Technical Sessions
Key to Session/Paper Numbers

A Coatings for Use at High Temperatures

B Hard Coatings and Vapor Deposition Technology

C Advanced Materials for Modern Device Applications

D Coatings for Biomedical and Healthcare Applications

E Tribology & Mechanical Behavior of Coatings and Engineered Surfaces

EX Exhibition Keynote Lecture

F New Horizons in Coatings and Thin Films

G Applications, Manufacturing, and Equipment

PL Plenary Lecture

TS Topical Symposia

Program numbers are listed with the symposium letter first, the session number second, and the number of the paper last (i.e., A1-1-1= symposium A, session one, paper number one).

Symposium scheduling pointers:

- All morning sessions begin at 8:00 am except for Monday when the technical sessions begin at 10:00 am following the 8:00 am Plenary Session
- Monday and Thursday afternoon sessions start at 1:30 pm; Tuesday and Wednesday afternoon sessions starting times vary 1:30 - 2:10 pm. Most session lunch breaks start at 12:00 pm
- Invited speakers (marked as such in the program) are allotted 40 minutes. Contributed speakers are allotted 20 minutes

If you are making an oral presentation:

All technical session rooms are equipped with computers, LCD projectors, screens, laser pointers and microphones. Please test your presentation materials to be certain that they are compatible with the equipment being provided in the technical session rooms. The room used for the Presenter's Preview Screening is the Dover. Please allow ample time for the test, preferably the day before your presentation. The Preview Room's hours of operation are Sunday, 3:30-6:30 pm and Monday – Thursday 8:00 am–5:30 pm

If you are making a poster presentation:

Boards will be available for posting materials at 11:00 am until 3:00 pm on Thursday, May 1. Prior to entering the Town & Country Poster Session Hall, authors presenting a poster are required to check in at the table located in the Hall's doorway. Please be prepared to show photo identification as well as your registration badge. These forms of identification must match the name of the presenter of the poster in the ICMCTF program. A sign listing the paper's number, title, and presenting author will aid each presenter in locating the correct board where the poster is to be displayed. The board which is provided is approximately four feet by four feet. All poster materials MUST be posted by 3:00 pm. All presenters are required to be at their poster presentation during the entire session (5:00 - 7:00 pm); to promote discussion and for the author to answer attendee questions. Be forewarned, all poster materials will be discarded if not removed from the boards by 9:00 pm Thursday evening.

Plenary Lecture

8:00-9:45
Room: San Diego

Plenary Lecture Session

Professor

Sybrand van der Zwaag

TU Delft, Netherlands

”Self-healing Materials: An Alternative Approach to Create More Durable/Reliable Materials and Products”

Please see full abstract on the
Plenary Session Page

8:00 – 9:45 am
San Diego Room

Monday Morning, April 28, 2014

	Hard Coatings and Vapor Deposition Technology **Room: Royal Palm 1-3 - Session B1-1** **PVD Coatings and Technologies** **Moderators: A.N. Ranade**, The Boeing Company, US, **S. Weißmantel**, University of Applied Sciences Mittweida, Germany, **J.W. Lee**, Ming Chi University of Technology, Taiwan	**Hard Coatings and Vapor Deposition Technology** **Room: Sunset - Session B5-1** **Hard and Multifunctional Nano-Structured Coatings** **Moderators: J. Paulitsch**, Vienna University of Technology, Austria, **J. Houska**, University of West Bohemia, Czech Republic
10:00 am	**B1-1-1** Composition Control in Zr-Cu-Ni-Al Thin Film Metallic Glass for Improvement of Mechanical and Anti-microbial Properties, **J.L. LEE**, K.C. HSU, J.G. DUH, National Tsing Hua University, Taiwan	**B5-1-1** Hard Multifunctional Hf-B-Si-C Films Prepared by Pulsed Magnetron Sputtering, **P. MARES**, J. KOHOUT, J. VLCEK, J. HOUSKA, R. CERSTVY, P. ZEMAN, University of West Bohemia, Czech Republic, M. ZHANG, J. JIANG, E. MELETIS, University of Texas at Arlington, US, S. ZUZJAKOVA, University of West Bohemia, Czech Republic
10:20 am	**B1-1-2** Low-Temperature, High-Rate Growth of Dense, Hard and Stress-free Refractory Ceramic Alloy Coatings, **G. GRECZYNSKI**, J. LU, J. JENSEN, Linköping University, IFM, Thin Film Physics Division, Sweden, I. PETROV, J. GREENE, University of Illinois at Urbana-Champaign, US, W. KÖLKER, S. BOLZ, C. SCHIFFERS, O. LEMMER, CemeCon AG, Germany, L. HULTMAN, Linköping University, IFM, Thin Film Physics Division, Sweden	**B5-1-2** Influence of Hf on the Structure, Thermal Stability and Oxidation Resistance of Ti-Al-N Coatings, Y. XU, Central South University, China, L. CHEN, Central South University and Zhuzhou Cemented Carbide Cutting Tools Co., LTD, China, **Y. DU**, Central South University, China, F. PEI, Central South University and Zhuzhou Cemented Carbide Cutting Tools Co., LTD, China, Y. PENG, Central South University, China
10:40 am	**B1-1-3** Estimating Metastable Phase Formation During Magnetron Sputtering, **K. CHANG**, D. MUSIC, D. LANGE, M. TO BABEN, H. BOLVARDI, J. SCHNEIDER, RWTH Aachen University, Germany	**B5-1-3** Growth of Hard Amorphous Ti-B-Si-N Coatings by Cathodic Arc Evaporation, **H. FAGER**, Thin Film Physics Division, IFM, Linköping University, Sweden, J. ANDERSSON, Seco Tools AB, Swedon, J. LU, J. JENSEN, L. HULTMAN, Thin Film Physics Division, IFM, Linköping University, Sweden
11:00 am	**B1-1-4** Microstructure and Superhardness Effects of VC/TiC Nanoscale Multilayer Films, **J.L. YUE**, J. CHEN, X.C. DONG, Central South University, China, G.Y. LI, Shanghai Jiaotong University, China	**B5-1-4** Structure, Oxidation Resistance and High Temperature Tribological Properties of CrTiAlN Coatings, **J. LIN**, K. COULTER, P. LEE, Southwest Research Institute, US, W. SPROUL, Reactive Sputtering, Inc., US
11:20 am	**B1-1-5 Invited** Recent Developments in Industrial Scale Pulsed Laser Deposition Technology for Thin Films, **J. LIIMATAINEN**, V. KEKKONEN, Picodeon, Ltd., Finland	**B5-1-5** Growth of $AlYB_{14}$ Thin Films by HPPMS, **O. HUNOLD**, D. MUSIC, Y.-T. CHEN, S. MRÁZ, J. SCHNEIDER, RWTH Aachen University, Germany
11:40 am	Invited talk continued.	
	Hysitron: Focused Topic Session **"Advancements in Thin Film Characterization"** **12:15-1:15 pm** **Royal Palm 1-3**	

Monday Morning, April 28, 2014

	Advanced Materials for Modern Device Applications **Room: Sunrise - Session C1** **Recent Advances in Optical Thin Films and Nanomaterials** **Moderators:** Taiwan, **L. Martinu**, Polytechnique Montreal, Canada	**Tribology & Mechanical Behavior of Coatings and Engineered Surfaces** **Room: California - Session E1-1** **Friction, Wear, and Lubrication: Effects and Modeling** **Moderators: M. Chandross**, Sandia National Laboratories, US, **O.L. Eryilmaz**, Argonne National Laboratory, US, **K. Polychronopoulou**, Khalifa University of Science, Technology & Research, UAE
10:00 am	**C1-1 Invited** Challenges and Perspectives of Optical Interference Coatings: FromTelecom and Space to Security and Consumer Electronics Applications, **R. SARGENT**, J. OCKENFUSS, D. HENDRIX, JDSU, US	**E1-1-1 Invited** Contact and Friction of Rough Adhesive Surfaces, **M. ROBBINS**, Johns Hopkins University, US, L. PASTEWKA, Fraunhofer IWM, Germany, T. SHARP, Johns Hopkins University, US
10:20 am	Invited talk continued.	Invited talk continued.
10:40 am	**C1-3** Assessment of the Mechanical Properties of Optical Coatings by *in situ* Real-time Approaches, **SCHMITT, T**. POIRIÉ, E. BOUSSER, L. MARTINU, J.E. KLEMBERG-SAPIEHA, Polytechnique Montreal, Canada	**E1-1-3** Wear Phenomena of ta-C Under Ultra-low Friction Conditions, **S. MAKOWSKI**, V. WEIHNACHT, F. SCHALLER, A. LESON, Fraunhofer IWS, Germany
11:00 am	**C1-4** Low Temperature Deposition of Thermochromic VO_2 Optical Coatings Using HiPIMS, S. LOQUAI, B. BALOUKAS, R. VERNHES, O. ZABEIDA, **J.E. KLEMBERG-SAPIEHA**, L. MARTINU, Polytechnique Montreal, Canada	**E1-1-4** Temperature-induced Low Friction of Sputtered Si-containing Amorphous Carbon Coatings, **O. JANTSCHNER**, Montanuniversität Leoben, Austria, S. FIELD, Teer Coatings Limited, Miba Coating Group, UK, K. ZORN, MIBA High Tech Coatings, Austria, D. MUSIC, J. SCHNEIDER, RWTH Aachen University, Germany, C. MITTERER, Montanuniversität Leoben, Austria
11:20 am	**C1-5** The Characteristics of Heavily Ga-doped ZnO Films with High Carrier Concentration for use in Plasmonics, **T. YAMAMOTO**, H. SONG, J. NOMOTO, H. MAKINO, Kochi University of Technology, Japan	**E1-1-5** The Aging and Temperature effects of DLC Coatings, **H. RONKAINEN**, VTT Technical Research Centre of Finland, K. HOLMBERG, VTT Technical Resesearch Centre of Finland, A. LAUKKANEN, VTT Technical Research Centre of Finland
11:40 am	**C1-6 Invited** Smart Optical Coating Systems for Energy Efficient Building Envelopes, **C.M. LAMPERT**, Star Science, US	**E1-1-6** Nanoscale Sliding Friction Phenomena at the Interface of Diamond-like Carbon and Tungsten, **P. STOYANOV**, Kennametal, Inc., US, P. ROMERO, M. DIENWIEBEL, M. MOSELER, Fraunhofer-Institute for Mechanics of Materials IWM, Germany
12:00 pm	Invited talk continued.	**E1-1-7** Scratch Testing for Diamond-like Coatings Evaluation at Micro and Nano-scale, F.L.C. LUCAS, University of Paraiba Valley IP&D/UNIVAP, São Jose dos Campos - SP, Brazil, S.F. FISSMER, Technologic Institute of Aeronautics, ITA/CTA, São Jose dos Campos - SP, Brazil, **L.V. SANTOS**, University of Paraiba Valley IP&D/UNIVAP, São Jose dos Campos - SP, Brazil, D.S. SILVA, Institute of Chemistry, University of Campinas - UNICAMP, Campinas SP, Brazil, C.A.R. COSTA, E.M. LANZONI, F. GALEMBECK, National Nanotechnology Laboratory at the National Center for Energy and Materials Research, Campinas SP, Brazil
12:20 pm	**C1-8** Potential Impact of Ambient Gases and Oxygen Partial Pressure on Structural, Hydrophobic, Optical and Electrical Property of Nanostructured HfO_xN_y Film, **V. DAVE**, Indian Institute of Technology Roorkee, India, P.K. MISHRA, Ranchi University, India, H.O. GUPTA, R. CHANDRA, Indian Institute of Technology Roorkee, India	**E1-1-8** Failure Mechanisms of DLC Coated Ti-6Al-4V and CoCr Biomedical Materials under Cyclic High Combined Contact Stresses, **Y. CHEN**, X. NIE, University of Windsor, Canada

Monday Morning, April 28, 2014

	New Horizons in Coatings and Thin Films Room: Royal Palm 4-6 - Session F5 Coatings for Compliant Substrates Moderator: N.R. Moody, Sandia National Laboratories, US	Applications, Manufacturing, and Equipment Room: Tiki - Session G4 Coatings for Machining Advanced Materials and for use in Advanced Manufacturing Methods Moderators: D. Kurapov, Oerlikon Balzers Coating AG, Liechtenstein, R. Cremer, KCS Europe GmbH, Germany
10:00 am	**F5-1** Electromechanical Properties of ZNO:Al Thin Films on Polymer Substrates for Optoelectronics Applications, **D. MOHAMMED**, University of Birmingham, UK, R. WADDINGHAM, A. FLEWITT, University of Cambridge, UK, S. KUKUREKA, University of Birmingham, UK	**G4-1** Nobel Wear Resistant Coating System for AHSS Stamping Die, **K. YAMAMOTO**, K. OZAKI, Kobe Steel Ltd., Japan, T. KASHI, Nippon Koshuha Steel Co., Ltd., Japan, H. YAMASHITA, Kams Co. Ltd., Japan
10:20 am	**F5-2** Low Temperature Titanium Dioxide Diffusion Barrier Layers on PEN Using Spatial Atomic Layer Deposition, **M. AGHAEE**, P. MAYDANNIK, Lappeenranta University of Technology, Finland, P. JOHANSSON, Tampere University of Technology, Finland, K. LAHTINEN, D. CAMERON, Lappeenranta University of Technology, Finland, J. KUUSIPALO, Tampere University of Technology, Finland	**G4-2** Development of (Cr,Al)ON Coatings using Middle Frequency Magnetron Sputtering and Investigations on Tribological Behavior against Polymers, K. BOBZIN, N. BAGCIVAN, **T. BRÖGELMANN**, Surface Engineering Institute - RWTH Aachen University, Germany
10:40 am	**F5-3 Invited** Stretch to the Limit: Ductility of Thin Metal Films on Polymer and Elastomer Substrates, **T. LI**, University of Maryland, US	**G4-3 Invited** Tailoring Wear Resistant PVD Coatings for Metal Cutting Applications, **E. GÖTHELID**, Sandvik Coromant, Sweden
11:00 am	Invited talk continued.	Invited talk continued.
11:20 am	**F5-5** Small Diameter Circular Ion Sources for Surface Engineering of Polymers, **F. PAPA**, Gencoa Ltd., US, D. MONAGHAN, V. BELLIDO-GONZALEZ, R. BROWN, A. AZZOPARDI, L. SORZABAL-BELLIDO, Gencoa Ltd., UK	**G4-5** Investigation of Suitability of CVD Diamond Thick Film Tool Coatings for High Performance Cutting of Ti6Al4V Super Alloys, **F. DEGEN**, F. KLOCKE, T. BERGS, M. BUSCH, Fraunhofer Institute for Production Technology IPT, Germany
11:40 am	**F5-6** Mechanical Design of Organic Light Emitting Diodes on Polymer Substrates, **S.J. BULL**, Newcastle University, UK	**G4-6 Invited** Technology Trends in Coated Cemented Carbides for High Demanding Applications CVD, PVD, Cutting Tool, **C. CZETTL**, M. POHLER, CERATIZIT Austria GmbH, Austria
12:00 pm	**F5-7** On the Response of Ti-6Al-4V and Ti-6Al-7Nb Alloys to a Nitron-100 Treatment, J.C. AVELAR-BATISTA WILSON, **S. BANFIELD**, J. HOUSDEN, Tecvac Ltd, UK, C. OLIVERO, P. CHAPON, Horiba Jobin Yvon S.A.S., France	Invited talk continued.
12:20 pm	**F5-8** A Comparison of Nanoindentation Pile-up in Bulk Materials and Thin Films, **N. MOHARRAMI**, S.J. BULL, Newcastle University, UK	
	Hysitron: Focused Topic Session **"Advancements in Thin Film Characterization"** **12:15-1:15 pm** **Royal Palm 1-3**	

Monday Afternoon, April 28, 2014

	Hard Coatings and Vapor Deposition Technology Room: Royal Palm 1-3 - Session B1-2 PVD Coatings and Technologies **Moderators: A.N. Ranade**, The Boeing Company, US, **S. Weißmantel**, University of Applied Sciences Mittweida, Germany, **J.W. Lee**, Ming Chi University of Technology, Taiwan	Hard Coatings and Vapor Deposition Technology Room: Sunset - Session B5-2 Hard and Multifunctional Nanostructured Coatings **Moderators: J. Paulitsch**, Vienna University of Technology, Austria, **J. Houska**, University of West Bohemia, Czech Republic
1:30 pm	**B1-2-1** High-temperature Sputter Deposition of $Ti_{1-x}Al_xN$/TiN Multilayer Coatings on Powder-metallurgical High-speed Steels, T. WEIRATHER, K. CHLADIL, Montanuniversität Leoben, Austria, B. SARTORY, Materials Center Leoben Forschung GmbH, Austria, D. CALISKANOGLU, Böhler Edelstahl GmbH & Co KG, Austria, R. CREMER, KCS Europe GmbH, Germany, W. KÖLKER, CemeCon AG, Germany, **C. MITTERER**, Montanuniversität Leoben, Austria	**B5-2-1** The Selection of Interfaces for Achieving Super- and Ultrahardness, **S. VEPREK**, Technical University Munich, Germany, V. IVASHCHENKO, Institute of Problems of Material Science, NAS of Ukraine, Ukraine, M. VEPREK-HEIJMAN, Technical University Munich, Germany
1:50 pm	**B1-2-2** Wear Protective Coating for Cutting Tools Applications Deposited by S3p™, D. KURAPOV, S. KRASSNITZER, T. BACHMANN, J. HAGMANN, W. KALSS, **M. ARNDT**, H. RUDIGIER, Oerlikon Balzers Coating AG, Liechtenstein	**B5-2-2** Comparison of TiSiN and TiSiVN Films Deposited by DC and HIPIMS Reactive Magnetron Sputtering Techniques, F. FERNANDES, University of Coimbra, Portugal, T. POLCAR, University of Southampton, UK, **A. CAVALEIRO**, University of Coimbra, Portugal
2:10 pm	**B1-2-3 Invited** Internal Oxidation of Nanolaminated Coatings, **Y.I. CHEN**, National Taiwan Ocean University, Taiwan	**B5-2-3** Structure and Properties of Novel Al-based PVD Nanostructured/Amorphous Coatings, **J. LAWAL**, A. LEYLAND, A. MATTHEWS, University of Sheffield, UK
2:30 pm	Invited talk continued.	**B5-2-4** The Modifying Effect of Cu and Ni on Nanostructuring and Properties of ARC - PVD Coatings Based on Titanium Nitride, **D.S. BELOV**, I.V. BLINKOV, A.O. VOLKHONSKIY, National University of Science and Technology "MISIS", Russian Federation
2:50 pm	**B1-2-5** Ion Energy Distributions in DC Arc Plasma from Compound Cathodes, I. ZHIRKOV, O. VOZNIY, **J. ROSEN**, Thin Film Physics Division, IFM, Linköping University, Sweden	**B5-2-5** Low Temperature Synthesis of Mo_2BC Thin Films, **H. BOLVARDI**, J. EMMERLICH, S. MRÁZ, RWTH Aachen University, Germany, M. ARNDT, H. RUDIGIER, OC Oerlikon Balzers AG, Liechtenstein, J. SCHNEIDER, RWTH Aachen University, Germany
3:10 pm	**B1-2-6** Filtered Cathodic Vacuum Arc Processes for Nano-scale Layering of Wear-resistant Structure on High Speed Steel Tools, **A. VERESCHAKA**, M. VOLOSOVA, S. GRIGORIEV, A. VERESCHAKA, Moscow State University of Technology (MSUT "STANKIN"), Russian Federation, A. BATAKO, Liverpool John Moores University, UK	**B5-2-6 Invited** Nanostructured Coatings with Adaptive Friction and Thermal Properties, **A.A. VOEVODIN**, Air Force Research Laboratory, US, C. MURATORE, University of Dayton, US, J.J. HU, J. GENGLER, Air Force Research Laboratory, US, D. STONE, S.M. AOUADI, University of North Texas, US, O. JANTSCHNER, C. MITTERER, R. RACHBAUER, Montanuniversität Leoben, Austria, P.H. MAYRHOFER, Vienna University of Technology, Austria, D. MUSIC, J. SCHNEIDER, RWTH Aachen University, Germany
3:30 pm	**B1-2-7** Structure and Corrosion Properties of TiN Films Deposited by Combined HIPIMS-DCMS Process, **P.EH. HOVSEPIAN**, A.A. SUGUMARAN, A.P. EHIASARIAN, Sheffield Hallam University, UK	Invited talk continued.
3:50 pm	**B1-2-8** Ternary Carbonitride Coatings deposited by High Power Impulse Magnetron Sputtering, **T. HIRTE**, R. FEUERFEIL, V. PEREZ-SOLORZANO BORRAGAN, Robert Bosch GmbH, Germany, M. SCHERGE, Fraunhofer Institute for Mechanics of Materials, IWM, Germany	**B5-2-8** Synthesis and Characterization of Multifunctional Me-B-C (Me = Cr, Nb, Mo) Thin Films Deposited by DC Magnetron Sputtering, **P. MALINOVSKIS**, N. NEDFORS, U. JANSSON, Uppsala University, Angstrom Laboratory, Sweden, J. LU, P. EKLUND, L. HULTMAN, Linköping University, IFM, Thin Film Physics Division, Sweden
4:10 pm	**B1-2-9 Invited** Laser Assisted and Arc Technologies for Hard Carbon Film Deposition – An Overview from the Beginning up to the Industrial Application, **H.J. SCHEIBE**, Fraunhofer Institute for Material and Beam Technology IWS, Germany	**B5-2-9** High Temperature Properties of Hexagonal Structured ZrAlN Thin Films, **L. ROGSTRÖM**, N. NORRBY, Linköping University, IFM, Nanostructured Materials, Sweden, M. AHLGREN, Sandvik Coromant, Sweden, N. SCHELL, Helmholtz-Zentrum Geesthacht, Germany, J. BIRCH, Linköping University, IFM, Thin Film Physics Division, Sweden, M. ODÉN, Linköping University, IFM, Nanostructured Materials, Sweden
4:30 pm	Invited talk continued.	**B5-2-10** Multi-Scale Mechanical Properties of Nanocrystalline Coatings Revealed by Micro- and Nano-Mechanical Tests, **J. ZÁLEŠÁK**, Erich Schmid Institute, Austrian Academy of Sciences, Austria, M. BARTOSIK, P.H. MAYRHOFER, Vienna University of Technology, Austria, J. KECKES, Montanuniversität Leoben, Austria
4:50 pm	**B1-2-11** Super-hard Tetrahedral Amorphous Carbon Films (ta-C) with Low Internal Stress -The Potential of the Pulsed Laser Deposition Technique, **K. GUENTHER**, University of Applied Sciences Mittweida, Germany, V. WEIHNACHT, Fraunhofer IWS, Germany, S. WEIßMANTEL, Univ. of Applied Sciences Mittweida, Germany	
5:10 pm	**B1-2-12 Withdrawn** Structure and Properties of Nitride Coatings, Prepared by PIII&D Using Multicomponent As-cast TiAl-based Cathodes, V. BELOUS, V. VASYLIEV, A. LUCHANINOV, V. MARININ, E. RESHETNYAK, V. STREL'NITSKIJ, National Science Center "Kharkov Institute of Physics and Technology", Ukraine, S. GOLTVYANYTSYA, **V. GOLTVYANYTSYA**, Real Ltd., Ukraine	

Welcome Mixer 6:00 - 7:30 pm in the Atlas Foyer
Sponsored by Oerlikon Balzers

Monday Afternoon, April 28, 2014

	Coatings for Biomedical and Healthcare Applications **Room: Sunrise - Session D1** **Surface Functionalization, Drug Delivery, and Anti-microbial Coatings** **Moderators: S. Rodil Posada**, Universidad Nacional Autonoma de Mexico, Mexico, **D.V. Shtansky**, National University of Science and Technology "MISIS", Russian Federation	**Tribology & Mechanical Behavior of Coatings and Engineered Surfaces** **Room: California - Session E2-1** **Mechanical Properties and Adhesion** **Moderators: J. Michler**, EMPA (Swiss Federal Laboratories for Materials Science and Technology), Switzerland, **R. Chromik**, McGill University, Canada, **D.F. Bahr**, Purdue University, US
1:30 pm	**D1-1** Wetting and Biocompatible Properties of Oxygen Plasma Treatment on Diamond-like Carbon Thin Films, **C. JONGWANNASIRI**, Nippon Institute of Technology, Japan, A. KHANTACHAWANA, King Mongkut's University of Technology Thonburi, Thailand, S. WATANABE, Nippon Institute of Technology, Japan	**E2-1-1 Invited** Thin Film Adhesion can be Measured From The Morphology of Telephone Cord Buckles, J.-Y. FAOU, S. GRACHEV, CNRS/Saint-Gobain, France, G. PARRY, Grenoble INP-CNRS-UJF, France, **E. BARTHEL**, CNRS/Saint-Gobain, France
1:50 pm	**D1-2** Preparation and Assessment of Bone Morphogenetic Proteins Immobilized Titanium Dioxide on Titanium Surface for Bone Implant, **H.W. SHU**, Feng Chia University, Taiwan, H.T. CHEN, China Medical University Hospital, Taiwan, C.J. CHUNG, Central Taiwan University of Science and Technology, Taiwan, J.L. HE, Feng Chia University, Taiwan	Invited talk continued.
2:10 pm	**D1-3 Invited** Biofilm formation and consequences in dental implants: New insights, **A. ALMAGUER-FLORES**, Universidad Nacional Autónoma de México, Mexico	**E2-1-3** Interface Delamination Study of Diamond-Coated Carbide Tools Considering Coating Fractures, P. LU, The University of Alabama, US, X. XIAO, Research & Development Center,General Motors Corporation, US, **K. CHOU**, The University of Alabama, US
2:30 pm	Invited talk continued.	**E2-1-4** Grain Structure Effect on the Stochastic Distribution of Local Adhesion Strength at Metal/Dielectric Layer Interface in Copper Wiring Systems, **N. SHISHIDO**, C. CHEN, S. KAMIYA, K. KOIWA, Nagoya Institute of Technology, Japan, M. OMIYA, Keio University, Japan, H. SATO, M. NISHIDA, Nagoya Institute of Technology, Japan, T. NAKAMURA, T. SUZUKI, Fujitsu Laboratories Limited, Japan, T. NOKUO, T. SUZUKI, JEOL, Japan
2:50 pm	**D1-5** Medical Coating Innovations: Antimicrobial PVD Coatings, **C. ACIKGOZ**, C. PINERO, V. DERFLINGER, A. JANSSEN, H. RUDIGIER, Oerlikon Balzers Coating AG, Liechtenstein	**E2-1-5** Evaluation of Scratch Adhesion Resistance on Boride Coatings Formed on the Surface of AISI 304 Steel, G. RODRÍGUEZ-CASTRO, **L.F. JIMÉNEZ-TINOCO**, Instituto Politecnico Nacional, Mexico, J.V. MÉNDEZ-MÉNDEZ, I. ARZATE-VÁZQUEZ, Instituto Politecnico Nacional, CNMN, Mexico, J. MARTÍNEZ-TRINIDAD, I. CAMPOS-SILVA, Instituto Politecnico Nacional, Mexico
3:10 pm	**D1-6** Surface Modification of Biodegradable Magnesium Alloys *via* Plasma-based Methods, **G.S. WU**, P.K. CHU, City University of Hong Kong, Hong Kong Special Administrative Region of China	**E2-1-6** Incoherent Interface Effect in the Mechanical Properties of Cu/W and Zr/Nb Nanomultilayers, **E. FRUTOS TORRES**, Czech Technical University in Prague, Czech Republic, M. CALLISTI, University of Southampton, UK, M. KARLIK, Czech Technical University in Prague, Czech Republic, T. POLCAR, University of Southampton, UK
3:30 pm	**D1-7** Corrosion Resistance, Anti-microbial Properties of Cu-Zr-Ag-Al Thin Film Metallic Glass with Various Cu/Zr Ratio in PBS Solution, **K.C. HSU**, J.G. DUH, National Tsing Hua University, Taiwan	**E2-1-7** Interface Toughness Optimization of Metal/Oxide Interfaces for Functional Coatings, **J. ZECHNER**, C. FRANTZ, R. KOODAKAL, L. PHILIPPE, J. MICHLER, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland
3:50 pm	**D1-8** Comparison of anti-HER2 Immobilization Using Three Different Techniques on Al-AlN-Al Thin Films, **M. HERNÁNDEZ**, I. GONZÁLEZ, H. GARCÍA, J. OSEGUERA, ITESM-CEM, Mexico	**E2-1-8 Invited** Using Nanoindentation to Assess Fracture Toughness and Interface Adhesion of Thin Coating, **J. CHEN**, Newcastle University, UK
4:10 pm	**D1-9** Formation and Characterization of Nanostructured Bioactive Apatite Coating on TiVAl Alloys, Y. GREISH, A. AL SHAMSI, A. AYESH, United Arab Emirates University (UAEU), UAE, **K. POLYCHRONOPOULOU**, Khalifa University, UAE	Invited talk continued.
4:30 pm		**E2-1-10** Yb:fiber Laser Surface Texturing of Stainless Steel Substrate, with MCrAlY Deposition and CO_2 Laser Treatment, **V. TELEGINSKI**, D. CHAGAS, Instituto Tecnológico de Aeronáutica (ITA), Brazil, J.C. SANTOS, J. AZEVEDO, G. VASCONCELOS, Instituto de Estudos Avançados (IEAv), Brazil
4:50 pm		**E2-1-11** Design and Evaluation of a Novel Testing Method for Surfaces Subjected to Combined Impact and Sliding or Rolling Loads, **P. EPAMINONDA**, C. REBHOLZ, University of Cyprus, Cyprus
5:10 pm		**E2-1-12 WITHDRAWN** Prevention of Ice and Snow Accumulation in Cold Environments, **R. FILLION**, A.R. RIAHI, A. EDRISY, University of Windsor, Canada
	Welcome Mixer 6:00 - 7:30 pm in the Atlas Foyer **Sponsored by Oerlikon Balzers**	

Monday Afternoon, April 28, 2014

	New Horizons in Coatings and Thin Films **Room: Royal Palm 4-6 - Session F1** **Nanomaterials, Nanofabrication, and Diagnostics** **Moderators: Y. Yamada-Takamura**, Advanced Institute of Science and Technology, Japan, **C. Ciobanu**, Colorado School of Mines, US	**Applications, Manufacturing, and Equipment** **Room: Tiki - Session G2** **Additive Manufacturing** **Moderators: D. Pappas,** EP Technologies, LLC, US, **X. Nie**, University of Windsor, Canada
1:30 pm	**F1-1 Invited** In Situ Diagnostics during Plasma Synthesis and Passivation of Group IV Nanocrystals, **S. AGARWAL**, Colorado School of Mines, US	**G2-1 Invited** Thin Films in a Thick 3D Printed World: How Thin Film will Enable 3D Printing., **K. CHURCH**, nScrypt Inc., US
1:50 pm	Invited talk continued.	Invited talk continued.
2:10 pm	**F1-3** Synthesis Of Copper Oxide Nanomaterials For Solar Cell Applications, **A. BHAUMIK**, K. GHOSH, Missouri State University, US	**G2-3** Barium Hexaferrite, Yttrium Iron Garnet and ZnS/Diamond Composite Thick Films Formed by the Aerosol Deposition Method, **C. EDDY, JR.**, U.S. Naval Research Laboratory, US, S. JOHNSON, American Association for Engineering Education, US, S.-F. CHENG, M.-J. PAN, F. KUB, U.S. Naval Research Laboratory, US
2:30 pm	**F1-4** Synthesis by Reactive Magnetron Sputtering and Characterization of Nanostructured n-type and p-type Semiconductor Coatings as Dodecane Sensors, **M. ARAB POUR YAZDI**, A. TAGUETT, IRTES-LERMPS-UTBM, France, J. SANCHEZ, UMR CNRS 6249, Université de Franche Comté, France, E. MONSIFROT, SARL DEPHIS, France, P. BRIOIS, IRTES-LERMPS-UTBM, France, F. BERGER, UMR CNRS 6249, Université de Franche Comté, France, A. BILLARD, IRTES-LERMPS-UTBM, France	**G2-4 Invited** Laser Consolidation – Converting 3D Design to Net-shape Functional Metallic Components, **L. XUE**, National Research Council, Canada
2:50 pm	**F1-5** Improved Dielectric and Magnetic Properties in Hexagonal-$Ymn_{1-x}Fe_xO_3$ (x=0, 0.1) Thin Films Deposited by Pulsed Laser Deposition, **S. CHAUHAN**, R. CHANDRA, P. DUBEY, S. SRIVASTAVA, A.S. RAJPUT, Indian Institute of Technology Roorkee, India	Invited talk continued.
3:10 pm	**F1-6 Invited** Formation of Metallic Glass Nanowires by Gas Atomization, **K. NAKAYAMA**, Tohoku University, Japan	**G2-6** Protective Coatings of Ultra High Toughness – Ceramic-based Composite Inspired from Natural Armors, **T.H. HSU**, P.Y. CHEN, National Tsing Hua University, Taiwan
3:30 pm	Invited talk continued.	**G2-7 Invited** 3D Printing (aka Additive Manufacturing): From Prototypes to Uniquely Designed Production Parts, **R. WICKER**, University of Texas at El Paso, US
3:50 pm	**F1-8** Namomechanical Properties of Platinum Thin Films Synthesized by Atomic Layer Deposition, M.A. MAMUN, D. GU, H. BAUMGART, A.A. ELMUSTAFA, **D. NMINIBAPIEL**, Old Dominion University, US	Invited talk continued.
4:10 pm	**F1-9** Improving Electrochemical Performance of Silicon Based Anodes by Forming a Well-Aligned CuSi Helices via an Oblique Angle Co-deposition Method for LIB, B.D. POLAT, Istanbul Technical University, Turkey, L. ERYILMAZ, R. ERCK, Argonne National Laboratory, US, **O. KELES**, Istanbul Technical University, Turkey, A. ERDEMIR, K. AMINE, Argonne National Laboratory, US	
4:30 pm	**F1-10** Relaxation Phenomena and Modeling Processes in Lithium Heptagermanate Li2Ge7O15 Crystals, **Y. OBAIDAT**, King Khalid University, Saudi Arabia	
4:50 pm	**F1-11** The Synthesis and Optoelectronic Properties of Fluorinated Vanadium Oxide Nanowires, **K.Y. PAN**, National Tsing Hua University, Taiwan, K.C. CHEN, H.C. SHIH, Chinese Culture University, Taiwan	

Welcome Mixer 6:00 - 7:30 pm in the Atlas Foyer
Sponsored by Oerlikon Balzers

Tuesday Morning, April 29, 2014

	Hard Coatings and Vapor Deposition Technology Room: Royal Palm 1-3 - Session B1-3 PVD Coatings and Technologies **Moderators: A.N. Ranade**, The Boeing Company, US, **S. Weißmantel**, University of Applied Sciences Mittweida, Germany, **J.W. Lee**, Ming Chi University of Technology, Taiwan	Hard Coatings and Vapor Deposition Technology Room: Sunset - Session B5-3 Hard and Multifunctional Nano-Structured Coatings **Moderators: J. Paulitsch**, Vienna University of Technology, Austria, **J. Houska**, University of West Bohemia, Czech Republic
8:00 am	**B1-3-1** Properties of Composite ZrO_2-Al_2O_3 Coatings Deposited by Pulsed-DC Magnetron Sputtering and Filtered Vacuum Arc Techniques, I. ZUKERMAN, NRC-Negev, Israel, A. RAVEH, Advanced Coatings Center, Rotem Industries Ltd, Israel, **R.L. BOXMAN**, Tel Aviv University, Israel, J.E. KLEMBERG-SAPIEHA, L. MARTINU, École Polytechnique de Montréal, Canada	**B5-3-1** Struture of CrN/NbN Nano-scale Multilayer Coating Deposited by Cathodic Arc Technique, J. ARAUJO, R. SOUZA, University of São Paulo, Brazil, N. LIMA, Energetic and Nuclear Research Institute, Brazil, **A.P. TSCHIPTSCHIN**, University of São Paulo, Brazil
8:20 am	**B1-3-2** Cutting Performance Comparison of Thick PVD Nitride Coating and CVD Oxide Coating in High Speed Turning of Cast Iron, **M. ABE**, K. YAMAMOTO, S. TANIFUJI, Kobe Steel Ltd., Japan	**B5-3-2** The Role of a Superelastic Interlayer on the Tribological Behaviour of Hard Coatings, **M. CALLISTI**, National Centre for Advanced Tribology Southampton, UK, B. MELLOR, T. POLCAR, University of Southampton, UK
8:40 am	**B1-3-3** The Structure and Composition Analyses of Tungsten Oxides Thin Film by PVD Process, C. LI, National Central University, Taiwan, J.H. HSIEH, Ming Chi Institute of Technology, Taiwan, **B.Q. HUANG**, National Central University, Taiwan	**B5-3-3 Invited** Contemporary Thin Film Ceramics Behaviour in the Extreme Environments, **V. VISHNYAKOV**, Manchester Metropolitan University, UK
9:00 am	**B1-3-4** Plasma-activated High-rate Deposition of Titanium Dioxide Coatings by Electron Beam, Spotless Arc and Dual Crucible Technology, **C. METZNER**, B. SCHEFFEL, G. MATTAUSCH, TH. MODES, Fraunhofer FEP, Germany	Invited talk continued.
9:20 am	**B1-3-5** An Investigation Into the Improvement of the Corrosion Behaviour of PVD Coatings, **JL. DAURE**, KT. VOISEY, PH. SHIPWAY, University of Nottingham, UK, DA. STEWART, Rolls-Royce plc, UK	**B5-3-5** The Microstructure and Mechanical Properties Evaluation of Cr-Si-B-N/Ti-Si-B-N Multilayered Thin Films, **L.C. HSU**, J.W. LEE, Ming Chi University of Technology, Taiwan
9:40 am	**B1-3-6** Effect of Cathode Composition on Cathodic Arc Synthesis of Multi-element Material from Compound Cathodes, **I. ZHIRKOV**, J. ROSEN, Thin Film Physics Division, IFM, Linköping University, Sweden	**B5-3-6** Study of Sensing Properties of Zinc Oxide and Cu-doped Zinc Oxide Nanowires, **Y.W. YEH**, C.P. LIU, National Cheng Kung University, Taiwan, R.C. WANG, National Kaohsiung University, Taiwan, J.L. HUANG, National Cheng Kung University, Taiwan
10:00 am	**B1-3-7** Investigations on Erosion Behavior of TiAlSiN Nanocomposite Coatings Deposited by High Speed-physical Vapor Deposition, K. BOBZIN, N. BAGCIVAN, T. BRÖGELMANN, **B. YILDIRIM**, RWTH Aachen University, Germany	**B5-3-7** Fabrication of n-type ZnO and p-type Cu_2O Nanostructures and its Photoelectrochemical Properties, **Y.H. CHEN**, Y.M. SHEN, National Cheng Kung University, Taiwan, S.C. WANG, Southern Taiwan University, Taiwan, J.L. HUANG, National Cheng Kung University, Taiwan
10:20 am	**B1-3-8** High-Rate Deposition of AlTiN and Related Coatings with Dense Morphology by Central Cylindrical DC Magnetron Sputtering, **M. JILEK**, SHM s.r.o., Czech Republic, F. MENDEZ MARTIN, Montanuniversität Leoben, Austria, P.H. MAYRHOFER, Vienna University of Technology, Austria, S. VEPREK, Technical University Munich, Germany	**B5-3-8 Moved to BP60** Fabrication and Characterization of Tungsten-Yttrium Coatings for Nuclear Reactor Applications, **G. MARTINEZ**, University of Texas at El Paso, US, C. RAMANA, University of Texas at El Paso
10:40 am	**B1-3-9 Invited** Oxidation Resistance and their Applications of Multicomponent TiAlSiN and CrAlSiN Hard Coatings Synthesized by Cathodic Arc Evaporation, **Y. CHANG**, National Formosa University, Taiwan	
11:00 am	Invited talk continued.	
11:20 am	**B1-3-11** Oriented Cubic Al-Ti-N Films with Large Compressive Stress Deposited by Dual Source Type Reactive Plasma Deposition System, **K. TANAKA**, M. TAKAHASHI, Mitsubishi Materials Corporation, Japan	
11:40 am	**B1-3-12** Oxidation Resistance and Mechanical Properties of CrTaSiN Coatings Prepared using Co-sputter Deposition, Y.I. CHEN, **H.H. WANG**, National Taiwan Ocean University, Taiwan	

Exhibition Hall Opens Today
Town & Country/San Diego/Golden West
12:00 - 7:00 pm
Enjoy lunch in the Exhibition Hall 12:15 pm

Tuesday Morning, April 29, 2014

	Coatings for Biomedical and Healthcare Applications **Room: Sunrise - Session D2-1** **Coatings for Bio-corrosion, Tribo-corrosion and Bio-tribology** **Moderators: J. Geringer**, Ecole Nationale Supérieure des Mines de Saint Etienne, France, **T. Shokuhfar**, Michigan Technological University, US	**Tribology & Mechanical Behavior of Coatings and Engineered Surfaces** **Room: California - Session E2-2** **Mechanical Properties and Adhesion** **Moderators: J. Michler**, EMPA (Swiss Federal Laboratories for Materials Science and Technology), Switzerland, **R. Chromik**, McGill University, Canada, **D.F. Bahr**, Purdue University, US
8:00 am		**E2-2-1 Invited** Tensile Deformation Behavior in Highly Nanotwinned Cu and CuAl Alloys, **A. HODGE**, University of Southern California, US
8:20 am	**D2-1-2** Properties of Waterborne Polyurethane/Graphene Coatings, **M. RAHMAN**, Q. HABIB, King Fahd University of Petroleum and Minerals, Saudi Arabia	Invited talk continued.
8:40 am	**D2-1-3 Invited** Corrosion and Tribological Film of CoCrMo Metal-on-Metal Hip Replacement, **Y. LIAO**, P. PANIGRAPHI, Northwestern University, US, M. MATHEW, R. POURZAL, A. FISCHER, M. WIMMER, Rush University Medical Center, US, L. MARKS, Northwestern University, US	**E2-2-3** Electromechanical and Chemomechanical Performance of Laser Oxide Coatings on Metallic Substrates, **S.K. LAWRENCE**, Purdue University, US, D. ADAMS, Sandia National Laboratories, US, D.F. BAHR, Purdue University, US, N.R. MOODY, Sandia National Laboratories, US **STUDENT AWARD FINALIST**
9:00 am	Invited talk continued.	**E2-2-4** Room Temperature Nanoindentation Creep of Nanograined NiTiW Shape Memory Thin Films, **N. KAUR**, D. KAUR, Indian Institute of Technology Roorkee, India
9:20 am	**D2-1-5** Electrochemical and Tribocorrosion Aspects of Mixed Metal Contacts in Hip Prostheses, D. ROYHMAN, M. RUNA, M. WIMMER, J. JACOBS, N. HALLAB, **M. MATHEW**, Rush University Medical Center, US	**E2-2-5 Invited** Deformation and Fracture of Metal Films on Polymer Substrates, **M.J. CORDILL**, V. MAIER, Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Austria, J. BERGER, O. GLUSHKO, Erich Schmid Institue of Materials Science, Austrian Academy of Sciences, Austria, J. PAULITSCH, Vienna University of Technology, Austria
9:40 am	**D2-1-6** Hydrothermal Deposition of Bio-resorbable Calcium-Phosphate Coating on AZ31 Magnesium for Implant Application, **S. KAABI FALAHIEH ASL**, Nanyang Technological University, School of Mechanical & Aerospace Engineering, Singapore Institute of ManufacturingTechnology, Singapore, N. SANDOR, Singapore Institute of Manufacturing Technology, Singapore, M.J. TAN, Nanyang Technological University , School of Mechanical & Aerospace Engineering,, Singapore	Invited talk continued.
10:00 am	**D2-1-7 Invited** Layers of Nanocrystallines and Tribofilm on Artificial Hip Implants Surfaces Induced by Bio-tribo-corrosion Processes, **Y. YAN**, Key Laboratory for Environmental Fracture (MOE), University of Science and Technology Beijing, China	**E2-2-7** Numerical Evaluation of Cohesive and Adhesive Failure Modes During the Indentation of Coated System with Compliant Substrate, **N. FUKUMASU**, R. SOUZA, University of São Paulo, Brazil
10:20 am	Invited talk continued.	
10:40 am	**D2-1-9** Fretting Corrosion of Co-Cr-Mo Alloy with Ti: Specific Tribocorrosive Behavior and Benefits in Comparison with Usual Metallic Alloys Dedicated to Orthopedic Implants, **S. NAKAHARA**, Department of Material Processing, Japan, A. TOWAREK, Warsaw University of Technology, Poland, K. UEDA, Department of Material Processing, Japan, T. NARUSHIMA, Tohoku University, Japan, J. GERINGER, Ecole Nationale Supérieure des Mines de Saint Etienne, France	
11:00 am	**D2-1-10** Studies of Unbleached Cotton Fabric Treated with TiO_2 Anchored by Diamond-like Carbon Film: Microbiological Inhibition Growth Rate With and Without UV Exposition, **E.D. SANTOS**, D.F. FURTADO, F.S. MIRANDA, F.L.C. LUCAS, R.S. PESSOA, H.S. MACIEL, Universidade do Vale do Paraíba, Brazil, E. ESPOSITO, Universidade Federal de São Paulo, Brazil, L.V. SANTOS, Universidade do Vale do Paraíba, Brazil	
	Exhibition Hall Opens Today **Town & Country/San Diego/Golden West** **12:00 - 7:00 pm** **Enjoy lunch in the Exhibition Hall 12:15 pm**	

Tuesday Morning, April 29, 2014

	New Horizons in Coatings and Thin Films Room: Royal Palm 4-6 - Session F2-1 High Power Impulse Magnetron Sputtering (HIPIMS) **Moderators: D. Lundin**, Université Paris-Sud 11, France, **S. Konstantinidis**, University of Mons, Belgium	Topical Symposia Room: Tiki - Session TS1 Mechanical Properties Challenges for Greener Energy Applications and Emissions Reduction **Moderators: G. Dadheech**, General Motors Research and Development Center, US
8:00 am	**F2-1-1** Imaging Of Self-Organized Plasma Structures In DC Magnetron Sputtering And HiPIMS Discharges, **M. PANJAN**, S. LOQUAI, J.E. KLEMBERG-SAPIEHA, L. MARTINU, École Polytechnique de Montréal, Canada	**TS1-1 Invited** Surface Engineering for Improving the Performance and Durability of Lithium Ion Batteries, **Y.T. CHENG**, University of Kentucky, US
8:20 am	**F2-1-2** Ionized Sputtering with a Pulsed Hollow Cathode Magnetron, **F. FIETZKE**, B.-G. KRÄTZSCHMAR, Fraunhofer Institute for Electron Beam and Plasma Technology FEP, Germany	Invited talk continued.
8:40 am	**F2-1-3** High-rate Reactive High-power Impulse Magnetron Sputtering of Densified Zirconium Dioxide Films, **J. VLCEK**, J. REZEK, University of West Bohemia, Czech Republic	**TS1-3** How Residual Stresses Affect the Elastic Properties of Ni, P. GADAUD, **X. MILHET**, Pprime Institute - UPR CNRS 3346 - Université de Poitiers - ENSMA - France, O. HUBERT, ENS Cachan, France, P.O. RENAULT, C. COUPEAU, Pprime Institute - UPR CNRS 3346 - Université de Poitiers - ENSMA - France
9:00 am	**F2-1-4** $CuInSe_2$ Thin Film Photovoltaic Absorber Layers by HIPIMS at Low Temperature, **A.P. EHIASARIAN**, D. LOCH, Sheffield Hallam University, UK, V. SITTINGER, Fraunhofer IST, Germany	**TS1-4** Strength and Fatigue Lifetime of Silicon in Hydrogen Atmosphere, **U. ARASU**, S. KAMIYA, H. IZUMI, Nagoya Institute of Technology, Japan
9:20 am	**F2-1-5 Invited** Plasma Spokes and Particle Transport in HiPIMS Discharges, **A. HECIMOVIC**, T. DE LOS ARCOS, V. SCHULZ-VON DER GATHEN, J. WINTER, Institut for Experimental Physics II, Ruhr-Universität Bochum, Germany	**TS4 Session Continues Immediately Following TS1 in the same room. See Page 12**
9:40 am	Invited talk continued.	
10:00 am	**F2-1-7** Effects of Cr and Ta Interlayers on the Adhesion and Mechanical Properties of CN_x Thin Films Deposited by HiPIMS on Steel Substrates, **K.D. BAKOGLIDIS**, S. SCHMIDT, G. GRECZYNSKI, J. LU, E. BROITMAN, L. HULTMAN, Linköping University, IFM, Thin Film Physics Division, Sweden	
10:20 am	**F2-1-8** Comparison of CrN/AlN Multilayer Coatings Deposited via Middle Frequency Pulsed and High Power Pulsed Magnetron Sputtering, N. BAGCIVAN, K. BOBZIN, **R.H. BRUGNARA**, Surface Engineering Institute - RWTH Aachen University, Germany	
10:40 am	**F2-1-9** Microstructure and Electrical Transport Properties of HIPIMS-Deposited ZnO Thin Films, **A.N. REED**, P.J. SHAMBERGER, Air Force Research Laboratories, Wright-Patterson AFB, C. MURATORE, University of Dayton, US, J.E. BULTMAN, University of Dayton Research Institute, US, A.A. VOEVODIN, Air Force Research Laboratory, Materials and Manufacturing Directorate, US	
11:00 am	**F2-1-10** A Comparative Study of Nanocomposite TiBCN Coatings Deposited by DC Magnetron Sputtering, Pulse DC Magnetron Sputtering and Deep Oscillation Magnetron Sputtering, **B. WANG**, M. KAUFMAN, G. BOURNE, W. SPROUL, J. LIN, Colorado School of Mines, US	
	Exhibition Hall Opens Today **Town & Country/San Diego/Golden West** **12:00 - 7:00 pm** **Enjoy lunch in the Exhibition Hall 12:15 pm**	

Topical Symposia
Room: Tiki - Session TS4

Graphene and 2D Nanostructures
Moderators: C. Teichert, Montanuniversität Leoben, Austria, **M. Chhowalla**, Rutgers University, US, **J. Huang**, Northwestern University, US

	TS1 in Previous Time Slots located in the same room. See Page 11	
9:20 am	**TS4-5** Synthesis, Properties, and Application of Two-dimensional Nano-Yttrium Oxide, **X. HE**, H. LIANG, Texas A&M University, US	
9:40 am	**TS4-6** Toward Growth of Few Layer Hexagonal Boron Nitride via Pulsed Laser Deposition, **N. GLAVIN**, Air Force Research Laboratory and Birck Nanotechnology Center, Purdue University, US, M. CHECK, M. JESPERSEN, University of Dayton Research Institute, US, J. GENGLER, Spectral Energies, LLC, US, T. FISHER, School of Mechanical Engineering and Birck Nanotechnology Center, Purdue University, US, A.A. VOEVODIN, Materials and Manufacturing Directorate, Air Force Research Laboratory, US	
10:00 am	**TS4-7 Invited** Reduction and Healing of Graphene Oxyde in Carbon Monoxide Atmosphere, **C. CIOBANU**, Colorado School of Mines	
10:20 am	Invited talk continued.	
10:40 am	**TS4-9** Mobility and Preferential Edge-Site Binding of Metal Adatoms on Graphene, **T. HARDCASTLE**, C. SEABOURNE, University of Leeds, UK, R. ZAN, Manchester, UK, R. BRYDSON, University of Leeds, UK, U. BANGERT, Manchester, UK, Q. RAMASSE, SuperSTEM Laboratory, Daresbury, UK, K. NOVOSELOV, Manchester, UK, A. SCOTT, University of Leeds, UK **STUDENT AWARD FINALIST**	
11:00 am	**TS4-10** High Energy Density Asymmetric Supercapacitor Based on Nitrogen Doped Graphene, **F.N. SARI**, J.-M. TING, National Cheng Kung University, Taiwan	
11:20 am	**TS4-11 Invited** Graphene-based Supercapacitors, **R.B. KANER**, L. WANG, J. HWANG, S. DUBIN, M. LI, H. WANG, University of California, Los Angeles, US, M. EL-KADY, Cairo University, Egypt, M. MOUSAVI, Tarbiat Modares University, Iran	
11:40 am	Invited talk continued.	
12:00 pm	**TS4-13** Characterization of 2D Nanomaterials with Spectroscopic Imaging Ellipsometry, P. THIESEN, Accurion GmbH, Germany, **G. HEARN**, Accurion Inc., US, U. WURSTBAUER, A. HOLLEITNER, B. MILLER, E. PARZINGER, Technische Universität München, Germany, U. WURSTBAUER, Columbia University, US, C. ROLING, Technische Universität München, Germany	**Exhibition Hall Opens Today** **Town & Country/San Diego/Golden West** **12:00 - 7:00 pm** **Enjoy lunch in the Exhibition Hall 12:15 pm**
12:20 pm	**TS4-14** Effect of Laser Irradiation on Structural and Electrical Properties of CVD Grown Graphene, **K. GHOSH**, M. LANGHOFF, A. BHAUMIK, Missouri State University, US, W. MITCHEL, Air Force Research Laboratory, AFRL/RXA, WPAFB, US, G.S. TOMPA, N. SBROCKEY, E. GALLO, T. SALAGAJ, Structured Materials Industries Inc., US	

Tuesday Morning, April 29, 2014

Exhibitors Keynote Lecture

11:00 am-12:00 pm
Room: California

Exhibition Keynote Lecture

TIMOTHY WEIHS
Johns Hopkins University, US

"Driving Commercial Applications and Exploring Scientific Questions with Reactive Multilayer Foils"

See Keynote Lecture Page for Abstract

11:00 am – 12:00 pm
California Room

Exhibition Hall Opens Today
Town & Country/San Diego/Golden West
12:00 - 7:00 pm
Enjoy lunch in the Exhibition Hall 12:15 pm

Tuesday Afternoon, April 29, 2014

	Hard Coatings and Vapor Deposition Technology **Room: Royal Palm 1-3 - Session B1-4** **PVD Coatings and Technologies** **Moderators: A.N. Ranade**, The Boeing Company, US, **S. Weißmantel**, University of Applied Sciences Mittweida, Germany, **J.W. Lee**, Ming Chi University of Technology, Taiwan	**Advanced Materials for Modern Device Applications** **Room: Sunset - Session C4-1** **Thin Films for Energy Related Applications** **Moderators: K. Yu**, Lawrence Berkeley National Laboratory, US, **J. Partridge**, RMIT University, Australia
1:30 pm		**C4-1-1 Invited** Intermediate Band Materials for High Efficiency Solar Cells, **Y. OKADA**, The University of Tokyo
1:50 pm		Invited talk continued.
2:10 pm	**B1-4-3** Structural, Mechanical and Tribological Properties of VN Thin Films Fabricated by PVD, H. AHMAD AGHDAM, Ataturk University, Turkey, **I. EFEOGLU**, K.V. EZIRMIK, H. CICEK, M. TAHMASEBIAN MYANDOAB, Atatürk University, Turkey, Ö. BARAN, Erzincan University, Turkey	**C4-1-3** Growth of Cu_2ZnSnS_4 by Reactive Magnetron Co-sputtering, **P-A. CORMIER**, University of Mons, Belgium, G. GUISBIERS, Materia Nova Research Center, Belgium, O. LOZANO-GARCIA, S. LUCAS, University of Namur, Belgium, R. SNYDERS, University of Mons, Belgium
2:30 pm	**B1-4-4** Compressive Intrinsic Stresses in Thin Films are Caused by Atom Insertion into Grain Boundaries, **D. MAGNFÄLT**, IFM Linköping University, Sweden, A. FILLON, Groupe de Physique des Matériaux, University of Rouen, France, R. BOYD, U. HELMERSSON, K. SARAKINOS, IFM Linköping University, Sweden, G. ABADIAS, Pprime Institute - UPR CNRS 3346 - Université de Poitiers - ENSMA - France	**C4-1-4** Preparation of Cu_2ZnSnS_4 Thin Films Using Pulsed Electrodeposition and Sulfurization, **L.J. WANG**, J.-M. TING, National Cheng Kung University, Taiwan
2:50 pm	**B1-4-5** Model for Growth Stress in Polycrystalline Films: Comparison with Growth on Lithographically-patterned and Randomly-nucleated Films, **E. CHASON**, C.-H. CHEN, A. ENGWAL, Brown University, US, J.-W. SHIN, LAM Reserearch, US, S.J. HEARNE, Sandia National Laboratories, US, L.B. FREUND, University of Illinois at Urbana-Champaign, US	**C4-1-5** Solid-State Solar Cell-Based on $CH_3NH_3PbI_3$ Perovskite Sensitizer and Mesoporous Anatase TiO_2 Beads, **F. FIRDAUSI**, J.-M. TING, National Cheng Kung University, Taiwan
3:10 pm	**B1-4-6** Influence of Tantalum on Structure, Electrical Resistivity and Corrosion Behavior of Sputtered Molybdenum Films, **A. HOFER**, Montanuniversität Leoben, Austria, N. REINFRIED, PLANSEE SE, Business Unit Coating, Austria, G. MORI, C. MITTERER, Montanuniversität Leoben, Austria	**C4-1-6** Preparation of Inkjet-printed Titanium Monoxide as p-Type Absorber Layer for Photovoltaic Purpose, **T.T.N. NGUYEN**, Y.H. CHEN, J.L. HE, Feng Chia University, Taiwan
3:30 pm	**B1-4-7** The Fabrication and Property Evaluation of Zr-Ti-B-Si Thin Film Metallic Glass Materials, **Y.L. DENG**, J.W. LEE, Ming Chi University of Technology, Taiwan	**C4-1-7** Magnetron Sputtering Deposition of Pd-Ag Thin Film Membranes onto Tubular Ceramic Supports for Hydrogen Separation, A.I. PEREIRA, University of Minho, Campus Azurém, Portugal, P. PEREZ, A. MENDES, L.M. MADEIRA, University of Porto, Portugal, **C.J. TAVARES**, University of Minho, Campus Azurém, Portugal
3:50 pm	**B1-4-8** The Effect of Pulse and Bias DC Voltage on Crystallization of TiNi Shape Memory Thin Films Deposited by Unbalanced Magnetron Sputtering, **H. CICEK**, I. EFEOGLU, Atatürk University, Turkey, Ö. BARAN, Erzincan University, Turkey, Y. TOTIK, Atatürk University, Turkey	**C4-1-8** Structural Evolution of Bias Sputtered $LiNi_{0.5}Mn_{1.5}O_4$ Thin Film Cathodes for Lithium Ion Batteries, **S.-H. SU**, K.-F. CHIU, H.-J. LEU, Feng Chia University, Taiwan
4:10 pm	**B1-4-9** Influences of TMS Flow Rates on the Structure and Mechanical Properties of Cr-Si-C-N Thin Films Deposited by Pulsed DC Reactive Magnetron Sputtering, **D.H. KAO**, National Taiwan University of Science and Technology, Taiwan, J.W. LEE, Ming Chi University of Technology, Taiwan, C.J. WANG, National Taiwan University of Science and Technology (NTUST), Taiwan	**C4-1-9** CdSe Quantum Dots Decorated Doped and Pure α- Fe_2O_3 Thin Films for Hydrogen Production, **A. IKRAM**, S. SAHAI, S. RAI, S. DASS, R. SHRIVASTAV, V. SATSANGI, Dayalbagh Educational Institute, India
4:30 pm	**B1-4-10** Growth of Silicon Germanium Nanowires by Physical Vapor Deposition, K. MAHMOOD, **M. ASGHAR**, The Islamia University of Bahawalpur, Pakistan, A. ALI, GC University Faisalabad, Pakistan	
	Exhibition Hall Opens Today **Town & Country/San Diego/Golden West** **12:00 - 7:00 pm** **Enjoy lunch in the Exhibition Hall 12:15 pm** **Exhibition Reception-TC/SD/GW** **5:30-7:00 pm** **Reception drinks compliments of Plansee**	

Tuesday Afternoon, April 29, 2014

	Coatings for Biomedical and Healthcare Applications **Room: Sunrise - Session D2-2** **Coatings for Bio-corrosion, Tribo-corrosion, and Bio-tribology** **Moderators: J. Geringer**, Ecole Nationale Supérieure des Mines de Saint Etienne, France, **T. Shokuhfar**, Michigan Technological University, US	**Tribology & Mechanical Behavior of Coatings and Engineered Surfaces** **Room: California - Session E1-2** **Friction, Wear, and Lubrication: Effects and Modeling** **Moderators: M. Chandross**, Sandia National Laboratories, US, **O.L. Eryilmaz**, Argonne National Laboratory, US, **K. Polychronopoulou**, Khalifa University of Science, Technology & Research, UAE
1:30 pm		
1:50 pm		
2:10 pm	**D2-2-3 Invited** Discovering Nanotechnology and Picotechnology for Medical Applications, **T. WEBSTER**, Northeastern University, US	**E1-2-3** On the Effect of Substrate Structure on the Tribological Behavior of Coatings: an Orthogonal Design Study, **V. FRIDRICI**, J. YANG, P. KAPSA, LTDS - Ecole Centrale de Lyon, France
2:30 pm	Invited talk continued.	**E1-2-4** Investigation of Quaternary Metal Oxide Coatings for High Temperature Solid Lubrication, **V. AGEH**, H. MOHSENI, T. SCHARF, University of North Texas, US
2:50 pm	**D2-2-5** Improved Corrosion Resistance of Mg-Y-RE Alloy Coated with Niobium Nitride, **W.H. JIN**, G.S. WU, P.H. LI, P.K. CHU, City University of Hong Kong, Hong Kong Special Administrative Region of China	**E1-2-5** Wear Characteristics of Mixed Lubricious Oxide Coatings, **S. DIXIT**, Plasma Technology Inc., US, A. ERDEMIR, O.L. ERYILMAZ, Argonne National Lab, US, R. DIXIT, DRS Research, US
3:10 pm	**D2-2-6** Achieving Controlled Degradation and Better Biocompatibility of Magnesium by a Combination of Microarc Oxidation and Highly Textural Lamellar Mesostructured $Mg(OH)_2$ Coatings, **S. NELLAIAPPAN**, I.S. PARK, M.H. LEE, Chonbuk National University, Jeonju, Republic of Korea	**E1-2-6** Empirical Interaction Potentials for Transition Metal Dichalcogenides from Force Matching Algorithm and Ab Initio Simulation, **P. NICOLINI**, T. POLCAR, Czech Technical University in Prague, Czech Republic
3:30 pm	**D2-2-7** Improvement of Titanium Wear and Corrosion Resistance by Plasma Electrolytic Oxidation: Effects of Applied Voltage and Annealing Treatment, **C. LAURINDO**, R.D. TORRES, P. SOARES, Pontificia Universidade Católica do Paraná, Brazil, J. GILBERT, S. MALI, Syracuse University, NY, US	**E1-2-7 Invited** Local Friction of Rough Contact Interfaces with Rubbers using Contact Imaging Approaches, **A. CHATEAUMINOIS**, C. FRETIGNY, ESPCI / CNRS, Paris, France
3:50 pm	**D2-2-8** Microstructure And Physical Properties Of Thermal Spraying AZO Coatings, **M.S. LEU**, Material and Chemical Research Laboratories, Industrial Technology Research Institute, Taiwan	Invited talk continued.
4:10 pm	**D2-2-9 Invited** Significance of Corrosion and Tribocorrosion in Dentistry, **V. BARÃO**, University of Campinas (UNICAMP), Piracicaba Dental School, Brazil, M. MATHEW, Rush University Medical Center, US, L. FAVERANI, W. ASSUNÇÃO, Sao Paulo State University (UNESP), Brazil, J. YUAN, University of Illinois at Chicago, US, M.F. MESQUITA, University of Campinas (UNICAMP), Piracicaba Dental School, Brazil, C. SUKOTJO, University of Illinois at Chicago, US	**E1-2-9** The Role of Mechanical Property Mismatch Between Film and Substrate on the Tribology Behavior of (Ti,Al,Si)N Coated Systems, **X. HUANG**, T.M. SHAO, State Key Laboratory of Tribology, Tsinghua University, China
4:30 pm	Invited talk continued.	**E1-2-10** Stress Analysis of TiSiN Coatings Using Scratch Testing and Raman Spectroscopy, **J. RESTREPO**, Universidad Nacional Autónoma de México - Instituto de Investigaciones en Materiales, Mexico, E. CAMPS, Instituto Nacional de Investigaciones Nucleares, Mexico, S. MUHL, Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Mexico
4:50 pm		**E1-2-11** Tribology of Silica Nanoparticle-Reinforced Hydrophobic Sol-Gel Derived Composite Coatings, **D. BANERJEE**, A. KESSMAN, E. CHAMBERS, K. SIERROS, D. CAIRNS, West Virginia University, US
5:10 pm		**E1-2-12** Friction Effects During the Extrusion of Al Alloy Through Severe Plastic Deformation, **A. SAHAI**, K. HANSRAJ, Dayalbagh Educational Institute, Agra, India
	Exhibition Hall Opens Today **Town & Country/San Diego/Golden West** **12:00 -7:00 pm** **Enjoy lunch in the Exhibition Hall 12:15 pm**	**Exhibition Reception** **TC/SD/GW 5:30-7:00 pm** **Drinks compliments of Plansee**

Tuesday Afternoon, April 29, 2014

	New Horizons in Coatings and Thin Films Room: Royal Palm 4-6 - Session F2-2 High Power Impulse Magnetron Sputtering (HIPIMS) **Moderators: D. Lundin**, Université Paris-Sud 11, France, **S. Konstantinidis**, University of Mons, Belgium	Applications, Manufacturing, and Equipment Room: Tiki - Session G1 Innovations in Surface Coatings and Treatments **Moderators: M. Arndt,** OC Oerlikon Balzers AG, Liechtenstein, **C. Metzner**, Fraunhofer FEP, Germany
1:30 pm		
1:50 pm	**F2-2-2** HiPIMS Deposition of Titania Coatings for Photocatalytic Applications, **G. WEST**, Dalton Research Institute, Manchester Metropolitan University, UK, M. RATOVA, Queen's University, UK, P. KELLY, Dalton Research Institute, Manchester Metropolitan University, UK	
2:10 pm	**F2-2-3 Invited** Reactive HiPIMS of Oxides: Discharge Current Evolution and Hysteresis Behaviour, **T. KUBART**, Uppsala University, Angstrom Laboratory, Sweden, D. LUNDIN, Université Paris-Sud 11, France, U. HELMERSSON, Linköping University, IFM, Plasma and Coatings Physics, Sweden	**G1-3** Engineered Coatings for Machining High Temperature Alloys and Stainless Steel, **A. INSPEKTOR**, C. MCNERNY, M. ROWE, M. BEBLO, N. WAGGLE, Kennametal Incorporated, US
2:30 pm	Invited talk continued.	**G1-4** State-of-the-Art in Al_2O_3 Deposition by Industrial-Scale Dual Magnetron Sputtering, **D. DIECHLE**, V. SCHIER, Walter AG, Germany
2:50 pm	**F2-2-5** Chopped-HiPIMS for the Deposition of Films of Ti, TiN and Ti-Si-N, **P. BARKER**, J. PATSCHEIDER, EMPA (Swiss Federal Laboratories for Materials Science and Technology), Switzerland	**G1-5 Invited** Coating Design at Work, **J. RECHBERGER**, Fraisa SA, Switzerland
3:10 pm	**F2-2-6** Cr and CrN Thin Films Deposited by HiPIMS-DOMS, **J.C. OLIVEIRA**, F. FERREIRA, R. SERRA, A. CAVALEIRO, SEG-CEMUC, University of Coimbra, Portugal	Invited talk continued.
3:30 pm	**F2-2-7** Effect of Synchronized Pulsed BIAS on the Properties of Reactive HiPIMS Sputtered Al-Cr-N Thin Films, **G MARK**, J. LOEFFLER, M. MARK, MELEC GmbH, Germany	**G1-7** A Novel Mathematical Approach to Surface Engineering Subject to Blistering, **M.H. NAZIR**, Z. KHAN, M. HADFIED, Bournemouth University, UK
3:50 pm	**F2-2-8** The Influence of Deposition Parameters on the Structure and Properties of Aluminum Nitride Coatings Deposited by High Power Impulse Magnetron, **C.T. CHANG**, Y.C. YANG, National Taipei University of Technology, Taiwan, J.W. LEE, Ming Chi University of Technology, Taiwan	**G1-8** Wettability Control of Nano-columnar DLC Coating by Electron Beam Post-Treatment, **T. AIZAWA**, Shibaura Institute of Technology, Japan, F. HOE, University Malaysia Technology, Malaysia
4:10 pm	**F2-2-9** Investigation of Negative Ions in Reactive HIPIMS Discharges Operating in Different Inert Gases, M. BOWES, The University of Liverpool, UK, **P. KELLY**, Surface Engineering Group, Manchester Metropolitan University, UK, J. BRADLEY, University of Liverpool, UK	
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Wednesday Morning, April 30, 2014

	Coatings for Use at High Temperatures **Room: Sunrise - Session A1-1** **Coatings to Resist High Temperature Oxidation, Corrosion and Fouling** **Moderators: M. Weaver**, The University of Alabama, US, **V. Kolarik**, Fraunhofer Institute for Chemical Technology ICT, Germany, **D. Litton**, Pratt & Whitney, US	**Hard Coatings and Vapor Deposition Technology** **Room: Royal Palm 1-3 - Session B4-1** **Properties and Characterization of Hard Coatings and Surfaces** **Moderators: C. Mulligan**, US Army ARDEC, Benet Laboratories, US, **J. Lin**, Southwest Research Institute, US, **U. Beck**, BAM Berlin, Germany
8:00 am	**A1-1-1** Modification of Aluminide Bond Coatings for EB-PVD TBCs with Pd and Pt Using a Novel CHC-PVD Method, **R. SWADZBA**, Institute for Ferrous Metallurgy, Poland, T. JUNG, Fraunhofer IST, Germany, U. SCHULZ, DLR - Deutsches Zentrum für Luft- und Raumfahrt, Germany, L. SWADZBA, M. HETMANCZYK, B. MENDALA, B. WITALA, Silesian University of Technology, Poland	**B4-1-1** Development of a Systematical Methodology for Predicting Coated Milling Tools' Efficiency Including its Qualification Based on a Comparison of PVD-Coatings Deposited by the DC- and HIPIMS-Process, M. BUSCH, F. KLOCKE, T. BERGS, **M. OTTERSBACH**, Fraunhofer Institute for Production Technology IPT, Germany, K.-D. BOUZAKIS, E. BOUZAKIS, Aristoteles University of Thessaloniki, Greece
8:20 am	**A1-1-2** Modeling of the Interdiffusion Between a γ- Ni-Al Alloy and a Pt Coating for Thermal Barrier Coating System Applications, **P. AUDIGIÉ**, A. ROUAIX-VANDE PUT, CIRIMAT, University of Toulouse, France, A. MALIÉ, S. HAMADI, Snecma, SAFRAN Group, France, D. MONCEAU, CIRIMAT, University of Toulouse, France	**B4-1-2** Origin of Compressive Stress in CVD TiB_2 Hard Coatings, **N. SCHALK**, C. MITTERER, J. KECKES, Montanuniversität Leoben, Austria, C. CZETTL, Ceratizit Austria GmbH, Austria, M. PENOY, C. MICHOTTE, Ceratizit Luxembourg S.àr.l., Luxembourg
8:40 am	**A1-1-3** Role of Boron on Oxidation Behavior of NiCrAlYHfTi Alloy in H_2O and CO_2 Environments, **K.A. UNOCIC**, B.A. PINT, Oak Ridge National Laboratory, US	**B4-1-3 WITHDRAWN** Effect of Zr on Thermal Stability and Oxidation Resistance of Cr-Al-N, **L. CHEN**, Central South University, China
9:00 am	**A1-1-4** Effect of Overaluminizing on Microstructure and High-temperature Degradation of a CoNiCrAlY Coating, **D. NAUMENKO**, A. JALOWICKA, Forschungszentrum Jülich GmbH, Germany, M. ERNSBERGER, R. HERZOG, MAN Diesel & Turbo SE, Germany, L. SINGHEISER, W.J. QUADAKKERS, Forschungszentrum Jülich GmbH, Germany	**B4-1-4** An In-situ Study of the Fracture Toughness and Cracking Behaviour of the CrAlN/Si_3N_4 Nanocomposite Coatings, **S. LIU**, C.E. DAVIS, University of Cambridge, UK, X. ZENG, Singapore Institute of Manufacturing Technology, Singapore, W. CLEGG, University of Cambridge, UK **STUDENT AWARD FINALIST**
9:20 am	**A1-1-5** Comparison of the High Temperature Oxidation Behavior of the Nano and Conventional NiCrAlY Coatings Developed by LVOF Process, **N. RANA**, R. JAYAGANTHAN, S. PRAKASH, Indian Institute of Technology Roorkee, India	**B4-1-5** Mechanical Properties and Cutting Performance of MT-TiCN Coated Carbide Tools as a Funtion of Carbon Content, **A. PASEUTH**, H. FUKUI, S. OKUNO, H. KANAOKA, Sumitomo Electric Hardmetal Corp., Japan, Y. OKADA, Motherson Techno Tools Ltd.
9:40 am	**A1-1-6** Hot Corrosion Behavior of MCrAlY Coatings Containing Ru, Mo and Ir, **K. YUAN**, R. LIN PENG, Linköping University, Sweden, X.H. LI, Siemens Industrial Turbomachinery AB, Sweden, S. JOHANSSON, Linköping University, Sweden, Y.D. WANG, University of Science and Technology, Sweden	**B4-1-6** Influence of Oxygen Impurities on Structural, Mechanical Properties and Age Hardening of Ti-Al-N, **H. RIEDL**, Christian Doppler Laboratory for Application Oriented Coating Development at Vienna University of Technology, Austria, A. VLASOVA, Vienna University of Technology, Austria, R. RACHBAUER, Oerlikon Balzers Coating AG, Liechtenstein, S. KOLOZSVÁRI, Plansee Composite Materials GmbH, Germany, J. PAULITSCH, P.H. MAYRHOFER, Vienna University of Technology, Austria
10:00 am	**A1-1-7 Invited** Low Temperature Hot Corrosion of Disk Alloys, **J. NESBITT**, S. DRAPER, A. MARTONE, R. MILLER, J. SMIALEK, NASA Glenn Research Center, US	**B4-1-7** Structure, Mechanical and Adhesion Properties of CuZr Metallic Glass and CuZrN Nitride Thin Films, F. CHALLALI, F. TETARD, LSPM-CNRS, Université Paris 13, Sorbonne Paris-Cité, France, G. ABADIAS, Pprime Institute - UPR CNRS 3346 - Université de Poitiers - ENSMA - France, L. BELLIARD, UPMC, Paris,France, T. CHAUVEAU, O. BRINZA, **P. DJEMIA**, LSPM-CNRS, Université Paris 13, Sorbonne Paris-Cité, France
10:20 am	Invited talk continued.	**B4-1-8** Evaluation of Fracture Toughness of ZrN Hard Coatings using Internal Energy Induced Cracking, **J.-H. HUANG**, Y.-H. CHEN, G.P. YU, National Tsing Hua University, Taiwan
10:40 am	**A1-1-9** Nano-Structured Coatings For Supercritical Steam Turbines Applications, **F. PEREZ**, M. MATO, M. LASANTA, G. ALCALA, S. CASTAÑEDA, Universidad Complutense de Madrid, Spain	**B4-1-9** Modified W-S Coatings for Reducing Friction in Rubber Seal Applications, **A. MANAIA**, Instituto Pedro Nunes, Portugal, A. CAVALEIRO, Coimbra University, Portugal, T. POLCAR, University of Southampton, UK
11:00 am	**A1-1-10** Determination of the Sources of Intrinsic Stress-state for ß-NiAl Diffusion Coatings under Thermo-cyclic Oxidizing Conditions, **C. OSKAY**, M. GALETZ, M. RUDOLPHI, M. SCHÜTZE, DECHEMA-Forschungsinstitut, Germany	**B4-1-10** Effect of Annealing Treatment on Sputtered Cobalt Sensing Response Toward Inorganic Phosphate Ion, **Z. ENDUT**, MIMOS Berhad, Malaysia, M. HAMDI, W.J. BASIRUN, University of Malaya, Malaysia, A.Z. ABDULLAH, N.A. RAIS, MIMOS Berhad, Malaysia
11:20 am	**A1-1-11** Oxidation Resistance of Low Velocity Oxy Fuel Sprayed Al_2O_3-13TiO_2 Coating on Nickel Based Superalloys at 800ºC, N.K. MISHRA, **S.B. MISHRA**, R. KUMAR, MNNIT Allahabad, India	**B4-1-11** Mechanical and Electrochemical Behaviour of TiN and TiCN Deposited on XC48 Steel Substrates by Magnetron Sputtering, **N. SAOULA**, Division des Milieux Ionisés et Lasers, CDTA, Algeria
11:40 am	**A1-1-12** Influence of Process Parameters on the Microstructure of Aluminide Coatings Obtained by VPA on Directionally Solidified NI Superalloy, **B. WITALA**, L. SWADZBA, M. HETMANCZYK, B. MENDALA, G. MOSKAL, Silesian University of Technology, Poland, R. SWADZBA, Institute for Ferrous Metallurgy, Poland, L. KOMENDERA, Subcarpathian Aviation Cluster, Poland	
	Exhibition Hall Closes Today **Town & Country/San Diego/Golden West** **Wednesday, 10:00 am-2:00 pm** **Enjoy lunch in the Exhibition Hall 12:15 pm**	

Wednesday Morning, April 30, 2014

	Hard Coatings and Vapor Deposition Technology Room: Royal Palm 4-6 - Session B6	Advanced Materials for Modern Device Applications Room: Sunset - Session C4-2
	Coating Design and Architectures **Moderators: R. Daniel**, Montanuniversität Leoben, Austria, **S. Ulrich**, Karlsruhe Institute of Technology (KIT), Germany	**Thin Films for Energy Related Application** **Moderators: K. Yu**, Lawrence Berkeley National Laboratory, US, **J. Partridge**, RMIT University, Australia
8:00 am	**B6-1 Invited** Advances in Design and Architecture of TM-Al-N based Coatings for Severe Applications, **P.H. MAYRHOFER**, Vienna University of Technology, Austria	**C4-2-1** Study of Al_xO_{1-x} /Ti Thin-film System by Complex of Methods, A. NIKITENKOV, **N. NIKITENKOV**, Y. TYURIN, I. DUSHKIN, V. SYPCHENKO, O. VILHIVSKAYA, Tomsk Polytechnical University, Russian Federation
8:20 am	Invited talk continued.	**C4-2-2** Effect of Flow-channel Machining Condition on Coatings of AISI 1045 Steel Plate by Pack Chromization, **L.C. TSAI**, C.J. WANG, National Taiwan University of Science and Technology, Taiwan, C.T. YEH, M.D. GER, Chung Cheng Institute of Technology, National Defense University, Taiwan
8:40 am	**B6-3** Nonmetal Sublattice Population Induced Defect Structure in Transition Metal Aluminum Oxynitrides, K.P. SHAHA, H. RUEB, S. ROTERT, M. TO BABEN, D. MUSIC, **J. SCHNEIDER**, RWTH Aachen University, Germany	**C4-2-3 Invited** Zinc Oxide UV Photodetectors for use in Melanoma and Vitamin D Studies, **MW. ALLEN**, University of Canterbury, New Zealand
9:00 am	**B6-4** Theoretical Investigation of Phase Stability and Electronic Structure of Ordered and Disordered $Ti_{1-x}Mg_xN_y$ Alloys, **B. ALLING**, Linköping University, IFM, Thin Film Physics Division, Sweden	Invited talk continued.
9:20 am	**B6-5** Roads to Tougher Nanostructured Coatings for Cutting at Intermediate Temperatures, **M. MORSTEIN**, A. LÜMKEMANN, PLATIT AG, Switzerland, B. TORP, PLATIT Inc., US	**C4-2-5** Optimization of the Light Scattering Characteristics of Surface-textured AZO Films Prepared by Magnetron Sputtering, T. MINAMI, **T. MIYATA**, T. YAMANAKA, Kanazawa Inst. of Tech., Japan, J. NOMOTO, Kochi Univ. of Tech., Japan
9:40 am	**B6-6** Chemical and Structural Design Concepts for Increasing the Oxidation Resistance of Ti-Al-N based Coatings, **R. HOLLERWEGER**, Vienna University of Technology, Austria, D. HOLEC, Montanuniversität Leoben, Austria, M. ARNDT, R. RACHBAUER, Oerlikon Balzers Coating AG, Liechtenstein, P. POLCIK, Plansee Composite Mat. GmbH, Germany, J. PAULITSCH, P.H. MAYRHOFER, Vienna Univ. of Tech., Austria	**C4-2-6** Experimental and Theoretical Investigation of ScN-based Solid Solution for Thermoelectric Applications, **S. KERDSONGPANYA**, B. ALLING, P. EKLUND, Thin Film Physics Division, IFM, Linköping University, Sweden
10:00 am	**B6-7 Invited** Strategies for Knowledge-based Design of Thin Film Architecture at the Nanoscale, **K. SARAKINOS**, IFM Linköping University, Sweden	**C4-2-7** Processing and Characterization of Multilayer ZnO/Al doped ZnO Nanostrcutured Films, R. JAYAGANTHAN, IIT Roorkee, India, **A. RAHMAN**, NIT Srinagar, India
10:20 am	Invited talk continued.	**C4-2-8** Combinatorial Sputtering Exploration of Zn-Sn-O (ZTO) Composition Spreads, **S.Y. LI**, National Cheng Kung University, Taiwan, J.-M. TING, K.S. CHANG, National Central University, Taiwan
10:40 am	**B6-9** A Study of AlCr-based Coatings Deposited by Magnetron Sputtering Using Powder Metallurgical Targets, **S. KOLOZSVÁRI**, P. POLCIK, PLANSEE Composite Materials GmbH, Germany	**C4-2-9** Improved Thermal Stability of Bismuth Oxide Thin Films Presenting the Delta-cubic Phase, C.L. GOMEZ, O. DEPABLOS, P. SILVA-BERMUDEZ, S. MUHL, Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de Mexico, Mexico, A. ZEINERT, Laboratoire de Physique de la Matière Condensée, Université de Picardie Jules Verne, France, E. CAMPS, Instituto Nacional de Investigaciones Nucleares de Mexico, Mexico, **S.E. RODIL**, Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Mexico
11:00 am	**B6-10 Invited** Assessment of the Mechanical Performance of Oxide Coatings on Stainless Steels and Titanium Alloys in Corrosive Environments, **D.F. BAHR**, Purdue University, S.K. LAWRENCE, Purdue University, US, D. ADAMS, N.R. MOODY, Sandia National Laboratories, US, M. PANG, K.R. MORASCH, Washington State University, US	**C4-2-10 WITHDRAWN** Effect of Substrate and Surfactant over the Crystallization, Growth and Luminescence of ZnO Coatings, **S. BRAHMA**, National Cheng Kung University, Taiwan, S.A. SHIVASHANKAR, Indian Institute of Science Bangalore, India, J.-M. TING, National Cheng Kung University, Taiwan
11:20 am	Invited talk continued.	**C4-2-11** Characteristics of Optoelectronic Properties of AZO/Au/AZO Multilayer Thin Films Prepared by RF Magnetron Sputtering and Ion Sputtering for Transparent Electrode, **C.H. CHU**, National Cheng Kung University, Taiwan, H.W. WU, Kun Shan University, Taiwan, J.L. HUANG, National Cheng Kung University, Taiwan
11:40 am	**B6-12** The Enhanced Photothermal Phenomena of SiO2-Ag and TiO2-Ag Multi-layered Thin Film Structures and its use for the Annealing of TaN-(Ag,Cu) Thin Film, J.H. HSIEH, **Y.T. SU**, Ming Chi University of Technology, Taiwan, C. LI, National Central University, Taiwan	**C4-2-12** Characterization of 1,4-Bis-(2-dimethylaminoethylamino)-9,10-anthraquinione Films Based Molecular Device by Thermal Evaporation Technique, **S. BHATIA**, Kanya Maha Vidyalaya, India, R.K. BEDI, Guru Nanak Dev University, India

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Wednesday Morning, April 30, 2014

	Tribology & Mechanical Behavior of Coatings and Engineered Surfaces **Room: California - Session E1-3** **Friction, Wear, and Lubrication: Effects and Modeling** **Moderators: M. Chandross**, Sandia National Laboratories, US, **O.L. Eryilmaz,** Argonne National Laboratory, US, **K. Polychronopoulou**, Khalifa University of Science, Technology & Research, UAE	**Topical Symposia** **Room: Tiki - Session TS3** **Energetic Materials and Micro-structures for Nanomanufacturing** **Moderators: D. Adams**, Sandia National Laboratories, US, **C. Rossi**, LAAS-CNRS, France
8:00 am	**E1-3-1** Load Dependence of the Tribological Properties of Silver Tantalate Coatings at Elevated Temperatures, **S.M. AOUADI**, D. STONE, C. PAKSUNCHAI, C. CHANTHARANGSI, University of North Texas, US, H. GAO, University of California Merced, US, T. SCHARF, University of North Texas, US, A. MARTINI, University of California Merced, US	**TS3-1 Invited** 2-Tetrazene Derivatives as New Energetic Materials, Synthesis, Characterization and Energetic Properties, **C. MIRÓ SABATÉ**, H. DELALU, Universite de Lyon, France
8:20 am	**E1-3-2** Development of a New Instrument for Complex Micro-scale Abrasion Test, **G. MONTESANTI**, M. RENZELLI, University of Rome "Roma Tre", Italy, C. DI CESARE, Scienzia Machinale Srl, Italy, E. BEMPORAD, University of Rome "Roma Tre", Italy	Invited talk continued.
8:40 am	**E1-3-3 Invited** Surface Films at Tribo-interface in Hydrogen Gas, **J. SUGIMURA**, Kyushu University, Japan	**TS3-3** Detonation in Vapor-deposited Explosive Films at the Micro-scale, **R. KNEPPER**, M. MARQUEZ, A. TAPPAN, Sandia National Laboratories, US
9:00 am	Invited talk continued.	**TS3-4** Engineered Microstructures of Binary Energetic Thermites by Additive Micro-manufacturing Methods: Fabrication, Characterization and Performance, **K. SULLIVAN**, C. ZHU, J. KUNTZ, E. DUOSS, A. GASH, C. SPADACCINI, Lawrence Livermore National Laboratory, US
9:20 am	**E1-3-5** Friction Behavior at the Nanoscale of Nitrided and Post-oxidized Plain Steel, M. FREISLEBEM, C. MENEZES, F. COSTI, P. FERREIRA, C. AGUZZOLI, I. BAUMVOL, **C. FIGUEROA**, Universidade de Caxias do Sul, Brazil	**TS3-5 Invited** Revealing the Reaction Dynamics and Phase Evolution in Self-propagating Reactive Nanolaminates using Movie Mode DTEM, **T. LAGRANGE**, Lawrence Livermore National Laboratory, US, D. ADAMS, R. REEVES, Sandia National Laboratories, US, B.W. REED, G.H. CAMPBELL, Lawrence Livermore National Laboratory, US
9:40 am	**E1-3-6** Hardfacing Using Low Cost Ferro-alloy Powder Mixtures by Submerged Arc Welding, R. ZAHIRI, R. SUNDARAMOORTHY, **C. SUBRAMANIAN**, Black Cat Blades Ltd., Canada	Invited talk continued.
10:00 am	**E1-3-7** 3-D FIB Serial Sectioning to Determine Solidification and Wear Mechanisms in Laser Deposited Metal-Ceramic Coatings, J.E. MOGONYE, H. MOHSENI, R. BANERJEE, **T. SCHARF**, University of North Texas, US	**TS3-7** Effect of Mixing Conditions on Reaction Propagation for Blade Cast Energetic Thin Films, **K. MEEKS**, J. CANO, Texas Tech University, US, M. PANTOYA, Texas Tech University. US, A. APBLETT, Sandia National Laboratories, US
10:20 am	**E1-3-8** Tribological Behaviour of CrN Coating in Lubricated Contact, **B. PODGORNIK**, M. SEDLAČEK, M. GODEC, Institute of Metals and Technology, Slovenia	**TS3-8** Reaction Instabilities In Cobalt/Aluminum Nanolaminates Made By Sputter Deposition, D. ADAMS, **R. REEVES**, Sandia National Laboratories, US
10:40 am	**E1-3-9** The Effect of Adhesion-mitigating Coatings on Rolled Aluminum Surface Quality, **O.A. GALI**, Uinveristy of Windsor, Canada, M. SHAFIEI, J.A. HUNTER, Novelis Global Research and Technology Center, US, A.R. RIAHI, University of Windsor, Canada	**TS3-9** Modelling Al-based Reactive Nanolaminates Growth: Dealing with Hyperthermal Trajectories through Combined DFT and Kinetic Monte Carlo Techniques, **A. ESTEVE**, LAAS-CNRS, France
11:00 am	**E1-3-10 Invited** Ab Initio Investigation of Atomistic Mechanisms in Solid and Boundary Lubrication, **RIGHI**, CNR - Istituto Nanoscienze S3, Universita' di Modena e Reggio Emilia via Campi, Italy	**TS3-10** Interface-layer Formation in Reactive Al-based Thin Films Studied by Spectroscopy, First Principle Calculation and Nanocalorimetry, **Y. LU**, University of Texas at Dallas, US, L. GLAVIER, C. ROSSI, A. ESTEVE, A. HEMERYCK, LAAS-CNRS, France, Y. CHABAL, University of Texas at Dallas, US
11:20 am	Invited talk continued.	**TS3-11** Spark Ignitable NiAl Ball Milled Powders and Use Thereof for Bonding Applications, A. KYRIAKOU, V. HADJISOFOKLEOUS, University of Cyprus, Cyprus, I.E. GUNDUZ, Purdue University, US, A. HADJIAFXENTI, T. KYRATSI, C.C. DOUMANIDIS, **C. REBHOLZ**, University of Cyprus, Cyprus
11:40 am	**E1-3-12** Effect of Nitrogen Injection Surface Layer on the Tribological Performance of M50 Steel Tribo-parts, **B. PENG**, The First Research Academy of China Aerospace Science and Technology Corporation, China, C. ZHANG, Harbin Institute of Technology, China, L. JIA, L. CHI, The First Research Academy of China Aerospace Science and Technology Corporation, China, L. WANG, Harbin Institute of Technology, China	**TS3-12** Reactions in Single Ball-milled Particles of Ni/Al System, **I.E. GUNDUZ**, BA. MASON, Purdue University, US, LJ. GROVEN, South Dakota School of Mines and Technology, US, S. SON, Purdue University, US
	Exhibition Hall Closes Today **Town & Country/San Diego/Golden West** **Wednesday, 10:00 am-2:00 pm** **Enjoy lunch in the Exhibition Hall 12:15 pm**	

Wednesday Afternoon, April 30, 2014

	Coatings for Use at High Temperatures **Room: Sunrise - Session A1-2** **Coatings to Resist High Temperature Oxidation, Corrosion and Fouling** **Moderators: M. Weaver**, The University of Alabama, US, **V. Kolarik**, Fraunhofer Institute for Chemical Technology ICT, Germany, **D. Litton**, Pratt & Whitney, US	**Hard Coatings and Vapor Deposition Technology** **Room: Royal Palm 1-3 - Session B4-2** **Properties and Characterization of Hard Coatings and Surfaces** **Moderators: C. Mulligan**, US Army ARDEC, Benet Laboratories, US, **J. Lin**, Southwest Research Institute, US, **U. Beck**, BAM Berlin, Germany
1:30 pm	**A1-2-1 Invited** Some Results About the Interactions Between Reactivity, Interdiffusion and Creep in Coated Thin Wall Superalloy Systems, **D. MONCEAU**, E. ANDRIEU, CIRIMAT laboratory, University of Toulouse, France, S. DRYEPONDT, CIRIMAT laboratory, University of Toulouse, France; present address: ORNL, US, A. RAFFAITIN, CIRIMAT laboratory, University of Toulouse, France; present address: AIRBUS, France, D. TEXIER, CIRIMAT laboratory, University of Toulouse, France; present address: ENSMA, France	
1:50 pm	Invited talk continued.	
2:10 pm	**A1-2-3** Characterization of the Gradient of Mechanical and Physical Properties Existing in β-NiAlPt Coated Ni-based Single Crystal Superalloy by using Ultrathin Specimens, **D. TEXIER**, E. ANDRIEU, CIRIMAT, France, S. SELEZNEFF, A. LONGUET, Snecma, SAFRAN Group, France, D. MONCEAU, CIRIMAT, France	**B4-2-3** Observation of Hardness and Fracture Toughness Enhancement in Fe/VC Multilayer Films with Coherent Interfaces, C. WANG, Northwestern Polytechnical University, China, J.M. PUREZA, Universidade do Estado de Santa Catarina, Brazil, **Y.W. CHUNG**, Northwestern University, US
2:30 pm	**A1-2-4** The Effect of a Cr Adhesion Layer on the Protective Behavior of Al_2O_3 Coatings Against Metal Dusting, E. URIBE-LAM, O. SALAS, D. MELO-MAXIMO, ITESM-CEM, Mexico, L. MELO-MAXIMO, IPN, Mexico, J. OSEGUERA, ITESM-CEM, Mexico, **R.D. TORRES**, PUCPR, Brazil, R. DE SOUZA, USP, Brazil	**B4-2-4 Invited** Using High Temperature Nanomechanics in Coating Design for Improved Wear Resistance in Extreme Frictional Environments, **B. BEAKE**, Micro Materials Ltd., UK, G. FOX-RABINOVICH, McMaster University, Canada
2:50 pm	**A1-2-5 Invited** The Use of Advanced Surface Analytical Techniques to Investigate Early Oxidation Stages of Aluminides, **P. MARCUS**, Chimie ParisTech (ENSCP), France	Invited talk continued.
3:10 pm	Invited talk continued.	**B4-2-6** In-situ X-Ray Scattering Study of the Cubic to Hexagonal Transformation of AlN in $Ti_{1-x}Al_xN$, **N. NORRBY**, L. ROGSTRÖM, Linköping University, Sweden, M. JOHANSSON-JÕESAAR, Seco Tools AB, Sweden, N. SCHELL, Helmholtz-Zentrum Geesthacht, Germany, M. ODÉN, Linköping University, Sweden
3:30 pm	**A1-2-7** Study of the Electrochemical Behaviour of Aluminized Steel, **B. LEMMENS**, Ghent University, Belgium, B. CORLU, J. DE STRYCKER, Arcelor Mittal Global R&D Gent, Belgium, I. DE GRAEVE, Vrije Universiteit Brussel, Belgium, K. VERBEKEN, Ghent University, Belgium	**B4-2-7** Microstructural Study of Thermal Spray Pseudo-alloy Coatings Using X-ray Diffraction (XRD), **E.A. LOPEZ COVALEDA**, Universidad Nacional de Colombia
3:50 pm	**A1-2-8** Effects of Ceramic Particle Size on Corrosion Behaviors of Cold Sprayed SiC_p/Al 5056 CComposited Coatings, **Y.Y. WANG**, B. NORMAND, N. MARY, Insa De Lyon, France, H. LIAO, UTBM, France	**B4-2-8** Characteristic Change of Hydrogen Permeation in Stainless Steel Plate by BN Coating, **M. TAMURA**, The University of Electro-Communications, Japan
4:10 pm	**A1-2-9** Corrosion Resistance of Ni Coatings on Steel Deposited with Electrolytic Plasma Processing, **A. SMITH**, E. MELETIS, University of Texas at Arlington, US	**B4-2-9** Influence of Modulation Period on Properties of TiN/Ta Multilayer Films, **H.F. SHANG**, T.M. SHAO, Tsinghua University, China
4:30 pm	**A1-2-10** Effects of Mg on Morphologies and Properties of Hot Dipped Zn-Mg Coatings, **C.Z. YAO**, S.L. TAY, T.P. ZHU, W. GAO, The University of Auckland, New Zealand	**B4-2-10** Characterization, Mechanical Properties, Wear and Scratch Test Resistance of Various Commercial and Lab-developed Electroless Nickel Deposits, V. VITRY, **F. DELAUNOIS**, University of Mons, Belgium
4:50 pm	**A1-2-11** Influence of Ruthenium as an Alloying Element on the Corrosion Behaviour of Laser Treated AISI 316-NiTi, **B.A. OBADELE**, M.L. LEPULE, P.A. OLUBAMBI, Tshwane University of Technology, South Africa	**B4-2-11** In-situ TiNi/Al_2O_3/Fe Functional Composite Coating Using Hybrid Centrifugal Assisted Combustion Synthesis, R. MAHMOODIAN, Centre of Advanced Manufacturing and Material Processing (AMMP), Malaysia, **M. HAMDI**, University of Malaya, Malaysia
5:10 pm	**A1-2-12** Microstructure, Mechanical and Anti-corrosion Property Evaluation of Iron-based Thin Film Metallic Glasses, **L.T. CHEN**, Y.C. YANG, National Taipei University of Technology, Taiwan, J.W. LEE, Ming Chi University of Technology, Taiwan	**B4-2-12** Properties of Hybrid Satellite/W(WC) and Colmonoy/W(WC) Coating Systems, L. VERNHES, Velan, Canada, **M. AZZI**, Notre Dame University-Louize, Lebanon, J.E. KLEMBERG-SAPIEHA, École Polytechnique de Montréal, Canada
	Exhibition Hall Closes Today **Town & Country/San Diego/Golden West** **Wednesday, 10:00 am-2:00 pm**	**Awards Convocation-5:45 pm** **Golden West Room** **Honorary Lecturer-Dr. Jindrich Musil** **"Advanced Hard Nanocomposite Coatings with Unique Properties"** **Awards Reception will follow the Convocation at 7:30 pm** **Poolside**

Wednesday Afternoon, April 30, 2014

	Advanced Materials for Modern Device Applications **Room: Sunset - Session C5-1** **Thin Films for Active Devices** **Moderator: F. Tasnadi,** Linköping University, Sweden	**Tribology & Mechanical Behavior of Coatings and Engineered Surfaces** **Room: California - Session E2-3** **Mechanical Properties and Adhesion** **Moderators: J. Michler**, EMPA (Swiss Federal Laboratories for Materials Science and Technology), Switzerland, **R. Chromik**, McGill University, Canada, **D.F. Bahr**, Purdue University, US
1:30 pm	**C5-1-1 Invited** Recent Progress in Understanding Free-charge Carrier and Structural Properties of InN Thin Films, **V. DARAKCHIEVA**, Linköping University, IFM, Sweden	
1:50 pm	Invited talk continued.	**E2-3-2** High Temperature Creep of Gas Turbine Coatings, **J. DAVENPORT**, University of Cambridge, UK, M. HANCOCK, Rolls-Royce plc, UK, R. STEARN, W. CLEGG, University of Cambridge, UK
2:10 pm	**C5-1-3** Carrier Transport in Undoped CdO Films Grown by Atmospheric-pressure Chemical Vapor Deposition, **T. TERASAKO**, K. OHMAE, S. SHIRAKATA, Ehime University, Japan	**E2-3-3 Invited** High Temperature Yield Stress of Hard Coatings, **J.M. WHEELER**, R. RAGHAVAN, V. CHAWLA, EMPA (Swiss Federal Laboratories for Materials Science and Technology), Switzerland, M. MORSTEIN, PLATIT AG, Switzerland, J. MICHLER, EMPA (Swiss Federal Laboratories for Materials Science and Technology), Switzerland
2:30 pm	**C5-1-4 WITHDRAWN** Bipolar Resistive Switching in Zr-doped SiO_2 for RRAM Applications, **K.C. CHANG**, T.M. TSAI, T.C. CHANG, G.R. LIU, Y.C. PAN, National Sun Yat-Sen University, Taiwan, S.M. SZE, National Chiao Tung University, Taiwan	Invited talk continued.
2:50 pm	**C5-1-5** Investigating in Via-Contact-Type Amorphous Indium-Gallium-Zinc-Oxide Thin Film Transistors Two-Stage Rise Capacitance-Voltage Characteristics Degradation in Different Environment, **J.C. JHU**, T.C. CHANG, National Sun Yat-Sen University, Taiwan, G.W. CHANG, Y.H. TAI, National Chiao Tung University, Taiwan	**E2-3-5** Temperature Dependent Energy Loss and Internal Friction Measurement in Nanocrystalline Metal Thin Films, Y.-T. WANG, Y.-C. CHENG, F.-J. HSU, **M.-T. LIN**, National Chung Hsing University, Taiwan
3:10 pm	**C5-1-6 WITHDRAWN** Deposition and Characterization of Germanium Thin Films for Active Device Applications, H. MOHAMMED, M. DEBERRY, U. OBAHIAGBON, O. AKPA, **N. KORIVI**, K. DAS, Tuskegee University, US	**E2-3-6** Ni-Bi Composite Coatings Produced by Ionic Co-discharge Electrodeposition, **S.L. TAY**, C.Z. YAO, The University of Auckland, New Zealand, W. CHEN, Beijing Institute of Technology, China, W. GAO, The University y of Auckland, New Zealand
3:30 pm	**C5-1-7** Device Applications of Energetically Deposited Metal Oxide and Carbonaceous Thin Films, **J. PARTRIDGE**, E. MAYES, B. MURDOCH, M. KRACICA, RMIT University, Australia, S. ELZWAWI, MW. ALLEN, University of Canterbury, New Zealand, M. BILEK, University of Sydney, Australia, D. MCCULLOCH, RMIT University, Australia	**E2-3-7** Synthesis and Thermal Stability of Gold-Zinc Oxide Nano-Composite Thin Films for Electrical Contacts, **R.S. GOEKE**, J. MOGONYE, N. ARGIBAY, S.V. PRASAD, Sandia National Laboratories, US
3:50 pm	**C5-1-8** Bipolar Memristive Properties of TiO_2 Thin Film on Pt/p^{++}Si, S. GULLULU, T. KARACALI, **H. EFEOGLU**, Ataturk University, Turkey	**E2-3-8 Invited** In Situ Biaxial Mechanical Testing of Metallic Thin Films on Stretchable Substrate: Synchrotron Diffraction Versus Image Correlation Analyses, **P.O. RENAULT**, E. LE BOURHIS, R. GUILLOU, University of Poitiers, France, P. GOUDEAU, CNRS, France, D. FAURIE, University of Paris 13, France, G. GEANDIER, CNRS/Universite Lorraine, France, C. MOCUTA, D. THIAUDIERE, SOLEIL Synchrotron, France
4:10 pm	**C5-1-9** Transparent Conductive and Structural Characterization of Pulsed-laser-deposited ZnO and Sn-doped ZnO Films for Nanorods Growth, **W.C. HUNG**, M. CHEN, Minghsin University of Science and Technology, Taiwan	Invited talk continued.
4:30 pm	**C5-1-10** Improved Multiferrioc Properties of $Bi_{0.9-x}Sm_xLa_{0.1}FeO_3$/$Pb(Zr_{0.52}Ti_{0.48})O_3$ Multilayers Prepared by Pulsed Laser Deposition, **R. BARMAN**, D. KAUR, Indian Institute of Technology Roorkee, India	**E2-3-10** Effect of Plasma Spraying Parameters on Microstructure and Mechanical Properties of Titania-doped Yttria-stabilized Zirconia, **S. LISCANO**, L. GIL, UNEXPO, Venezuela (Bolivarian Republic of)
4:50 pm	**C5-1-11** Large Polarization in Lead Free Ferroelectric Thin Films Fabricated by Pulsed Laser Deposition, **Y. KOLEKAR**, University of Pune, India, A. BHAUMIK, Missouri State University, US, C.V. C. V. RAMANA, University of Texas at El Paso, US, K. GHOSH, Missouri State University, US	**E2-3-11** Effect of Plasma Nitriding Species on the Surface Properties of Tool Steels, **P. ABRAHA**, Meijo University, Japan, J. MIYAMOTO, Toba National College of Maritime Technology, Japan
5:10 pm	**C5-1-12 WITHDRAWN** Structural, Optical and Electrical Properties of Transparent p-NiO/n-FTO Hetero-junction, **D. TATAR**, Atatürk University, Turkey, F. BAKAN, Sabancı University, Turkey, K. CINAR, E.E. SUKUROGLU, Y. TOTIK, B. DUZGUN, Atatürk University, Turkey	
	Exhibition Hall Closes Today **Town & Country/San Diego/Golden West** **Wednesday, 10:00 am-2:00 pm**	**Awards Convocation-5:45 pm** **Golden West Room** **Honorary Lecturer-Dr. Jindrich Musil** **"Advanced Hard Nanocomposite Coatings with Unique Properties"** **Awards Reception will follow the Convocation at 7:30 pm** **Poolside**

Wednesday Afternoon, April 30, 2014

	New Horizons in Coatings and Thin Films **Room: Royal Palm 4-6 - Session F4** **New Oxynitride and Oxide-based Coatings** **Moderators: W. Kalss**, Oerlikon Balzers Coating AG, Liechtenstein, **M. Stüber,** Karlsruhe Institute of Technology, Germany	**Topical Symposia** **Room: Tiki - Session TS2-1** **Advanced Characterization of Coatings and Thin Films** **Moderators: M. Sebastiani**, University of Rome "Roma Tre", Italy, **R. Ghisleni**, EMPA (Swiss Federal Laboratories for Materials Science and Tech.), Switzerland
1:30 pm		**TS2-1-1** Synchrotron Nanodiffraction and X-TEM on Al-Ti-N based Hard Coatings with Different Morphologies, **M. BARTOSIK**, Vienna University of Technology, Austria, R. RACHBAUER, Oerlikon Balzers Coating AG, Liechtenstein, C. KRYWKA, University of Kiel and Helmholtz Zentrum Geesthacht, Germany, C.M. KOLLER, J. BERNARDI, Vienna University of Technology, Austria, J. KECKES, Montanuniversität Leoben, Austria, P.H. MAYRHOFER, Vienna University of Technology, Austria
1:50 pm	**F4-2** Effect of Oxygen Incorporation on the Structure and Elasticity of Ti-Al-N-O Coatings Synthesized by Cathodic Arc and High Power Pulsed Magnetron Sputtering, **M. HANS**, M. TO BABEN, D. MUSIC, J. EBENHÖCH, RWTH Aachen University, Germany, D. PRIMETZHOFER, Uppsala University, Sweden, D. KURAPOV, Oerlikon Balzers Coating AG, Liechtenstein, M. ARNDT, H. RUDIGIER, OC Oerlikon Balzers AG, Liechtenstein, J. SCHNEIDER, RWTH Aachen University, Germany	**TS2-1-2** Predictive Power of First-principles Calculations for the Electron Energy Loss Spectroscopy, **D. HOLEC**, Montanuniversität Leoben, Austria, L. ZHOU, P.H. MAYRHOFER, Vienna University of Technology, Austria
2:10 pm	**F4-3** Magnetron Sputtering of p-type $AgFeO_2$ Thin Films with the Delafossite Structure Using a Combinatorial Approach, **U. JANSSON**, F. MAO, T. NYBERG, T. THERSLEFF, Uppsala University, Sweden	**TS2-1-3** Local Lattice Strain as Stabilizing Factor of Metastable fcc-(Ti,Al)N in Nanoscaled TiN/(Ti,Al)N/AlN Multilayers, **U. RATAYSKI**, D. CHMELIK, C. WÜSTEFELD, F. HANZIG, M. MOTYLENKO, Institute of Materials Science , TU Bergakademie Freiberg, Germany, C. BAEHTZ, Helmholtz-Zentrum Dresden-Rossendorf, Germany, M. ŠÍMA, SHM s.r.o., Germany, D. RAFAJA, Institute of Materials Science , TU Bergakademie Freiberg, Germany
2:30 pm	**F4-4** Influence of Si Doping on Process Stability and Coating Properties During Arc Deposition of $(Al, Cr)_2O_3$, **L. LANDÄLV**, Linköping University, IFM, Thin Film Physics Division and Sandvik Coromant R&D, Sweden, E. GÖTHELID, M. AHLGREN, Sandvik Coromant R&D, Sweden, L. HULTMAN, B. ALLING, P. EKLUND, Linköping University, IFM, Thin Film Physics Division, Sweden	**TS2-1-4** Nucleation and Initial Growth of sp^2-BN Thin Films by Chemical Vapor Deposition, **M. CHUBAROV**, Linköping University, IFM, Thin Film Physics Division, Sweden, H. PEDERSEN, Linköping University, Sweden, Z. CZIGANY, Hungarian Academy of Sciences, Research Centre for Natural Sciences, Hungary, H. HÖGBERG, A. HENRY, Linköping University, IFM, Thin Film Physics Division, Sweden
2:50 pm	**F4-5 Invited** Synthesis-structure-property Relations of Al-oxide-based Coatings, **J. PAULITSCH**, C.M. KOLLER, Vienna University of Technology, Austria, R. RACHBAUER, J. RAMM, Oerlikon Balzers Coating AG, Liechtenstein, P. POLCIK, PLANSEE Composite Materials GmbH, Germany, D. HOLEC, Montanuniversität Leoben, Austria, P.H. MAYRHOFER, Vienna University of Technology, Austria	**TS2-1-5** Recent Advances in Glow Discharge Optical Emission Spectrometry GD-OES for Material Characterization, **P. HUNAULT**, C. MORIN, HORIBA Scientific, US, P. CHAPON, Horiba Jobin Yvon S.A.S., France
3:10 pm	Invited talk continued.	**TS2-1-6** New Insights into the Contribution of Auger Spectroscopy Towards Energy Applications: Auger Recent Performance Improvements, Complementarity with XPS and ToF-SIMS, "Imaging Cluster" Approach, **E. DE VITO**, S. JOUANNEAU, E. RADVANYI, W. PORCHER, A. BORDES, J.P. BARNES, CEA Grenoble, France, P. MARCUS, Chimie ParisTech (ENSCP), France
3:30 pm	**F4-7** Structure and Electronic Properties of $AlCrO_xN_{1-x}$ Thin Films Deposited by Reactive Magnetron Sputtering, **H. NAJAFI**, A. KARIMI, EPFL, Switzerland, M. MORSTEIN, PLATIT AG, Switzerland	**TS2-1-7 Invited** Microstructure Control of Metal Thin Films by Ion Irradiation, **R. SPOLENAK**, ETH Zurich, Switzerland
3:50 pm	**F4-8** Stoichiometry Gap in MF Sputtered CrON Thin Films, **M. RENZELLI**, M. SEBASTIANI, E. BEMPORAD, University of Rome "Roma Tre", Italy, H. KAPPL, M. FENKER, FEM Forschungsinstitut Edelmetalle & Metallchemie, Germany	Invited talk continued.
4:10 pm	**F4-9** Influence of the Power Supplied in the Optical Properties of ZrO_xN_y/ZrO_2, **J.E. ALFONSO**, M.J. PINZÓN, J.J. OLAYA, G. CUBILLOS, Universidad Nacional de Colombia Bogotá, Colombia	**TS2-1-9** A Novel Instrument and Methodology for the In-Situ Measurement of the Stress in Thin Films, **D.M. BROADWAY**, NASA Marshal Space Flight Center, US, M.O. OMOKANWAYE, Massachusetts Institute of Technology, US, B.D. RAMSEY, NASA Marshal Space Flight Center, US
4:30 pm	**F4-10** Influence of the Annealing in the Corrosion Resistance of $Bi_xTi_yO_z$ Coatings Deposited on Ti6Al4V, **M.J. PINZÓN**, J.E. ALFONSO, J.J. OLAYA, Universidad Nacional de Colombia Bogotá, Colombia	**TS2-1-10** New Approach for Tailoring Mechanical Properties and Residual Stress of a-C:H:W Coatings, **C. SCHMID**, TU Darmststadt, Physical Metallurgy, Germany, H. HETZNER, F. HILPERT, University of Erlangen-Nürnberg, Germany, K. DURST, TU Darmststadt, Physical Metallurgy, Germany
4:50 pm	**F4-11** Characterization of Microstructure and Basic Properties of Plasma Sprayed Oxides Coatings Modified by Submicrocrystalline Powders of Different Oxides, G. MOSKAL, Silesian University of Technology, Poland, **S. POLIS**, SUT, Poland	**TS2-1-11** Process Control of TiCN Thin Films Deposited by Cathodic Arc Evaporation with Combined Raman and Optical Emission Spectroscopy, **G. LEACH**, Simon Fraser University, Canada, M.H. SHIH, MingDao University, Taiwan, T. BURAI, Simon Fraser University, Canada, B.H. HSIAO, MingDao University, Taiwan, X.Z. ZHANG, A.S. SCHIFFER, Simon Fraser University, Canada, J.H. HUNG, Aurora Scientific Corp, Canada, D.Y. WANG, MingDao University, Taiwan
	Exhibition Hall Closes Today **Town & Country/San Diego/Golden West** **Wednesday, 10:00 am-2:00 pm**	**Awards Convocation-5:45 pm** **Golden West Room** **Honorary Lecturer-Dr. Jindrich Musil** **"Advanced Hard Nanocomposite Coatings with Unique Properties"** **Awards Reception will follow the Convocation at 7:30 pm** **Poolside**

Thursday Morning, May 1, 2014

	Coatings for Use at High Temperatures **Room: Sunrise - Session A1-3** **Coatings to Resist High Temperature Oxidation, Corrosion and Fouling** **Moderators: M. Weaver**, The University of Alabama, US, **V. Kolarik**, Fraunhofer Institute for Chemical Technology ICT, Germany, **D. Litton**, Pratt & Whitney, US	**Hard Coatings and Vapor Deposition Technology** **Room: Golden West - Session B2** **CVD Coatings and Technologies** **Moderators: E. Blanquet**, SIMaP CNRS/Grenoble INP/UJF, France, **M. Shiratani**, Kyushu University, Japan
8:00 am	**A1-3-1** High Temperature Oxidation Behavior of Al2O3/ Al Composite Coating on γ-TiAl, **Y. XU**, Nanjing University of Aeronautics and Astronautics, Q. MIAO, Nanjing University of Aeronautics and Astronauticsg, China, W. LIANG, X. YU, L. WANG, Q. JIANG, B. REN, J. YANG, Nanjing University of Aeronautics and Astronautics, China	**B2-1 Invited** Pulsed Direct Liquid Injection CVD: a High Potential Process for Advanced and Nanostructured Carbide and Nitride Coatings, **F. MAURY**, A. DOUARD, G. BOISSELIER, CIRIMAT, France, F. SCHUSTER, CEA, France
8:20 am	**A1-3-2** High-Temperature Oxidation of Al-Hf and Al-Hf-O Coatings, X. MAEDER, CSEM SA, Switzerland, M. DÖBELI, ETH Zurich, Switzerland, A. DOMMANN, EMPA, Switzerland, A. NEELS, CSEM SA, Switzerland, P. POLCIK, PLANSEE Composite Materials GmbH, Germany, H. RUDIGIER, B. WIDRIG, **J. RAMM**, Oerlikon Balzers Coating AG, Liechtenstein	Invited talk continued.
8:40 am	**A1-3-3** Hard Wear-resistant Mo-Si-B-(N) Coatings with Oxidation Resistance up to 1400^{0}C, **PH.V. KIRYUKHANTSEV-KORNEEV**, A. MEURISSE, A. BONDAREV, E.A. LEVASHOV, D.V. SHTANSKY, National University of Science and Technology "MISIS", Russian Federation	**B2-3** Niobium Nitride Thin Films Deposited by High Temperature Chemical Vapor Deposition, **F. MERCIER**, SIMaP CNRS/Grenoble INP/UJF, France, S. COINDEAU, CMTC-SIMaP, France, M. BENZ, SIMaP CNRS/Grenoble INP/UJF, France, A. CRISCI, T. ENCINAS, CMTC-SIMaP, France, G. RIADO, R. BOICHOT, A. MANTOUX, SIMaP CNRS/Grenoble INP/UJF, France, C. JIMENEZ, F. WEISS, LMGP CNRS/Grenoble INP, France, E. BLANQUET, M. PONS, SIMaP CNRS/Grenoble INP/UJF, France
9:00 am	**A1-3-4** On the Mechanisms and Mitigation of CMAS Attack on YSZ Thermal Barrier Coatings, K.-I. LEE, The University of Manchester, UK, **R. WU**, National Institute for Materials Science, Japan, P. XIAO, The University of Manchester, UK	**B2-4** Diamond Coatings for the Machining of Composite Materials used in Aerospace Industry, **B. MESIC**, M. FRANK, M. WODA, W. KOELKER, O. LEMMER, C. SCHIFFERS, CemeCon AG, Germany
9:20 am	**A1-3-5 Invited** On the Ways to Improve the Oxidation Resistance of the Nb-Si Composites System, **S. MATHIEU**, Université de Lorraine, France, S. KNITTEL, Snecma, SAFRAN Group, France, L. PORTEBOIS, Université de Lorraine, France, N. ADKINS, M. WICKINS, University of Birmingham, UK, C. SEEMÜLLER, M. HEILMAIER, Karlsruhe Institute of Technology (KIT), Germany, M. MULSER, Fraunhofer Institute for Manufacturing Technology and Advanced Materials, Germany, S. DRAWIN, Onera, France, R. BRAUN, DLR, Germany, M. VILASI, Université de Lorraine, France	**B2-5** CVD Titanium Aluminum Nitride Coatings for Cutting Applications, **D. STIENS**, T. MANNS, S. RUPPI, Walter AG, Germany
9:40 am	Invited talk continued.	**B2-6** Functionalization of Aluminium Nitride Grown by High Temperature Chemical Vapor Deposition, **M. PONS**, Grenoble Institute of Technology, France
10:00 am	**A1-3-7** Protection of Nb-Si Alloys by Diffusion Coatings Manufactured by the Halide Pack-cementation Technique: Influence of the Ti and Si Activities on the Coating Microstructure, **L. PORTEBOIS**, S. MATHIEU, M. VILASI, Université de Lorraine, France	**B2-7 Invited** Diagnostics of SiH4/H2 Plasma and Surface Reaction in Microcrystalline Silicon Deposition, **K. ISHIKAWA**, Y. ABE, A. FUKUSHIMA, Y. LU, S. KAWASHIMA, K. MIWA, K. TAKEDA, H. KONDO, M. SEKINE, M. HORI, Nagoya University, Japan
10:20 am	**A1-3-8** NiCrN Coatings for Forming and Moulding Applications, **P. NAVABPOUR**, H. SUN, K. COOKE, Teer Coatings Limited, Miba Coating Group, UK	Invited talk continued.
10:40 am	**A1-3-9** Chemical Inertness of Ta–Si–N Coatings with Lanthanum Borosilicate Glasses in Glass Molding Process, Y.I. CHEN, **Y.R. CHENG**, National Taiwan Ocean University, Taiwan, L.C. CHANG, Ming Chi University of Technology, Taiwan, Y.H. CHEN, Young Optics Inc., Taiwan	**B2-9** In-situ Measurements of Volume Fraction of cDusters in Films During Plasma CVD, **M. SHIRATANI**, S. TOKO, K. KOGA, N. ITAGAKI, H. SEO, Kyushu University, Japan
11:00 am	**A1-3-10** Control of Bon Coat Microstructure in HVOF Process for Thermal Barrier Coatings, **S. MYOUNG**, Z. LU, M. KIM, H.-S. KIM, Y. JUNG, Changwon National University, Republic of Korea	**B2-10** Microstructure and Wear Mechanisms of Texture-controlled CVD α-Al_2O_3 Coatings, R. M'SAOUBI, **T. LARSSON**, Seco Tools AB, Sweden
11:20 am	**A1-3-11** Multi-Component High-Entropy Alloy Coatings for Use in High Temperature Environments, **J. ALFANO**, M. WEAVER, The Univ. of Alabama, US	**B2-11** Grain Boundary Engineered α-Al_2O_3 Coatings, **S. RUPPI**, D. STIENS, T. MANNS, Walter AG, Germany
11:40 am	**A1-3-12** Performance of HVOF Sprayed Al_2O_3-CoCrAlTaY Coating on 12Cr-1Mo steel to Combat Hot Corrosion at 800°C, N. JEGADEESWARAN, RITM, India, M. RAMESH, NITK, Surathkal, India, **B. UDAYA**, NITK Surathkal, India	**B2-12** Growth Mechanism of Amorphous Phase Mixed α-Al2O3 Hard Coatings, **S. TATSUOKA**, K. SATO, N. IWASAKI, K. YAMAGUCHI, A. OSADA, Mitsubishi Materials Corporation, Japan
12:00 pm		**B2-13** Chemical Vapor Deposition of Epitaxial sp^2-Boron Nitride Thin Films, M. CHUBAROV, Linköping University, IFM, Thin Film Physics Division, Sweden, H. PEDERSEN, Linköping University, Sweden, H. HÖGBERG, **A. HENRY**, Linköping University, IFM, Thin Film Physics Division, Sweden
12:20 pm	**Elsevier Authors FTS: Focused Topic Session** **"How to Get Published"** **12:15-1:15 pm** **California Room**	**ICMCTF 2015 Planning Meeting** **12:00-12:45 pm** **Royal Palm 4-6**

Thursday Morning, May 1, 2014

	Hard Coatings and Vapor Deposition Technology **Room: Royal Palm 1-3 - Session B4-3** **Properties and Characterization of Hard Coatings and Surfaces** **Moderators: C. Mulligan**, US Army ARDEC, US, Benet Laboratories, **J. Lin**, Southwest Research Institute, US, **U. Beck**, BAM Berlin, Germany	**Advanced Materials for Modern Device Applications** **Room: Sunset - Session C5-2** **Thin Films for Active Devices** **Moderator: F. Tasnadi**, Linköping University, Sweden
8:00 am	**B4-3-1** Ion Beam Induced Damages on Metastable Nitride Coatings, **E. LEWIN**, Empa, Swiss Federal Laboratories for Material Science and Technology, Switzerland, J. PATSCHEIDER, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland	**C5-2-1** Characteristics of PECVD SiO_xN_{1-x} for Resistive Memory Application, **F. ZHOU**, YF. CHANG, University of Texas at at Austin, US, B. FOWLER, Privatran LLC, US, J.C. LEE, University of Texas at at Austin, US
8:20 am	**B4-3-2** Residual Stress Gradients in α-Al_2O_3 Coatings Determined by Pencil X-ray Nanodiffraction: the Influence of Blasting Media, **M. TKADLETZ**, Materials Center Leoben Forschung GmbH, Austria, J. KECKES, N. SCHALK, Montanuniversität Leoben, Austria, C. CZETTL, CERATIZIT Austria GmbH, Austria, C. MITTERER, Montanuniversität Leoben, Austria	**C5-2-2** Investigation of Temperature-Dependent Asymmetric Degradation Behavior Induced by Hot Carrier Effect in Oxygen Ambiance in In-Ga-Zn-O Thin Film Transistor, **B.W. CHEN**, T.C. CHANG, National Sun Yat-Sen University, Taiwan
8:40 am	**B4-3-3** Investigation on Interfacial Adhesion of Ti-6Al-4V/Nitride Coatings, **L. JIN**, A.R. RIAHI, K. FAROKHZADEH, A. EDRISY, University of Windsor, Canada	**C5-2-3** Investigating Characteristics and Reliabilities of Dual Gate a-InGaZnO Thin Film Transistor with an Etch Stop Layer, **P.Y. LIAO**, T.C. CHANG, National Sun Yat-Sen University, Taiwan
9:00 am	**B4-3-4** High Resolution Electron Microscopy Structure Determination of the Metastable Cubic SiNx Phase, A. FALLQVIST, L. HULTMAN, **P. PERSSON**, Linköping University, IFM, Thin Film Physics Division, Sweden	**C5-2-4** Wide Band-gap $CuInAlS_2$ Thin Film and Its Application to UV Detectors, **D.C. PERNG**, National Cheng Kung University, Taiwan, T.T. KAO, National Kaohsiung First University of Science and Technology, Taiwan, R.P. CHANG, National Cheng Kung University, Taiwan
9:20 am	**B4-3-5** Phosphorus Content Effect on the Chemical Reaction and Mechanical Properties of the Sn/Ni-*x*P Metallurgical System, C.E. HO, **C.W. FAN**, C.H. YANG, L.H. HSU, Yuan-Ze University, Taiwan	**C5-2-5** Room Temperature Acetone Sensing of Sulfonated Copper Phthalocyanine (TsCuPc) Modified ZnO Films, **A. BAL**, Amritsar College of Engineering and Technology, India, M. KAHLON, DAV Institute of Engineering and Technology, India
9:40 am	**B4-3-6 Invited** Mechanical Property Characterization of Coatings and Surfaces within the Nano- and Micro-Scale, **T. CHUDOBA**, ASMEC Advanced Surface Mechanics GmbH, Germany	**C5-2-6 WITHDRAWN** Influence of Supercritical CO_2 Fluid Treatment on Resistive Switching Behaviors of Ti-doped SiO_2 Thin Film, **T.M. TSAI**, K.C. CHANG, T.C. CHANG, G.R. LIU, J.P. JIANG, National Sun Yat-Sen University, Taiwan, S.M. SZE, National Chiao Tung University, Taiwan
10:00 am	Invited talk continued.	**C5-2-7** Surface Decoration using Pd Nanoislands for YBCO Superconducting Thin Film using Pulsed Laser Deposition, **M. ERTUGRUL**, D. TATAR, E. SONMEZ, M.T. YURTCAN, Ataturk University, Turkey
10:20 am	**B4-3-8** Growth of 3C-SiC Films on Si Substrates by Vapor-Liquid-Solid Tri-phase Epitaxy, **H.Y. LEE**, Y.L. LIANG, J.L. HUANG, X.D. QI, National Cheng Kung University, Taiwan	**C5-2-8** Abnormal Temperature-dependent Floating-body Effect on Hot-carrier Degradation in PDSOI n-MOSFET, **K.J. LIU**, T.C. CHANG, National Sun Yat-Sen University, Taiwan
10:40 am	**B4-3-9** Effect of Zwitterioinic Surfactants on the Coating Efficiency and Properties of Electroless Ni-P Coatings, **R. MURALIRAJA**, R. ELANSEZHIAN, Pondicherry Engineering College, India	**C5-2-9** Anomalous V_t Shifts after PBTI Stress by Fast I-V Measurement in Input/Output High-k/Metal Gate Stack, **S.H. HO**, National Chiao Tung University, Taiwan, T.C. CHANG, National Sun Yat-Sen University, Taiwan
11:00 am	**B4-3-10** High-resolution Transmission Electron Microscopy of Hard Zr-B-C-N Films, **M. ZHANG**, J. JIANG, P. KROLL, University of Texas at Arlington, US, J. VLCEK, P. STEIDL, J. KOHOUT, R. CERSTVY, University of West Bohemia, Czech Republic, E. MELETIS, University of Texas at Arlington, US	**C5-2-10** Investigation of Carrier Transport Behavior in Amorphous In-Ga-Zn-O Thin Film Transistors, **T.Y. HSIEH**, T.C. CHANG, P.Y. LIAO, National Sun Yat-Sen University, Taiwan
11:20 am	**B4-3-11** Enhancement of Scratch Resistance and Hydrophobicity on Polycarbonate via a Multifunctional Hybrid O/I Coating, **N. LE BAIL**, Ecole Centrale de Lyon, France, B. TOURY, Université Claude Bernard Lyon 1, France	
	Elsevier Authors FTS: Focused Topic Session **"How to Get Published"** **12:15-1:15 pm** **California Room**	**ICMCTF 2015 Planning Meeting** **12:00-12:45 pm** **Royal Palm 4-6**

Thursday Morning, May 1, 2014

	Tribology & Mechanical Behavior of Coatings and Engineered Surfaces **Room: California - Session E3-1** **Tribology of Coatings for Automotive and Aerospace Applications** **Moderators: S. Dixit**, Plasma Technology Inc., US, **A. Gies**, Oerlikon Balzers Coating AG, Liechtenstein, **G. Doll**, University of Akron, US	**New Horizons in Coatings and Thin Films** **Room: Royal Palm 4-6 - Session F3** **New Boron, Boride and Boron Nitride Based Coatings** **Moderators: A. Inspektor**, Kennametal Incorporated, US, **A. Henry**, Linköping University, IFM, Thin Film Physics Division, Sweden
8:00 am	**E3-1-1** Boundary Lubrication of W-DLC Coatings – from Laboratory to Real Engine, **T. POLCAR**, University of Southampton, UK, M. EVARISTO, SEG-CEMUC, University of Coimbra, Portugal, P. MUTAFOV, Czech Technical University in Prague, Czech Republic, A. CAVALEIRO, SEG-CEMUC, University of Coimbra, Portugal	**F3-1 Invited** BN Nanotubes and Nanosheets and their Utilization for Structural and Medical Applications, **D.V. SHTANSKY**, A. MATVEEV, M. KOVALSKII, I. BATENINA, K. FAERSTEIN, A. STEINMAN, National University of Science and Technology "MISIS", Russian Federation, D.M. TANG, National Institute for Materials Science, (NIMS),Japan, Y. BANDO, M. YAMAGUCHI, D.V. GOLBERG, National Inst. for Mat. Science, (NIMS), Japan
8:20 am	**E3-1-2** Catalytic Cracking of Lubricating Oils to Extract DLC Boundary Films at Sliding Interfaces, **A. ERDEMIR**, O.L. ERYILMAZ, Argonne National Laboratory, US	Invited talk continued.
8:40 am	**E3-1-3** Lubricated Tribological Behavior of VN-Cu Coatings, **G. RAMIREZ**, O.L. ERYILMAZ, A. ERDEMIR, Argonne National Laboratory, US	**F3-3** Effect of Boron Potential in the Mechanical Properties of the Borided Layers Obtained by Boron Diffusion at the Surface of AISI 316L Stainless Steel, **E. HERNÁNDEZ-SÁNCHEZ**, Y. DOMÍNGUEZ-GALICIA, Instituto Politecnico Nacional-UPIBI, Mexico, J. HERNÁNDEZ-SÁNCHEZ, Instituto Politecnico Nacional, R. CARRERA-ESPINOZA, Instituto Politécnico Nacional-ESIME, Mexico, C. OROZCO-ÁLVAREZ, Instituto Politécnico Nacional-UPIBI, México
9:00 am	**E3-1-4 WITHDRAWN** Composite Coatings with Ceramic Matrix Including Nanomaterials as Solid Lubricants for Oil Free Automotive Applications, A.. POSMYK, J. MYALSKI, **B. HEKNER**, Silesian University of Technology, Poland	**F3-4** Thermal Radiative Properties and Behavior at Very High Temperatures of Pyrolytic Boron Nitride Coating on C/C Composites for the Heat Shield of Solar Probe Missions, **E. BRODU**, M. BALAT-PICHELIN, C. MORIN, J-L. SANS, PROMES-CNRS, France
9:20 am	**E3-1-5** DLC Coating to Lower Friction Loss of Piston Rings in Internal Combustion Engines, **R. LAMMERS**, M. KENNEDY, S. HOPPE, Federal-Mogul Corporation, Germany	**F3-5 Invited** Cubic Boron Nitride Coatings - Fundamental Aspects During Film Growth And Challenges In Industrial Utilization, **S. ULRICH**, J. YE, H. LEISTE, M. STUEBER, Karlsruhe Institute of Technology (KIT), Germany
9:40 am	**E3-1-6** Improving Adhesion of Diamond Like Carbon (DLC) and its Tribological Properties, **D. ROMAGNOLI**, STS srl, Italy	Invited talk continued.
10:00 am	**E3-1-7 Invited** Few Layer Graphene: The Next Solid Lubricant?, **A. SUMANT**, D. BERMAN, Center for Nanoscale Materials, Argonne National Laboratory, US, A. ERDEMIR, Energy Systems Division, Argonne National Laboratory, US	**F3-7** Methanol Wetting Enthalpy on Few-layer Graphene Decorated Hierarchical Carbon Foam for Thermal Cooling Applications, **R. PAUL**, DN. ZEMLYANOV, RN. REIFENBERGER, Purdue University, US, A.A. VOEVODIN, Air Force Research Laboratory, Materials and Manufacturing Directorate, T. FISHER, Purdue University, US
10:20 am	Invited talk continued.	
10:40 am	**E3-1-9** Gold-Ceramic Nanocomposite Thin Films: The New Gold Standard, **N. ARGIBAY**, R.S. GOEKE, S.V. PRASAD, C.C. BATTAILE, M.T. DUGGER, Sandia National Laboratories, US	
11:00 am	**E3-1-10 Withdrawn** Novel Nano-impact Techniques for Determining the Onset of Fracture in Brittle Films, **J.E. MOGONYE**, S.V. PRASAD, Sandia National Laboratories, US	
	Elsevier Authors FTS: Focused Topic Session **"How to Get Published"** **12:15-1:15 pm** **California Room**	**ICMCTF 2015 Planning Meeting** **12:00-12:45 pm** **Royal Palm 4-6**

Topical Symposia
Room: Tiki - Session TS2-2

Advanced Characterization of Coatings and Thin Films
Moderators: M. Sebastiani, University of Rome "Roma Tre", Italy, **R. Ghisleni**, EMPA (Swiss Federal Laboratories for Materials Science and Technology), Switzerland

8:00 am	**TS2-2-1** Atomic Force Microscopy: A Powerful Tool for Ultrathin Metal/Polymer Assemblies Characterization, **D. SINISCALCO**, Université du Maine, France	
8:20 am	**TS2-2-2** Optimized Design of Surface Mechanical Testing Procedures, **G. FAVARO**, N. RANDALL, CSM Instruments, Switzerland, J. KOHL, University of San Diego, US, N. BIERWISCH, N. SCHWARZER, Saxonian Institute of Surface Mechanics, Germany	
8:40 am	**TS2-2-3 Invited** Deformation and Cracking of Hard Coatings, S. LIU, University of Cambridge, UK, J.M. WHEELER, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland, F. DI-GIOACCHINO, University of Cambridge, UK, X. ZENG, SIMTECH, Singapore, J. MICHLER, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland, **W. CLEGG**, University of Cambridge, UK	
9:00 am	Invited talk continued.	
9:20 am	**TS2-2-5** A Critical Comparison Between XRD and FIB Residual Stress Measurement Techniques in Thin Films, E. BEMPORAD, University of Rome "Roma Tre", Italy, M. BRISOTTO, L.E. DEPERO, **M. GELFI**, University of Brescia, Italy, A.M. KORSUNSKY, A. LUNT, University of Oxford, UK, M. SEBASTIANI, University of Rome "Roma Tre", Italy	
9:40 am	**TS2-2-6** From Interatomic Interaction Potentials via Einstein Field Equation Techniques to Time Dependent Contact Mechanics of Thin Films, **N. SCHWARZER**, Saxonian Institute of Surface Mechanics, Germany	
10:00 am	**TS2-2-7** Role of Activators on The Thermochemical Stability of Aluminide Coatings of Low Carbon Steel, B. AL-ANZI, Kuwait University, Kuwait, M. AL-NABHAN, Petrochemicals Industries Corporation, Kuwait, A.R. KHAN, **A. ALHAZZA**, Kuwait Institute for Scientific Research, Kuwait	
10:20 am	**TS2-2-8** Surface Topography Corrected Analysis of Indentation Tests, **M. FUCHS**, N. SCHWARZER, Saxonian Institute of Surface Mechanics, Germany	
10:40 am	**TS2-2-9** Electron Backscatter Diffraction Characterization of Blind Hole Fillings by Electrolytic Cu Deposition, **L.H. HSU**, C.E. HO, C.W. FAN, C.C. CNEN, M.K. LYU, Yuan-Ze University, Taiwan	
11:00 am	**TS2-2-10** Raman, Structural, Electronic and Optical Characteristics of Mo:ZnO and Mo:ZnO/Graphene Composite Films, **M.C. HSIEH**, H.S. KOO, Minghsin University of Science and Technology, Taiwan	
11:20 am	**TS2-2-11** Effect of Annealing Environment on the Optical, Electrical and Thermoelectric Properties of MBE Grown ZnO Thin Films, **K. MAHMOOD**, M. ASGHAR, The Islamia University of Bahawalpur, Pakistan, I. FERGUSON, M.A. HASAN, Y. RAJA, University of North Carolina, US, Y.A. XIE, Univ. of California, Los Angeles, US	
11:40 am	**TS2-2-12** Theoretical and Experimental Determination of the Cu Diffusivity in Molten Eutectic Sn–Ag System at 235 ° C– 280 ° C, C.E. HO, W.Z. HSIEH, C.S. LIU, **C.H. YANG**, Yuan-Ze University, Taiwan	
	Elsevier Authors FTS: Focused Topic Session **"How to Get Published"** **12:15-1:15 pm** **California Room**	**ICMCTF 2015 Planning Meeting** **12:00-12:45 pm** **Royal Palm 4-6**

Thursday Afternoon, May 1, 2014

	Coatings for Use at High Temperatures **Room: Sunrise - Session A2-1** **Thermal and Environmental Barrier Coatings** **Moderators: K.A. Unocic**, Oak Ridge National Laboratory, US, **V. Maurel**, Mines-ParisTech, France, **K. Lee,** Rolls Royce, US	**Hard Coatings and Vapor Deposition Technology** **Room: Royal Palm 1-3 - Session B4-4** **Properties and Characterization of Hard Coatings and Surfaces** **Moderators: C. Mulligan**, US Army ARDEC, US, Benet Laboratories, **J. Lin**, Southwest Research Institute, US, **U. Beck**, BAM Berlin, Germany
1:30 pm	**A2-1-1 Invited** Lifetime and Interaction of New Single and Double Layer EB-PVD Thermal Barrier Coatings with Volcanic Ash, **U. SCHULZ**, German Aerospace Center (DLR), Germany, A.U. MUNAWAR, University of Roma-Tre, Italy, P. MECHNICH, W. BRAUE, R. NARAPARAJU, German Aerospace Center (DLR), Germany	**B4-4-1** Nanostructural Analysis of Magnetron Sputtered HfAlN Thin Films Grown on MgO(001) by Atom Probe Tomography, **D. ENGBERG**, Linköping University, IFM, Thin Film Physics Division, Sweden, L. JOHNSON, Sandvik Coromant, Sweden, M. THUVANDER, Chalmers University of Technology, Department of Applied Physics, Sweden, L. HULTMAN, Linköping University, IFM, Thin Film Physics Division, Sweden
1:50 pm	Invited talk continued.	**B4-4-2** Investigations on the Diffusion Behaviour of Fe, Cr, and C in Arc Evaporated TiN- and CrN-based Coatings and Their Influence on the Thermal and Mechanical Properties, **C. SABITZER**, C. STEINKELLNER, B. LARRIEU, Vienna University of Technology, Austria, P. POLCIK, Plansee Composite Materials GmbH, Germany, M. ARNDT, R. RACHBAUER, Oerlikon Balzers Coating AG, Liechtenstein, J. PAULITSCH, P.H. MAYRHOFER, Vienna University of Technology, Austria
2:10 pm	**A2-1-3** Thermo-mechanical properties of calcium–magnesium alumino-silicate (CMAS) and CMAS infiltrated Electron Beam –Physical Vapor Deposited 7 wt. YSZ Thermal Barrier Coatings, **S. AHMADIAN**, E. JORDAN, University of Connecticut, US	**B4-4-3 Invited** Mechanical and Tribological Behavior of Nanocrystalline Ni-W Coatings: Importance of Grain Size and Grain Boundary State, **T. RUPERT**, University of California Irvine, US
2:30 pm	**A2-1-4 Invited** Mitigation of Deleterious Effects of Environmental Deposits on Thermal Barrier Coatings, **B. NAGARAJ**, General Electric Aviation, US	Invited talk continued.
2:50 pm	Invited talk continued.	**B4-4-5** Microstructure-Related Depth-Gradients of Mechanical Properties in Thin Nanocrystalline Films, **R. DANIEL**, Montanuniversität Leoben, Austria, A. RIEDL, Materials Center Leoben Forschung GmbH, Austria, T. SCHÖBERL, Montanuniversität Leoben, Austria, B. SARTORY, Materials Center Leoben Forschung GmbH, Austria, C. MITTERER, J. KECKES, Montanuniversität Leoben, Austria
3:10 pm	**A2-1-6** Degradation Study of 7 YSZ TBCs on Aero-engine Combustion Chamber Parts Due to Infiltration by Different CMAS Variants, **R. NARAPARAJU**, U. SHULZ, P. MECHNICH, DLR - Deutsches Zentrum für Luft- und Raumfahrt, Germany, P. DOEBBER, F. SEIDEL, MTU Maintance, Germany	**B4-4-6** Corrosion Resistance of Zirconium Oxynitride/Zirconia Thin Film Growth by Spray Pyrolysis-nitruration and DC Sputtering Magnetron Unbalance, G. CUBILLOS, **D. POSSO**, J.J. OLAYA, Universidad Nacional de Colombia Bogotá, Colombia
3:30 pm	**A2-1-7 Invited** Lifetime Influence on Different TBC Systems in Laboratory and in Practise, **W. STAMM**, Siemens Power Generation, Germany	**B4-4-7** Structural Characterization of NbAlN Coating Deposited on AISI D2 Steel by TRD Method, **E. ABAKAY**, S. SEN, U. SEN, Sakarya University, Turkey
3:50 pm	Invited talk continued.	**B4-4-8** Surface Hardening of IF Steel by Plasma Nitriding and Pre-shot Peening, A.P.A. MANFRIDINI, Universidade Federal de Minas Gerais, UFMG, Brazil, A.C. BOZZI, Universidade Federal do Espírito Santo, UFES, Brazil, J.C. AVELAR-BATISTA WILSON, Tecvac, Ltd., UK, **M.V. AUAD**, Auad Godoy Consultants, Brazil, C. GODOY, Universidade Federal de Minas Gerais, UFMG, Brazil
4:10 pm	**A2-1-9** Effect of Process Parameters on MCrAlY Bondcoat Roughness and Lifetime of APS-TBC Systems, W. NOWAK, **D. NAUMENKO**, Forschungszentrum Jülich GmbH, Germany, G. MOR, F. MOR, Flame Spray North America Inc., US, D.E. MACK, R. VASSEN, L. SINGHEISER, W.J. QUADAKKERS, Forschungszentrum Jülich GmbH, Germany	**B4-4-9** Influence of Cu Additions on the Mechanical and Wear Properties of NbN Coatings, **K.V. EZIRMIK**, S. ROUHI, Atatürk University, Turkey
4:30 pm	**A2-1-10 Invited** Protective Coatings for Gas Turbines, **NJ. SIMMS**, J. SUMNER, J.R. NICHOLLS, A. ENCINAS-OROPESA, Cranfield University, UK	
4:50 pm	Invited talk continued.	
5:10 pm	**A2-1-12** Study on Hot Corrosion Behavior of ZrO_2-Y_2O_3-Ta_2O_5 Thermal Barrier Coating in Turbine Simulated Environment, **M.H. HABIBI**, S. GUO, Louisiana State University, US	
	Elsevier Reviewer Workshop: **"How to Review a Paper"** **1:30-4:00 pm—Esquire Room** No Charge but **MUST** be pre-registered; please contact: J.Wijnen@elsevier.com	**Poster Session 5:00-7:00 pm** **Town & Country and San Diego Rooms** **Reception begins at 6:00 pm**

Thursday Afternoon, May 1, 2014

	Advanced Materials for Modern Device Applications **Room: Golden West - Session C3** **Advances in Electrode Materials for Modern Device Applications** **Moderators: T. Terasako**, Ehime University, Japan, **J.A. Zapien**, City University of Hong Kong, Hong Kong	**Tribology & Mechanical Behavior of Coatings and Engineered Surfaces** **Room: California - Session E3-2** **Tribology of Coatings for Automotive and Aerospace Applications** **Moderators: S. Dixit,** Plasma Technology Inc., US, **A. Gies**, Oerlikon Balzers Coating AG, Liechtenstein, **G. Doll**, University of Akron, US
1:30 pm	**C3-1** A Novel Hierarchical Aluminum-doped Zinc Oxide Thin Film for Flexible Thin-film Solar Cells, **X. HUANG**, F.Y. ZHANG, Xiamen University, China	**E3-2-1 Invited WITHDRAWN** Effect of Powder Manufacturing Methods on Aircraft Wear Coatings, **M. FRONING**, Boeing Research and Technology, US
1:50 pm	**C3-2** Evaluation of TiN-Coated Aluminum Electrodes for DC High Voltage Electron Guns, **M.A. MAMUN**, Old Dominion University, US, E. FORMAN, Thomas Jefferson National Accelerator Facility, US, R. TAUS, Loyola Marymount University, US, M. POELKER, Thomas Jefferson National Accelerator Facility, US, A.A. ELMUSTAFA, Old Dominion University, US	Invited talk continued.
2:10 pm	**C3-3** Effects of N_2O Addition During the Growth of ZnO Films using High-temperature H_2O Generated by a Catalytic Reaction, T. NAKAMURA, Y. OHASHI, N. YAMAGUCHI, E. NAGATOMI, T. KATO, Y. TAMAYAMA, **K. YASUI**, Nagaoka University of Technology, Japan	**E3-2-3** Solid Particle Erosion Resistant Nanolayered CrAlTiN and Multilayered CrAlTiN-AlTiN Coatings, **Q. YANG**, R. MCKELLAR, National Research Council, Canada
2:30 pm	**C3-4 WITHDRAWN** Conductivity and Morphology of Highly Textured In_2O_3(111) Films with Ultrathin In Seeding Layers, **C.C. YU**, K.S. YANG, National University of Kaohsiung, Taiwan	**E3-2-4** Microstructure and Properties of WC-Co(-Cr) HVOF Coatings Obtained from Standard, Superfine and Modified by Sub-microcrystalline Carbide Powders, K. SZYMAŃSKI, Silsian University of Technology, Poland, G. MOSKAL, **H. MYALSKA**, Silesian University of Technology, Poland
2:50 pm	**C3-5** Enhancement of Open-circuit Voltage on Organic Photovoltaic Devices by Al-doped TiO_2 Modifying Layer Produced by Sol-gel Method, R. VALASKI, C. ARANTES, C.A. ACHETE, Inmetro, Brazil, **M. CREMONA**, PUC-RIO, Brazil	**E3-2-5** Corrosion and Tribological Properties of Thick Diamond-like Carbon (DLC) Coatings Deposited using a Meshed-PIID Process, **R. WEI**, J. LIN, L. CASERES, V.Z. POENITZSCH, Southwest Research Institute, US
3:10 pm	**C3-6 Invited** Thermochromics and Electrochromics for Energy Efficient Fenestration, **C. GRANQVIST**, Uppsala University, Angstrom Laboratory, Sweden	**E3-2-6** MoSx/WC PVD Coatings for Harmonic Drive Gears in Space Applications Characterized by Vacuum Pin on Disc Tests and XPS, **C. GABLER**, AC²T research GmbH, Austria, A. MERSTALLINGER, Aerospace & Advanced Composites GmbH, Austria, M. JANSSON, Harmonic Drive AG, Germany, J.L. VIVIENTE, Tecnalia, Spain
3:30 pm	Invited talk continued.	**E3-2-7** Tribological Behaviour of the Non-Hydrogenated Diamond-like Carbon (DLC) Coatings Against Ti-6Al-4V: Effect of Surface Passivation by Alcohol, S. BHOWMICK, **A. BANERJI**, A. ALPAS, University of Windsor, Canada
3:50 pm	**C3-8** Degradation Mechanism of ZnO thin Film for TCO of Flexible a-Si:H PV Module due to Moisture, **J.-S. JEONG**, Korea Electronics Technology Institute, Republic of Korea	**E3-2-8 Invited** Diamond-like Carbon Nanocomposite Coatings to Mitigate Friction and Wear in Harsh Environments, **S.V. PRASAD**, J.E. MOGONYE, Sandia National Laboratories, US
4:10 pm	**C3-9** Growth Mechanism of Silver Chloride Nano Wires by Electrodeposition Route, **A.D. DERARDJA**, S.S.M. SEGHIR MECHOUAR, LaMSM, University of Batna, Algeria	Invited talk continued.
4:30 pm		**E3-2-10** Micro-scale Abrasion Behaviour of Electroless Ni-P-SiC Coating on Aluminium Alloy, M. FRANCO, **W. SHA**, S. MALINOV, Queen's University Belfast, UK
	Elsevier Reviewer Workshop: **"How to Review a Paper"** **1:30-4:00 pm—Esquire Room** No Charge but **MUST** be pre-registered; please contact: J.Wijnen@elsevier.com	**Poster Session 5:00-7:00 pm** **Town & Country and San Diego Rooms** **Reception begins at 6:00 pm**

Thursday Afternoon, May 1, 2014

	New Horizons in Coatings and Thin Films **Room: Royal Palm 4-6 - Session F6** **Thin Films and Coatings for Fuel Cells & Batteries** **Moderators: C. Ramana**, University of Texas at El Paso, US, **L. Lei,** Shanghai Jiaotong University, China	**Applications, Manufacturing, and Equipment** **Room: Tiki - Session G5** **Coatings, Pre-treatment, Post Treatment and Duplex Technology** **Moderators: T. Takahashi**, KCS Europe GmbH, Germany, **Y. Chang**, National Formosa University, Taiwan
1:30 pm	**F6-1 Invited** Surface Modification of Electrode Materials for Lithium-ion Batteries, **M. JULIEN**, Université Paris-6, France, A. MAUGER, UPMC, Paris, France, K. ZAGHIB, IREQ, Canada	**G5-1** Selective Wear Protection of Forging Dies through Localized Plasma Duplex Treatments, **H. PASCHKE**, M. WEBER, Fraunhofer IST, Germany, T. YILKIRAN, Institute of Forming Technology and Machines, Germany
1:50 pm	Invited talk continued.	**G5-2** The Boriding Process in CoCrMo Alloy: the Presence of Indentation Size Effect and Fracture Toughness on Cobalt Boride Coatings, I. CAMPOS-SILVA, D. BRAVO-BÁRCENAS, Instituto Politecnico Nacional, Mexico, H. CIMENOGLU, Istanbul Technical University, Turkey, U. FIGUEROA-LÓPEZ, ITESM-CEM, Mexico, **M. FLORES-JIMÉNEZ**, Instituto Politecnico Nacional, Mexico
2:10 pm	**F6-3** Experimental and Ab Initio Investigations on Textured Li-Mn-O Spinel Thin Film Cathodes, **J. FISCHER**, Karlsruhe Institute of Technology (KIT), Germany, D. MUSIC, RWTH Aachen University, Germany, T. BERGFELDT, C. ZIEBERT, S. ULRICH, H.J. SEIFERT, Karlsruhe Institute of Technology (KIT), Germany	**G5-3** Pre-treatment of Polymer Based Substrates and High Rate Deposition of Silicon Dioxide Films Using a New Dual Magnetron Plasma Source, **P. MORSE**, J. GERMAN, W. MEREDITH, D. CROWLEY, S. WILLIAMS, Sputtering Components Inc., US
2:30 pm	**F6-4** Production of Core–shell Copper/Tin/MWCNT Composite Electrodes for Li-ion Batteries, M. UYSAL, Sakarya University, Engineering Faculty, Turkey, T. CETINKAYA, Sakarya University, Turkey, **M. KARTAL**, Sakarya University, Engineering Faculty, Turkey, M. GULER, A. ALP, H. AKBULUT, Sakarya University, Turkey	**G5-4** Influence of Nitriding Parameters on the Tribological Properties and the Adhesion of Ti- and Cr-based Multilayer Designs, W. TILLMANN, **M. DILDROP**, T. SPRUTE, TU Dortmund University, Germany
2:50 pm	**F6-5** Influences of Feedstocks on the Processes and Microstructures of the Flame-sprayed SOFC Anode, **H.C. TSENG**, Y.C. YANG, National Taipei University of Technology, Taiwan	**G5-5** The Powder-Pack Nitriding Process: Growth Kinetics of Nitride layers on pure iron, I. CAMPOS-SILVA, Instituto Politecnico Nacional, Mexico, M. ORTIZ-DOMINGUEZ, Universidad Politecnica de Pachuca, Mexico, M. ELIAS-ESPINOSA, Itesm, Csf, Mexico, M. FLORES-JIMÉNEZ, L.F. JIMÉNEZ-TINOCO, **D. BRAVO-BÁRCENAS**, Instituto Politecnico Nacional, Mexico
3:10 pm	**F6-6** Li Ion Technology for Vehicle Electrification, **G. DADHEECH**, M. VERBRUGGE, General Motors Research and Development Center, US, S. SRIRAMULU, TIAX, Inc., US	**G5-6** Influence of Substrate Pre-treatments on Residual Stresses and Tribomechanical Properties of PVD Coatings, W. TILLMANN, **T. SPRUTE**, D. GRISALES, Technische Universität Dortmund, Germany
3:30 pm	Invited talk continued.	**G5-7 Invited** Improvement of Coating Performance by Combining Different PVD/PACVD Technologies and Surface Treatments, **M. EERDEN**, J. LANDSBERGEN, D. DOERWALD, M. HORSTINK, T. KRUG, IHI Hauzer Techno Coating BV, Netherlands Invited talk continued.
3:50 pm	**F6-8** Improvement on the Corrosion Behaviour and Surface Conductivity of Coblast Coatings by Pack Cementation, **A. OLADOYE**, J. CARTON, Dublin City University, Ireland, A. OLABI, University of the West of Scotland, UK	
4:10 pm		**G5-9** Effect of Mechanical Post-treatment Techniques on the Characteristics and Performance of Arc-evaporated AlTiN Coating in Dry Machining of Stainless Steel, A. SINGH, **S. GANGOPADHYAY**, National Institute of Technology Rourkela, India
	Elsevier Reviewer Workshop: **"How to Review a Paper"** **1:30-4:00 pm—Esquire Room** No Charge but **MUST** be pre-registered; please contact: J.Wijnen@elsevier.com	**Poster Session 5:00-7:00 pm** **Town & Country and San Diego Rooms** **Reception begins at 6:00 pm**

Thursday Afternoon, May 1, 2014

Topical Symposia
Room: Sunset - Session TS5

Plasma Diagnostics and Modeling
Moderators: A. Hecimovic, Ruhr Universität Bochum, Germany

1:30 pm	**TS5-1** Erosion Characteristics of AlCr Composite Cathodes in Cathodic Arc Plasma with Inert and Reactive Gas Atmospheres, **R. FRANZ**, Montanuniversität Leoben, Austria, P. POLCIK, PLANSEE Composite Materials GmbH, Germany, A. ANDERS, Lawrence Berkeley National Laboratory, US	
1:50 pm	**TS5-2** Plasma Characteristics of High Power Impulse Plasma Source (HiPIPS) For Low Temperature Diamond Growth, **V.Z. POENITZSCH**, R. WEI, J. LIN, K. COULTER, Southwest Research Institute, US	
2:10 pm	**TS5-3** Characterization of Transport of Sputtered Particles from Target to Substrate in Multiple Frequency Driven Discharges, **S. BIENHOLZ**, Ruhr-University Bochum, Germany, S. RIES, N. BIBINOV, P. AWAKOWICZ, Ruhr University Bochum, Germany	
2:30 pm	**TS5-4 Invited** Status and Challenges in Electrical Diagnostics of Processing Plasmas, **E. STAMATE**, Technical University of Denmark, Denmark	
2:50 pm	Invited talk continued.	
3:10 pm	**TS5-6** Study of Substrate Heating during Reactive Magnetron Sputtering, J. RESTREPO, Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México,, Mexico, **J. CRUZ**, S. MUHL, S.E. RODIL, Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Mexico	
3:30 pm	**TS5-7 Invited** Simulation of Magnetron Discharges and Modeling Approaches Towards HiPIMS, **A. PFLUG**, M. SIEMERS, T. MELZIG, L. SCHÄFER, Fraunhofer Institute for Surface Engineering and Thin Films IST, Germany, A. HECIMOVIC, T. DE LOS ARCOS, J. WINTER, Ruhr Universität Bochum, Germany	
3:50 pm	Invited talk continued.	
4:10 pm	**TS5-9** Time-resolved Plasma Diagnostics in Reactive High-power Impulse Magnetron Sputtering Discharges, N. BRITUN, M. PALMUCCI, R. SNYDERS, **S. KONSTANTINIDIS**, University of Mons, Belgium	
4:30 pm	**TS5-10** Measuring and Controlling the Plasma in Pulsed Laser Deposition of Thin Films, S. RAJENDIRAN, A. WEST, T. GANS, **E. WAGENAARS**, York Plasma Institute, University of York, UK	
4:50 pm	ROUND TABLE	

Elsevier Reviewer Workshop:
"How to Review a Paper"
1:30-4:00 pm—Esquire Room
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Poster Session 5:00-7:00 pm
Town & Country and San Diego Rooms
Reception begins at 6:00 pm

Coatings for Use at High Temperatures
Room: Town & Country and San Diego - Session AP

Symposium A Poster Session
5:00 pm

AP1

The Corrosion Resistance of Fe-W-Cr-Nb Alloy, AISI 1020, 420 Coatings Produced by Thermal Spray, **E.A. LOPEZ COVALEDA**, J.J. OLAYA, Universidad Nacional de Colombia, Colombia

AP2

Influence of Deposition Process Parameters on the Durability and Stresses in Films AlCrN, AlCrN Based and AlCrN/TiSiN, used in the Milling Machining of Super-duplex, **W. MATTES**, Centro Universitário Católica de Santa Catarina, Brasil, S. MARTINS, UFRN, Brasil, J. PAIVA JUNIOR, SENAI, Brasil

AP3

Galvanic Corrosion Resistance of a Magnesium Alloy AJ62 and Carbon Fibre Coupling Improved by Plasma Electrolytic Oxidation Process, **T. CHENG**, University of Windsor, Canada, S. CUI, University of Toronto, Canada, X. NIE, University of Windsor, Canada

AP6

Corrosion Inhibition of Mild Steel in Hydrochloric Acid Solution using Potassium Gluconate as Inhibitor, **O.L. AKANJI**, Tshwane University of Technology, South Africa

AP7

nc-TiN/a-SiN_x Thin Films Prepared by Means of High-Power Impulse and Pulsed–DC Magnetron Co-Sputtering, **M. ARAB POUR YAZDI**, IRTES-LERMPS-UTBM, France, F. LOMELLO, LRC CEA-IRTES-LERMPS-UTBM, France, F. SANCHETTE, LRC CEA-ICD LASMIS, Nogent International Center for CVD Innovation (Nicci), UTT Antenne de Nogent, France, F. SCHUSTER, CEA, France, A. BILLARD, IRTES-LERMPS-UTBM, France

AP8 Withdrawn

Isothermal Oxidation Behavior And Kinetics Of Thermal Barrier Coatings Produced By Cold Gas Dynamic Spray Technique, **K.M. DOLEKER**, A.C. KARAOĞLANLI, Bartın University, Turkey, A. TURK, Sakarya University, Turkey, I. OZDEMIR, Katip Celebi University, Turkey

AP9

Pulsed Laser Deposition and Properties of TiAlN Thin Films, E. CAMPS, **J. QUIÑONES-GALVAN**, National Institute for Nuclear Research, Mexico, S. MUHL, Universidad Nacional Autonoma de Mexico, E. GARCIA, Universidad Nacional Autónoma de Mexico, M. FLORES, Universidad de Guadalajara, Mexico

AP10

Diffusion Behaviour of NiAlRu Coatings on X750 Substrates, **L. FU**, M. WEAVER, The University of Alabama, US

AP11

High Temperature Oxidation of EB-PVD TBCs on Pt-diffused Single Crystal Ni Superalloy, **R. SWADZBA**, J. WIEDERMANN, Institute for Ferrous Metallurgy, Poland, T. JUNG, Fraunhofer IST, Germany, U. SCHULZ, DLR - Deutsches Zentrum für Luft- und Raumfahrt, Germany, L. SWADZBA, B. WITALA, Silesian University of Technology, Poland

AP12

Electric Arc Spray Coatings For The Naval Industry, **L. DIMATE**, J.J. OLAYA, J.E. ALFONSO, Universidad Nacional de Colombia Bogotá, Colombia

AP13

Effect of High-temperature Stress on the Hot-dipped Aluminide Mild Steel with NaCl Deposit, **C.Y. TUNG**, C.J. WANG, National Taiwan University of Science and Technology, Taiwan

AP14

Microstructure and Oxidation Resistance of Ti-B, Ti-B-N, and Ti-B-N-Si Films Deposited by High Power Impulse Magnetron Sputtering, **J. KIM**, J. JANG, E. AN, I.-W. PARK, D.-G. NAM, Korea Institute of Industrial Technology (KITECH), Busan, South Korea, Y. KIM, N. KANG, Pusan National University, South Korea, Y.-D. PARK, Dong-Eui University, South Korea

AP15

Laser Surface Aluminizing of SAE 4340 Steel, G. VASCONCELOS, **V. TELEGINSKI**, D. CHAGAS, R. BECKER, Institute for Advanced Studies, Brazil

AP16

Cyclic Oxidation Tests of Aluminide Coatings Produced by VPA Method on Directionally Solidified Ni Superalloy, **B. WITALA**, L. SWADZBA, M. HETMANCZYK, B. MENDALA, G. MOSKAL, Silesian University of Technology, Poland, R. SWADZBA, Institute for Ferrous Metallurgy, Poland, L. KOMENDERA, Subcarpathian Aviation Cluster, Poland

AP17

Oxidation Resistance of Titania-doped Yttria-stabilized Zirconia TBC Coatings, **S. LISCANO**, L. GIL, UNEXPO, Venezuela (Bolivarian Republic of)

AP18

Film Cooled Recession of SiC/SiC Ceramic Matrix Composites: Test Development, CFD Modeling and Experimental Observations, **D. ZHU**, B. SAKOWSKI, C. FISHER, NASA Glenn Research Center, US

AP20

In-situ Polymerization for Anti-corrosion Polyimide/Boron Nitride Hybrid Films with Different Polymer Configurations, **Y.C. HUANG**, W.T. WHANG, National Chiao Tung University, Taiwan

AP21

Characterization of Microstructure and Oxidation Resistance of Silicide Coatings on Mo, W and Nb, G. MOSKAL, **S. POLIS**, Silesian University of Technology, Poland

AP22

Experimental Study and Numerical Simulation of Thermal Barrier Coating Systems with Thermal Cycling, **J.G. ZHU**, W. CHEN, LIU, Jiangsu University, China, H.M. XIE, Tsinghua University, China

AP23

Hot Corrosion Studies of Thermal Sprayed Nanostructured Coatings Deposited by Mechanically Milled NiCrAlY Powder, **N. RANA**, R. JAYAGANTHAN, S. PRAKASH, Indian Institute of Technology Roorkee, India

Hard Coatings and Vapor Deposition Technology
Room: Town & Country and San Diego - Session BP

Symposium B Poster Session
5:00 pm

BP2

Investigation of Adhesion and Corrosion Properties of CrAlYN/CrY Multilayer Coatings Deposited by Unbalanced Magnetron Sputtering, M. TAHMASEBIAN MYANDOAB, I. EFEOGLU, K.V. EZIRMIK, E. ARSLAN, Y. TOTIK, **E.E. SUKUROGLU**, Atatürk University, Turkey, Ö. BARAN, Erzincan University, Turkey

BP3

DLAg and DLSiO Films with Good Tribological and Corrosion Resistance Properties for Aerospace Applications, **F.L.C. LUCAS**, Universidade do Vale do Paraíba, Brazil, P.A. RADI, S.F. FISSMER, Technologic Institute of Aeronautics, Brazil, P.M.S.C.M. LEITE, R.S. PESSOA, H.S. MACIEL, L.V. SANTOS, Universidade do Vale do Paraíba, Brazil

BP4

Production and Characterization of Niobium Carbide Coatings on Gray Cast Iron by Termorreactive Difussion/Deposition, **A.A. AMAYA A.**, O.E. PIAMBA TULCAN, J.J. OLAYA, Universidad Nacional de Colombia Bogotá, Colombia

BP5

Radiation Exposed Hydrogenated Amorphous Carbon Films: Microstructure and Wettability, K.C. HOFELMANN, M. PARTICHELLI, R.A.S. ZANON, Universidade do Estado de Santa Catarina, Brazil, C.A. ACHETE, InMetro - Instituto Nacional de Metrologia, Brazil, **J.M. PUREZA**, Universidade do Estado de Santa Catarina, Brazil, M.M. LACERDA, Universidade Federal do Rio de Janeiro, Brazil

BP6

Reactive and Non-reactive Deposition of Al-Cr-N Coatings using Metallic, Intermetallic, and Ceramic Target Material, **C. SABITZER**, Vienna University of Technology, Austria, S. KOLOZSVÁRI, Plansee Composite Materials GmbH, Germany, M. ARNDT, R. RACHBAUER, Oerlikon Balzers Coating AG, Liechtenstein, J. PAULITSCH, P.H. MAYRHOFER, Vienna University of Technology, Austria

BP7

Impact of Point Defects on Stability of $(Al_{1-x}Cr_x)_2O_3$ Phases from First Principles, **C.M. KOLLER**, Vienna University of Technology, Austria, J. RAMM, Oerlikon Balzers Coating AG, Liechtenstein, P. POLCIK, Plansee Composite Materials GmbH, Germany, D. HOLEC, Montanuniversität Leoben, Austria, J. PAULITSCH, P.H. MAYRHOFER, Vienna University of Technology, Austria

BP8

Synthesis and Characterization of Thin Films Doped with Cobalt by MOCVD, **N.E. MENDEZ LOZANO**, L.M. APATIGA CASTRO, Universidad Nacional Autonoma de Mexico, Mexico

BP9

Microstructure, Mechanical and Electrochemical Properties of Vanadium-Niobium Rich Carbide Layers Grown by TRD, **F. CASTILLEJO**, Universidad Santo Tomás Bogotá, Colombia, J.J. OLAYA, J.E. ALFONSO, Universidad Nacional de Colombia Bogotá, Colombia

BP10

Electrochemical and Tribological Properties of Cr-Nb Carbides produced by TRD Process., F. ALFONSO, Universidad Santo Tomas, Colombia, **J.J. OLAYA**, O. PIAMBA, Universidad Nacional de Colombia Bogotá, Colombia

BP12

Corrosion Protection Coatings with Atomic Layer Deposition, **E.M. HÄRKÖNEN**, University of Helsinki, Finland, S. TERVAKANGAS, J. KOLEHMAINEN, DIARC-Technology Inc., Finland, I. KOLEV, Hauzer Techno Coating B.V., The Netherlands, B. DÍAZ, J. SWIATOWSKA, V. MAURICE, A. SEYEUX, P. MARCUS, Chimie ParisTech (ENSCP), France, M. FENKER, FEM Forschungsinstitut Edelmetalle & Metallchemie, Germany, L. TÓTH, G. RÁDNOCZI, Research Centre for Natural Sciences HAS, Hungary, M. VEHKAMÄKI, M. RITALA, University of Helsinki, Finland

BP14

Investigation of Hysteresis Effect and Influence of Bias Voltage during Deposition of HPPMS Aluminum Oxide Coatings, K. BOBZIN, N. BAGCIVAN, **R.H. BRUGNARA**, S. BASTURK, RWTH Aachen University, Germany

BP15

Effect of Composition on Fracture Toughness of TiZrN Hard Coatings, **Y.F. CHEN**, J.-H. HUANG, National Tsing Hua University, Taiwan

BP16

Comparison of Corrosion Resistance of N-doped ZrO_2 Thin Films Deposited by HCD-IP and Grown by Heat Treating ZrN Thin Films in Vacuum, **S.A. CHOU**, J.-H. HUANG, National Tsing Hua University, Taiwan

BP17

Effect of Processing Parameters on Wear Resistance and Mechanical Properties of Thick TiN Film on D2 Steel Deposited by Unbalanced Magnetron Sputtering, **C.I. CHIU**, J.-H. HUANG, National Tsing Hua University, Taiwan

BP18

Effect of Substrate Bias on Structure and Mechanical Properties of Synthesis of (Ti, Zr)N Hard Coatings by DC Unbalanced Magnetron Sputtering, **H.A. CHEN**, G.P. YU, National Tsing Hua University, Taiwan

BP19

Effect of Temperature on Exchange Bias of $BiFeO_3$/FePt Bi-layer Films Epitaxial System Deposited by Radio-frequency Sputtering, **L.C. HUANG**, G.P. YU, National Tsing Hua University, Taiwan

BP20

Closed Drift Type Circular Ion Source, **J.-K. KIM**, K.-T. KIM, Y.-J. KANG, D.-G. KIM, S. LEE, Korea Institute of Materials Science, Korea

BP21

Mechanical Properties of CrSiN Coatings by Cathodic Arc Deposition with Different Arc Currents, **W.Y. HO**, Y.S. CHANG, B.Y. CHOU, C.L. LIN, MingDao University, Taiwan, C.S. HSU, Tatung University, Taiwan

BP22

Optical Properties Of Tetrahedral Amorphous Carbon Films And Their Potential For Lab-On-A- Chip, **K. GUENTHER**, University of Applied Sciences Mittweida, Germany, F. SONNTAG, Fraunhofer IWS, Germany, S. WEIßMANTEL, University of Applied Sciences Mittweida, Germany

BP23

Raman Study on Structural Changes of DLC Films Deposited on Curved Surfaces, **J. CHOI**, T. HATTA, T. KATO, The University of Tokyo, Japan

BP24

Effect of Amino Acid Additives on the Microstructure of Electrodeposited Nickel Films, **T. NAGAI**, K. HODOUCHI, H. MATSUBARA, Nagaoka University of Technology, Japan

BP25

Effect of Nb Content on Superelastic, Mechanical and Damping Properties of NiTi Shape Memory Thin Films, **N. KAUR**, D. KAUR, Indian Institute of Technology Roorkee, India

BP26

Mechanical Properties of TiAlSiN Coatings by Hybrid Process, **J.-H. YANG**, J.-I. JEONG, M.-A. SONG, J.-H. JUNG, Research Institute of Industrial Science and Technology, Republic of Korea

BP27

Electrochemical Characteristics of Heterostructural Nanolayer Tantalum Nitride Coatings, **F.B. WU**, K.Y. LIU, National United University, Taiwan

BP28

Ab Initio Studies on the Adsoprtion and Adhesive Transfer of Al and Fe to Nitride Coating Materials, **H. RIEDL**, Christian Doppler Laboratory for Application Oriented Coating Development at Vienna University of Technology, Austria, J. ZÁLEŠÁK, Montanuniversität Leoben, Austria, M. SOBIECH, Oerlikon Balzers Coating AG, Liechtenstein, P. POLCIK, Plansee Composite Materials GmbH, Germany, D. HOLEC, Montanuniversität Leoben, Austria, P.H. MAYRHOFER, Vienna University of Technology, Austria

BP29

Structure and Elastic Properties of Ternary Metal Nitride $Zr_{1-x}Ta_xN$ Alloys Thin films: Experimental Study and First-principles Calculations, **P. DJEMIA**, LSPM-CNRS, Université Paris 13, Sorbonne Paris-Cité, France, Q.-M. HU, Shenyang National Laboratory for Materials Science, China, M. BENHAMIDA, K. BOUAMAMA, Laboratoire Optoélectronique et Composants, Ferhat Abbas University, Algeria, L. BELLIARD, UPMC, Paris,France, G. ABADIAS, Pprime Institute - UPR CNRS 3346 - Université de Poitiers - ENSMA - France

BP30 WITHDRAWN

Morphological Transition of Fe Films on Si Substrates with an Fe_5Si_3 Intermediate Layer, **C.C. YU**, H. CHANG, National University of Kaohsiung, Taiwan, C.T. LIU, W.C. CHENG, National Taiwan University of Science and Technology, Taiwan, Y.D. YAO, National Pingtung University of Education, Taiwan

BP31

Electrical and Reliability Characteristics of HfO_2 Gate Dielectric Under Oxygen Treatment, Y.L. CHENG, **T.C. BO**, National Chi-Nan University, Taiwan

BP32

Effect of Ion Irradiation on NI Films Prepared on a Flexible Substrate Material Using Unbalanced Magnetron Sputtering Assisted by Inductively Coupled Plasma, **T. KODA**, H. TOYOTA, Hiroshima Institute of Technology, Japan

BP33

Effects of Deposition Conditions on ZNO Thin Film Prepared Using RF Magnetron Sputtering, **Y. TAKIGUCHI**, H. TOYOTA, Hiroshima Institute of Technology, Japan

BP34

Microstructure and Properties of Vanadium Nitride Hard Coating Prepared by Arc Ion Plating, **T. EOM**, M. YOON, B. SONG, C. YUN, S. SONG, TaeguTec, Republic of Korea, B. MIN, Yeungnam University, Republic of Korea

BP35

Selective Textured Deposition of Ti(C,N), **L. VON FIEANDT**, M. BOMAN, Uppsala University, Sweden, T. LARSSON, O. ALM, J. LAURIDSEN, Seco Tools AB, Sweden, J. PERSSON, E. LINDAHL, Sandvik Coromant R&D Materials and Processes, Sweden

BP36

Reduction of Coercivity in Graded X/FePt (X=CoPt, FePd, FePt) Thin Films with Perpendicular Anisotropy, **S.H. LIU**, Feng Chia University, Taiwan, S.N. HSIAO, National Synchrotron Radiation Research Center, Taiwan, S.K. CHEN, Feng Chia University, Taiwan, H.Y. LEE, National Synchrotron Radiation Research Center, Taiwan

BP37

Effect Of The Concentration Of V In Corrosion Resistance Of Vanadium Carbide Coatings Deposited By The Thermoreactive Deposition Diffusion Process (Trd), **A. ORJUELA**, J.E. ALFONSO, J.J. OLAYA, Universidad Nacional de Colombia Bogotá, Colombia

BP38

Thermal Effects On Steels At Laser Method Of Separation, **D. MANAS**, Tomas Bata University in Zlin, Czech Republic, M. MANAS, Tomas Bata University in Zlin, Faculty of Applied Informatics, Czech Republic, M. STANEK, M. OVSIK, Tomas Bata University in Zlin, Czech Republic

BP40

Production and Characterization of Vanadium Carbide Coatings on Gray Cast Iron by Termorreactive Diffusion / Deposition, A.A. AMAYA A., J.J. OLAYA, **O.E. PIAMBA TULCAN**, Universidad Nacional de Colombia Bogotá, Colombia

BP41

Effect of the Concentration Of Nb In Corrosion Resistance Of Niobium Carbide Coatings Deposited by the Thermoreactive Deposition Diffusion Process (TRD), A. ORJUELA, **R. RINCÓN**, Fundacion Universitaria Los Libertadores, Colombia, L. ARDILA, Universidad Nacional de Colombia Bogotá, Colombia

BP42

Characteristic of Multiferroic $BiFeO_3/LaNiO_3$ Superlattice Structures Prepared by RF Sputtering, **H.Y. LEE**, National Synchrotron Radiation Research Center, Taiwan, Y.T. LIU, National Chiao Tung University, Taiwan

BP43

Evaluation of the Erosion-corrosion of Nanocomposite (Fe, 25Cr, 5B, 6Mo, 15W, 3Mg, 4C, 12Ni, 2Si) Deposited on AISI-SAE 4340. Steel through Thermal Spray Arc, F.A. LAVERDE, **J.E. ALFONSO**, J.J. OLAYA, Universidad Nacional de Colombia Bogotá, Colombia

BP44

Morphological and Electrochemical Characterization of $V_XNb_YC_Z$ Coatings Produce by Thermo-reactive Diffusion, **S.A. CASTRO HERMOSA**, J.E. ALFONSO, J.J. OLAYA, Universidad Nacional de Colombia Bogotá, Colombia

BP45

Influence of Magnetron Sputtering Conditions on WTi and Ta Thin Films: Microstructure-stress-electrical Conductivity Relationship, **P.O. RENAULT**, E. LE BOURHIS, A. LE PRIOL, University of Poitiers, France, P. MULLER, Sofradir, France, H. SIK, SAGEM Défense Sécurité, France

BP46

Influence of Reducing Agent on Electroless (Ni-P) Coating Process and Optimization of Process Parameters using Taguchi Technique, **M. RAJARAMAN**, E. RASU, Pondicherry Engineering College, India

BP47

Mechanical and Tribological Properties of Nanocomposite Ti-B-N-Si Films Deposited by High Power Impulse Magnetron Sputtering, **J. JANG**, J. KIM, E. AN, I.-W. PARK, D.-G. NAM, Korea Institute of Industrial Technology (KITECH), Busan, South Korea, K.H. KIM, I. PARK, Pusan National University, South Korea

BP48

Structural Investigation of Y- and Hf-Doped TiAlSiCN Coatings, **PH.V. KIRYUKHANTSEV-KORNEEV**, K.A. KUPTSOV, A.N. SHEVEYKO, National University of Science and Technology "MISIS", Russian Federation, C. ROJAS, A. FERNANDEZ, Instituto de Ciencia de Materiales de Sevilla, Spain, D.V. SHTANSKY, National University of Science and Technology "MISIS", Russian Federation

BP50

Preparation and Characterization of (111)-oriented Ti1-xAlxN Thin Films on Monocrystalline Aluminium Nitride by Reactive Chemical Vapor Deposition, H. SHIMODA, **F. MERCIER**, S. LAY, E. BLANQUET, SIMaP CNRS/Grenoble INP/UJF, France

BP51

Microstructure and Mechanical Properties of Carbon/carbon Composites with the Fiber Surface Modification by Carbon Nanofibers, **J. CHEN**, L. HUANG, P. XIAO, X. XIONG, Central South University, China

BP52

Effect of the Interlayer Thickness on the Adhesion Property of the CrZrN Coatings Deposited on AISI H13 Steel, **K.-S. KIM**, H.-K. KIM, J.H. LA, S.-M. KIM, S.-Y. LEE, Korea Aerospace University, Korea

BP53

Effect of Gas Pressure and Exciting Voltage on the Plasma Stability of a Pulsed-DC Hollow Cathode Discharge, A. BENKENSTEIN, **K. BÖBEL**, MÜLLER, Robert Bosch GmbH, Germany, B. DZUR, Ilmenau University of Technology, Germany

BP55

Structure and Mechanical Properties of Ta Alloyed Cr-Al-N Coatings, **R. HOLLERWEGER**, L. ZHOU, Vienna University of Technology, Austria, D. HOLEC, Montanuniversität Leoben, Austria, R. RACHBAUER, Oerlikon Balzers Coating AG, Liechtenstein, P. POLCIK, Plansee Composite Materials GmbH, Germany, P.H. MAYRHOFER, Vienna University of Technology, Austria

BP56

Mechanical and Tribological Properties of TiAlSiN Nanocomposite Coatings Deposited by a High Power Impulse Magnetron Sputtering, **M.K. LEI**, B. WU, Y.G. LI, Z.L. WU, X.P. ZHU, Dalian University of Technology, China

BP57

Sputtered Thin Film Metallic Glass as Underlayer for Sn Whisker Mitigation, W. DIYATMIKA, **J.P. CHU**, Y. YEN, W.Z. CHANG, C. HSUEH, National Taiwan University of Science and Technology, Taiwan

BP58

Tribocorrosion Properties of Duplex *MAO/DLC* Coatings on Ti6Al4V Alloys, E.E. SUKUROGLU, **Y. TOTIK**, E. ARSLAN, I. EFEOGLU, Atatürk University, Turkey

BP59

Effect of Coating Thickness on the Silt Erosion Properties of Ternary Metal Nitride Thin Films prepared by Magnetron Sputtering, V. ARYA, BHEL R&D, India, **P. DUBEY**, R. CHANDRA, Indian Institute of Technology Roorkee, India

BP60

Fabrication and Characterization of Tungsten-Yttrium Coatings for Nuclear Reactor Applications, **G. MARTINEZ**, University of Texas at El Paso, US, C. RAMANA, University of Texas at El Paso

Thursday Afternoon Poster Sessions

Advanced Materials for Modern Device Applications
Room: Town & Country and San Diego - Session CP

Symposium C Poster Session
5:00 pm

CP1

Computational Investigations of Stress Evolution during Thin Film Growth, **X.X. YU**, W. LI, T. KAUB, G.B. THOMPSON, The University of Alabama, US

CP3

Effect of O_2 Plasma Treatment on Physical, Electrical, and Reliability Characteristics of Low Dielectric Constant Material, Y.L. CHENG, **B.H. LIN**, National Chi-Nan University, Taiwan

CP4

Gas Sensing of SnO_2 Nanoparticles and Pt/SnO_2 Nanoparticles by Thermal Decomposition Process, **S.C. WANG**, T.W. YANG, B.J. HUANG, Southern Taiwan University of Science and Technology, Taiwan

CP5

Ab Initio Evaluation of the Potential use of Sc-based III-Nitrides in Optoelectronics, S. ZHANG, University of Cambridge, UK, **D. HOLEC**, Montanuniversität Leoben, Austria, G. FU, C. HUMPHREYS, University of Cambridge, UK, P.H. MAYRHOFER, Vienna University of Technology, Austria, MA. MORAM, Imperial College London, UK

CP6

Field-enhanced Light Instability under Visible and Ultraviolet Light Irradiation on Amorphous In-Ga-Zn-O Thin Film Transistors, **K.J. LIU**, T.C. CHANG, T.Y. HSIEH, National Sun Yat-Sen University, Taiwan

CP7

Modifications in Structure and Properties of Nickel Oxide Films after Argon Ion Beam Bombardment, S.C. CHEN, C.K. WEN, Ming Chi University of Technology, Taiwan, **T.Y. KUO**, Institute of Materials Science and Engineering, National Taiwan University, Taiwan, C.S. WANG, Ming Chi University of Technology, Taiwan, H.C. LIN, Institute of Materials Science and Engineering, National Taiwan University, Taiwan

CP8

Characterization and Properties of NiO Films Produced by RF Magnetron Sputtering with Oxygen Ion Source Assistance, S.C. CHEN, **C.K. WEN**, Ming Chi University of Technology, Taiwan, T.Y. KUO, Institute of Materials Science and Engineering, National Taiwan University, Taiwan, W.C. PENG, Ming Chi University of Technology, Taiwan, H.C. LIN, Institute of Materials Science and Engineering, National Taiwan University, Taiwan

CP9

Temperature Dependent Obliquely Deposited Anti-contamination Coating of HfO_2 for Glass Insulators, **V. DAVE**, A. SANGER, H.O. GUPTA, R. CHANDRA, Indian Institute of Technology Roorkee, India

CP10

Resistive Switching Characteristics of Silicon Oxide Based RRAM with Titanium Doping, **T.M. TSAI**, K.C. CHANG, T.C. CHANG, G.R. LIU, J.P. JIANG, National Sun Yat-Sen University, Taiwan, S.M. SZE, National Chiao Tung University, Taiwan

CP11

Crystalline Structure of ZnO thin Films Grown on A-plane Sapphire Substrates Using High-temperature H_2O Produced by a Pt-catalyzed H_2-O_2 Reaction, Y. OHASHI, T. NAKAMURA, N. YAMAGUCHI, T. TAKEUCHI, Y. TAMAYAMA, **K. YASUI**, Nagaoka University of Technology, Japan

CP13

Effects of Thickness on the Characteristics of p-type Cu_2O Thin Film for all Oxide Solar Cell using Reactive Sputtering, Y.S. JUNG, H.W. CHOI, **K.H. KIM**, Gachon University, Republic of Korea

CP14

Characteristics of SiH4-containing Plasma Generated by ICP-CVD Mixed with H2, B2H6 and PH3, J.H. HSIEH, **H.S. LIN**, Ming Chi University of Technology, Taiwan, C. LI, National Central University, Taiwan

CP15

Low Contact Resistance Carbon Thin Films as Current Collectors for Lithium Ion Batteries, S.K. CHEN, K.-F. CHIU, S.-H. SU, S.H. LIU, K.-H. HOU, **C.-C. HSIAO**, Feng Chia University, Taiwan

CP16

Effects of Temperature on Instabilities Caused by Charge-trapping Phenomenon in Dual Gate Amorphous In-Ga-Zn-O Thin-film Transistors, **P.Y. LIAO**, T.C. CHANG, National Sun Yat-Sen University, Taiwan

CP17

Effects of Uniaxial Mechanical Strain on Amorphous In-Ga-Zn-O Thin Film Transistors Fabricated on Flexible Polyimide Substrates, **B.W. CHEN**, T.C. CHANG, National Sun Yat-Sen University, Taiwan

CP18

Correlation Between Temperature-dependent Carrier Transport Behavior and Self-heating Effect in Amorphous In-Ga-Zn-O Thin Film Transistors, **T.Y. HSIEH**, T.C. CHANG, P.Y. LIAO, National Sun Yat-Sen University, Taiwan

CP19

Effect of Selenization Temperature on the Formation of Cu(In,Ga)$(Se,S)_2$ Phtovoltaic Absorber by Selenization and Sulfurization of CuGa/In/Se Metal Precursors, J. KOO, S. LEE, **W.K. KIM**, Yeungnam University, Republic of Korea

CP20

Effect of the Sputtering Conditions of Co-sputtered Cu-In-Ga Precursors on Cu(InGa)Se_2 Photovoltaic Absorber Formation, **J. PARK**, W.K. KIM, Yeungnam University, Republic of Korea

CP21

Structural Characteristics and Properties of Gallium Nitride Thin Films Prepared by Radio Frequency Magnetron Sputtering, Y.K. CHO, **J.H. KIM**, Chungbuk National University, Republic of Korea

CP22

N_2O Plasma Treatment Suppression of Temperature-dependent Point Defect Formation in Amorphous Indium-Gallium-Zinc-Oxide Thin Film Transistors, **J.C. JHU**, National Chiao Tung University, Taiwan, T.C. CHANG, National Sun Yat-Sen University, Taiwan, G.W. CHANG, Y.H. TAI, National Chiao Tung University, Taiwan

CP23

Properties of CNTs/PEDOT:PSS (spin-coated) Thin Films as Flexible Transparent Electrodes, **B.J. KIM**, S.H. HAN, J.S. PARK, Hanyang University, Republic of Korea

CP24

Effects of Substrate Corona-pretreatment on Properties of Flexible Transparent CNT Electrodes, **S.H. HAN**, B.J. KIM, J.S. PARK, Hanyang University, Republic of Korea

CP25

Effects of Hot-pressing on Structural, Optical, and Electrical Properties of Silicon-incorporated Zinc Oxide Thin Films, **K.W. CHA**, S.H. LEE, W. KIM, J.S. PARK, Hanyang University, Republic of Korea

CP26

Effects of Air Exposure and Thermal Treatment on Properties of SZO Films and Characteristics of SZO-based Thin Film Transistors, **S.H. LEE**, K.W. CHA, W. KIM, J.S. PARK, Hanyang University, Republic of Korea

CP27 **WITHDRAWN**

Effect of Molecular Structure of the Starting Precursor Materials over the Crystallization, Growth and Luminescence of ZnO Coatings, **S. BRAHMA**, National Cheng Kung University, Taiwan, S.A. SHIVASHANKAR, Indian Institute of Science Bangalore, India, J.-M. TING, National Cheng Kung University, Taiwan

CP28

High Electrical Conductivity of Orientedly-assembled Sb_2Se_3 Nanostructured Films, H.C. CHANG, **T.H. CHEN**, K.S. KE, C.H. CHEN, National Chiao Tung University, Taiwan

CP29 **WITHDRAWN**

A Germanium/Silicon Heterojunction Field Effect Transistor Photodetector Fabricated on Silicon-on-insulator, H. MOHAMMED, M. DEBERRY, U. OBAHIAGBON, O. AKPA, M. AWAAH, **N. KORIVI**, K. DAS, Tuskegee University, US

CP34

Influence of Pre-metal / Post-metal Annealing on Reliability with High-k/Metal Gate Metal-oxide Semiconductor Field Effect Transistors, **Y.H. LU**, T.C. CHANG, National Sun Yat-Sen University, Taiwan

CP36

The Effect of Hydrogen Ion on Resistance Switching Characteristic of Hf-doped Silicon Oxide RRAM, **T.J. CHU**, T.C. CHANG, T.M. TSAI, K.C. CHANG, Y.E. SYU, M.C. CHEN, National Sun Yat-Sen University, Taiwan

CP37

Dynamic Gate-Induced-Drain-Leakage Stress Associated Hot Carrier Degradation in HfO_2/TiN n-channel Metal-Oxide-Semiconductor Field-Effect Transistors, **J.Y. TSAI**, T.C. CHANG, National Sun Yat-Sen University, Taiwan, C.E. CHEN, S.H. HO, National Chiao Tung University, Taiwan

CP38

Investigation of Hot Carrier Stress in p-channel Double Diffused Drain Metal-Oxide-Semiconductor Transistors with Different Shallow Trench Isolation Structures, **C.E. CHEN**, National Chiao Tung University, Taiwan, T.C. CHANG, National Sun Yat-Sen University, Taiwan, H.M. CHEN, National Chiao Tung University, Taiwan, B. YOU, National Sun Yat-Sen University, Taiwan, T.Y. TSENG, National Chiao Tung University, Taiwan

CP39

Anomalous Degradation Behaviors under Illuminated Gate Bias Stress in a-Si:H Thin Film Transistor, **M.Y. TSAI**, T.C. CHANG, A.K. CHU, T.Y. HSIEH, K.Y. LIN, National Sun Yat-Sen University, Taiwan

CP40

Investigation on Degradation Behavior with UV Light Treatment under Negative Bias Illumination Stress in a-InGaZnO Thin Film Transistor, **H.M. CHEN**, National Chiao Tung University, Taiwan, T.C. CHANG, M.Y. TSAI, National Sun Yat-Sen University, Taiwan, Y.H. TAI, National Chiao Tung University, Taiwan

CP41

Hydrolysis-Induced Abnormal On-Current Degradation and Current Crowding Behavior under Negative Gate Bias Stress in a-InGaZnO Thin Film Transistors, **K.H. LIU**, National Chiao Tung University, Taiwan, T.C. CHANG, M.C. CHEN, National Sun Yat-Sen University, Taiwan, W.C. CHOU, National Chiao Tung University, Taiwan

CP43

Effect of Annealing Temperature on the Optical, Electrical and Thermoelectric Properties of MOCVD Grown ZnO, **K. MAHMOOD**, M. ASGHAR, The Islamia University of Bahawalpur, Pakistan, L. NA, Y. RAJA, I. FERGUSON, University of North Carolina, US

CP44

One Step Synthesis of Cobalt Ferrites ($CoFe_2O_4$) Nanoparticles by Hydrothermal Method and Optical Properties, **A. AL-SHIHRI**, A. KALAM, King Khalid University, Saudi Arabia, G. DU, Zhejiang Normal University, China

CP45

Effect of Electron Beam Radiation on Electrical and Optical Properties of Multilayered Tin Oxide Thin Films, **K.I. MADDANI**, SDMCET, India, J.S. BHAT, Karnatak University, India

CP46

TiO_2:Nb Transparent Conductive Thin Films Treated by a Post Hot-wire Annealing in a Reducing H_2 Atmosphere, M.V. CASTRO, L. REBOUTA, P. ALPUIM, M.F. CERQUEIRA, University of Minho, Portugal, E. ALVES, N.P. BARRADAS, Ion Beam Laboratory (ITN), Portugal, **C.J. TAVARES**, University of Minho, Campus Azurém, Portugal

CP47

Thermo-mechanical Behavior of Die Attach Film on Flexible PCB Substrate for Multi Chip Package, **J.-O. BANG**, Sungkyunkwan University, Republoic of Korea, K.S. KIM, Sungkyunkwan University, Republic of Korea, Y.M. LEE, Samsung Electro-Mechanics Co., Republic of Korea, S.B. JUNG, Sungkyunkwan University, Republic of Korea

CP48

Optimization of n-Oxide Thin-film Formation in Heterojunction Solar Cells Using Thermally Oxidized p-Cu2O Sheets, **Y. NISHI**, T. MIYATA, T. MINAMI, Kanazawa Institute of Technology, Japan

CP49

Study on Aluminum Hot-dip Copper Process and the Interface Microstructure of Copper-clad Aluminum Bimetallic Material, **X. CHEN**, Georgia Institute of Technology, US, X. TANG, Z. WANG, X. HUI, University of Science and Technology Beijing, China, M. LI, Georgia Institute of Technology, US

Coatings for Biomedical and Healthcare Applications
Room: Town & Country and San Diego - Session DP

Symposium D Poster Session
5:00 pm

DP1

Biocompatibility and Antimicrobial Performance of TiZrCN Coatings, H.L. HUANG, China Medical University and Hospital, Taiwan, Y. CHANG, **Y.C. YANG**, National Formosa University, Taiwan, C.H. LAI, T.M. SHIEH, China Medical University and Hospital, Taiwan

DP2

Biocompatibility and Electrochemical Behavior of Nanotubular Anodized TiO2 Layer for Implant Applications, E. MUNDARAY, **L. GIL**, Universidad Nacional Experimental Politécnica (UNEXPO), Venezuela (Bolivarian Republic of), F. ALVAREZ, Fundación Instituto de Estudios Avanzados (IDEA), Venezuela (Bolivarian Republic of), L. HERNANDEZ, Universida Nacional Experimental Politécnica (UNEXPO), Venezuela (Bolivarian Republic of)

DP3

Low Temperature Pasteurization via High Density Plasma Oxidation, **T. AIZAWA**, Shibaura Institute of Technology, Japan, Y. SUGITA, YS-Electric Industry, Co. Ltd., Japan

DP4

Biomolecular Modification of Zirconia Surface for Enhenced Biocompatibility, S.K. HSU, H.C. HSU, Central Taiwan University of Science and Technology, Taiwan, W.F. HO, Da-Yeh University, Taiwan, K.H. LEE, **S.C. WU**, Central Taiwan University of Science and Technology, Taiwan

DP5

Surface Modification of Blood-contacting Biomaterials by Plasma-Polymerized Super-Hydrophobic Films, C.R. HSIAO, Feng Chia University, Taichung, Taiwan, C.W. LIN, Central Taiwan University of Science and Technology, Taiwan, C.M. CHOU, Taichung Veterans General Hospital, Taiwan, **C.J. CHUNG**, Central Taiwan University of Science and Technology, Taiwan, J.L. HE, Feng Chia University, Taiwan

DP6

Influence of Non-Photoresist Lithography on Cell Activity of Titanium, **J.-H. KANG**, M.-H. LEE, W.-S. SEO, Korea Institute of Ceramic Engineering and Technology, Korea, S.-W. LEE, Kyung Hee University, Korea, H.-J. CHOI, Yonsei University, Korea

DP7

Investigation of an a-TiC_x Film as the Interlayer of Fluorinated DLC on a Ti6Al4V Substrate- an Approach to the Anti-corrosive and Mechanical Properties, C.-C. CHOU, H.-Y. CHEN, **M.-K. HSU**, National Taiwan Ocean University, Taiwan, Republic of China

DP8

Effects of the Plasma Electrolytic Oxidation Method in the CaP Enriched Titanium Oxide Layer Physicochemical and Corrosion Properties, **C. LAURINDO**, R.D. TORRES, P. SOARES, Pontificia Universidade Católica do Paraná, Brazil, S. MALI, J. GILBERT, Syracuse University, NY

DP9

Silicon-substituted Hydroxyapatite Coating on Biomedical Ti-Nb-Zr Alloy Using Cyclic Electrochemical Deposition Method, **Y.H. JEONG**, W.A. BRANTLEY, The Ohio State University, US, H.C. CHOE, Chosun University, Korea

DP10

Nanotube Shape and Morphology Control of Ti-6Al-4V by Various Applied Potential for Drug Doping and Bioactive Materials Coating, **H.C. CHOE**, Chosun University, Republic of Korea

DP11

Electrochemically Hydroxyapatite-precipitated Nanotubular Ti-35Ta-xNb Alloys, **C.I. JO**, Chosun University, Korea, Republic of Korea, H.C. CHOE, Chosun University, Republic of Korea

DP12

Nanotube Formation Phenomena on Ti-25Nb-xZr Alloys with Zr Content and Applied Potential, **I.S.BYEON. BYEON**, H.C. CHOE, Chosun University, Republic of Korea

DP13

The Tribocorrosion of CoCrMo Alloys Coated with TiAlPtN/TiAlPt Multilayers, **M. FLORES**, Universidad de Guadalajara, Mexico, E. ANDRADE, Universidad Nacional Autónoma de México, Mexico, O. JIMENEZ, Universidad de Guadalajara, Mexico

DP14

Enhanced Corrosion Resistance and Hemocompatibility of Biomedical NiTi Alloy by Atmospheric-pressure Plasma Polymerized Fluorine-rich Coating, **P.H. LI**, City University of Hong Kong, Hong Kong Special Administrative Region of China, L.M. LI, City University of Hong Kong, China, W.H. WANG, The University of Hong Kong, China, W.H. JIN, City University of Hong Kong, China, X.M. LIU, Hubei University, China, K.W.K. YEUNG, The University of Hong Kong, China, P.K. CHU, City University of Hong Kong, Hong Kong Special Administrative Region of China

DP15

Enhanced Osteogenic Activity on Platform of Titanate Nanotube Arrays, **X.M. ZHANG**, L.M. LI, W.H. JIN, P.H. LI, City University of Hong Kong, Hong Kong Special Administrative Region of China, L.Z. ZHAO, The Fourth Military Medical University, China, K.F. HUO, Huazhong University of Science and Technology, China, P.K. CHU, City University of Hong Kong, Hong Kong Special Administrative Region of China

DP16

The Effect of PEO Process Parameters on the Tribocorrosion Properties of TiO_2 Coatings, E.E. SUKUROGLU, H. FARZI, Atatürk University, Turkey, **S. SUKUROGLU**, Gümüşhane University, Turkey, Y. TOTIK, E. ARSLAN, I. EFEOGLU, Atatürk University, Turkey

Tribology & Mechanical Behavior of Coatings and Engineered Surfaces

Room: Town & Country and San Diego - Session EP

Symposium E Poster Session

5:00 pm

EP1

Tribology of Hydrogenated and Hydrogen-free Diamond-like Carbon Coatings in Biofuel Systems at Elevated and at Higher Temperatures, **A. DORNER-REISEL**, R. LIEBERWIRTH, S. SVOBODA, University of Applied Sciences Schmalkalden, Germany, K. GÜNTHER, University of Applied Sciences Mittweida, Germany, C. HIMCINSCHI, Technische Universität Bergakademie Freiberg, Germany, S. WEIßMANTEL, University of Applied Sciences Mittweida, Germany, G. IRMER, Technische Universität Bergakademie Freiberg, Germany

EP2

Optimizing Wear and Hydrophobic Properties of Cr-N/Al-N Multilayer Coatings, **Y. YANG**, National Kaohsiung First University of Science and Technology, Taiwan

EP3

Microstructure and Properties of WC-Co-(Cr) Coatings Modified by Sub-microcrystalline Carbides Obtained by Different Methods of High Velocity Spray Process, K. SZYMAŃSKI, G. MOSKAL, **H. MYALSKA**, Silesian University of Technology, Poland

EP5

Thermo-mechanical Stability Analysis of Sputtered DCB on Al_2O_3 for Aerospace Hybrid Power Converter, **J.-S. JEONG**, Korea Electronics Technology Institute, Republic of Korea

EP6

Wear and Friction Behavior of Fe2B Layers Formed According to a Mathematical Model of the Growth Kinetics, **E.E. VERA CARDENAS**, M. ORTIZ-DOMINGUEZ, Universidad Politécnica de Pachuca, Mexico, R. LEWIS, University of Sheffield, UK, J.L. BERNAL PONCE, Universidad Politécnica de Pachuca, Mexico, F. NAVA LEANA, Universidad Politecnica de Pachuca, Mexico, M.A. FLORES-RENTERÍA, Universidad Politécnica de Pachuca, Mexico

EP7

Dimensioning Indentation and Scratch Tests for Thin Films, **M. FUCHS**, N. SCHWARZER, N. BIERWISCH, Saxonian Institute of Surface Mechanics, Germany

EP8

A Comparative Study About the Wear Resistance of Hard Coatings Obtained by Three Different Hardening Diffusion Processes at the Surface of AISI 4140 Steel, J. HERNÁNDEZ-SÁNCHEZ, **E. HERNÁNDEZ-SÁNCHEZ**, Instituto Politecnico Nacional, Mexico, Y. DOMÍNGUEZ-GALICIA, M.E. ROSALES PEÑA ALFARO, Instituto Politecnico Nacional-UPIBI, Mexico, J.J. CORONEL-HERNÁNDEZ, Universidad Autónoma de Querétaro, Mexico

EP9

The Corrosion Resistance and the Adhesion Strength of Double Layered Zn-Mg Thin Films, **J.H. LA**, K.S. KIM, S.-Y. LEE, Korea Aerospace University, Republic of Korea, J.J. LEE, Seoul National University, Republic of Korea, W.Y. JEUNG, Korean Institute of Science and Technology, Republic of Korea

EP10

Scratch and Wear Behavior of AlTiN/TiN Nanolayer Coatings, H. ÇALIŞKAN, Bartın University, Turkey, **M. PANJAN**, P. PANJAN, M. ČEKADA, Jozef Stefan Institute, Slovenia, A.C. KARAOĞLANLI, Bartın University, Turkey

EP11

The Friction and Wear Properties at Room Temperature and Vacuum Atmosphere of Ti/TiB_2/MoS_2 Graded-Composite Coatings Deposited by CFUBMS, Ö. BARAN, Erzincan University, Turkey, F. BIDEV, **H. CICEK**, Atatürk University, Turkey, L. KARA, Karadeniz Technical University, Turkey, I. EFEOGLU, Atatürk University, Turkey, T. KÜÇÜKÖMEROĞLU, Karadeniz Technical University, Turkey

EP12

Instrumented Indentation Hardness and Sliding Wear Characteristics of a Sequential Plasma Process of AISI 316L Austenitic Steel, after Pre-shot Peening, M.R. MENEZES, Universidade Federal de Minas Gerais, UFMG, Brazil, J.C. AVELAR-BATISTA WILSON, Tecvac, Ltd., UK, **M.V. AUAD**, Auad Godoy Consultants, Brazil, A.C. BOZZI, Universidade Federal de Espirito Santo, UFES, Brazil, C. GODOY, Universidade Federal de Minas Gerais, UFMG, Brazil

EP13

Tribological Properties of Solid Lubricant W-S-N Coatings, **P. MUTAFOV**, T. POLCAR, Czech Technical University in Prague, Czech Republic, M. EVARISTO, A. CAVALEIRO, SEG-CEMUC, University of Coimbra, Portugal

EP14

Characterisation of Amorphous Carbon Coatings for Tribological Applications in Challenging Environments, **J. COOPER**, University of Sheffield, UK, DA. STEWART, Rolls Royce, UK, A. LEYLAND, A. MATTHEWS, University of Sheffield, UK

EP15

Analysis of Sliding Wear Tests of Plasma Processed AISI 316L, M.C.S. DUARTE, Universidade Federal de Minas Gerais, UFMG, Brazil, A.C. BOZZI, Universidade Federal do Espírito Santo, UFES, Brazil, **C. GODOY**, Universidade Federal de Minas Gerais, UFMG, Brazil

EP16

Comparision of the Tribological Behavior of VN-Cu and MoN-Cu Coatings at High Temperature, G. RAMIREZ, **T.A.L. DE LIMA BURGO**, O.L. ERYILMAZ, A. ERDEMIR, Argonne National Laboratory, US

EP17

Microstructure Characterization and Mechanical Properties of Multicomponent CrAlSiTiVN Hard Coating, **Y. CHANG**, National Formosa University, Taiwan

EP18

Investigation of Hard Coatings with the Instrumented Indentation Test, **T. HAAS**, B. BINDER, G. BOSCH, H.P. VOLLMAR, Helmut Fischer GmbH, Germany

EP19 **WITHDRAWN**

Glassy Carbon Coatings Deposited on Hybrid Structure of Composite Materials, A.. POSMYK, J. MYALSKI, **B. HEKNER**, Silesian University of Technology, Poland

EP21

Tribological and Corrosion Properties of Ni/MWCNT Nanocomposites Produced by Pulse Electro Co-deposition, **M. KARTAL**, Sakarya University, Turkey, H. GUL, Duzce University, Gumusova Vocational School, Turkey, M. UYSAL, A. ALP, H. AKBULUT, Sakarya University, Turkey

EP22

Wear Behavior of CBN Coated Carbide Tools in Milling of Ti6Al4V Alloy, **H. ÇALIŞKAN**, B. KURŞUNCU, A.C. KARAOĞLANLI, Bartın University, Turkey

EP25

Reactively Sputtered Chromium Carbide/Carbon Glass-like Films for Sliding Electrical Contact Applications, **K. NYGREN**, Uppsala University, Sweden, M. SAMUELSSON, A. FLINK, H. LJUNGCRANTZ, Impact Coatings AB, Sweden, A.K. RUDOLPHI, U. JANSSON, Uppsala University, Sweden

EP26

Mechanical and Tribological Characterization of ZrN Coatings on Titanium Modified Austenitic Stainless Steel, **M.F. WANI**, National Institute of Technology Hazratbal, India

EP27

Application of a DLC-coating for Improving Hydrostatic Piston Shoe Bearing Performance under Boundary Lubrication Conditions, S.-M. KIM, S.-R. LEE, **S.-Y. LEE**, Y.S. HONG, C.-H. KIM, Korea Aerospace University, Korea

EP28

The Effect of Deposition Parameters on the Tribological Properties of TiAlCrNbN Thin Films, L. KARA, Karadeniz Technical University, Turkey, Ö. BARAN, Erzincan University, Turkey, T. KÜÇÜKÖMEROĞLU, Karadeniz Technical University, Turkey, **I. EFEOGLU**, Atatürk University, Turkey

EP29

Improvement of Fatigue Property of Magnesium Alloy by Coating Thin Film Metallic Glass, **C.H. CHANG**, J.P. CHU, National Taiwan University of Science and Technology (NTUST), Taiwan, P.K. LIAW, University of Tennessee, US

New Horizons in Coatings and Thin Films
Room: Town & Country and San Diego - Session FP

Symposium F Poster Session
5:00 pm

FP1

Preparation of *n*-ZnO and *p*-CuO Films and Their Heterojunctions by Chemical Bath Deposition Based Technique, **T. TERASAKO**, T. MURAKAMI, S. SHIRAKATA, Ehime University, Japan

FP2

Low Temperature Atomic Layer Deposition of ZnO Thin Films on Cellulose Nanofibers for low Cost Dye-Sensitized Solar Cells, **K.N. HA**, Korea Institute of Industrial Technology (KITECH), Korea, E. AN, Korea Institute of Industrial Technology (KITECH), Busan, South Korea, W.-J. LEE, Pusan National University, South Korea, I.-W. PARK, Korea Institute of Industrial Technology (KITECH), Busan, South Korea, S.-H. KWON, Y. PARK, Pusan National University, South Korea

FP3

Characterization of ZnO Nanotubes Grown by Supercritical CO_2 Fluid Mixed with Ethanol Solution, **K.C. CHANG**, T.M. TSAI, T.C. CHANG, G.R. LIU, H.C. HUANG, T.F. YOUNG, D.S. GAN, National Sun Yat-Sen University, Taiwan

FP4

High Power Impulse Magnetron Sputter Deposited IGZO on Flexible Substrate and its Thin-film Transistor Performance, **Y.H. CHEN**, R.C. KE, J.L. HE, Feng Chia University, Taiwan

FP5

Measurement of Ionized Metal Flux Fraction in HiPIMS by Retarding Field QCM Analyzer, **T. KUBART**, Uppsala University, Angstrom Laboratory, Sweden, M. CADA, Z. HUBICKA, Institute of Physics of the ASCR, v.v.i., Czech Republic

FP6

Improving the Absorption of Visible Light of Iron Silicide Thin Film by Pinhole Fabrication, **H.F. HSU**, Y.T. CHANG, G.Y. LI, National Chung Hsing University, Taiwan

FP7

Synthesis, Structure and Optical Properties of Tungsten Oxynitride Thin Films, **C. RAMANA**, A.J. MORENO-TARANGO, E. RUBIO, R. VEMURI, University of Texas at El Paso, US

FP8

Enhanced Exchange Bias and Mechanical Properties of Al Incorporated Ni–Mn–Sb Ferromagnetic Shape Memory Alloy Thin Flms, **R. BARMAN**, D. KAUR, Indian Institute of Technology Roorkee, India

FP9

Synthesis and Water Splitting Characterization of Ordered (Cu, Zn) Oxide Nanowire Arrays by PAM Template Assisted Method During Electrochemical Deposition, Y.M. SHEN, National Cheng Kung University, Taiwan, S.C. WANG, Southern Taiwan University, Taiwan, J.L. HUANG, **Y.H. CHEN**, National Cheng Kung University, Taiwan

FP11

Evaluation of the Nanomechanical Properties of Vanadium Thin Films Prepared by RF Magnetron Sputtering, M.A. MAMUN, K. ZHANG, H. BAUMGART, A.A. ELMUSTAFA, **D. NMINIBAPIEL**, Old Dominion University, US

FP12

Oriented Lanthanum Silicate Thin Film Electrolytes for IT-SOFCS, **J.C. OLIVEIRA**, M. MACATRÃO, A. CAVALEIRO, SEG-CEMUC, University of Coimbra, Portugal

FP13

Microstructure and Electronic Properties of Intrinsic and W-Doped Gallium Oxide Thin Films Made by Sputter-Deposition, C. RAMANA, University of Texas at El Paso, **E. RUBIO**, A. MIRANDA-GALLARDO, University of Texas at El Paso, US

FP14

Purification of Commercial CNT Sheet Material for Composite Fabrication, **A.R. HOPKINS**, H.A. KATZMAN, The Aerospace Corporation, US

FP15

Growth of Boron Nitride at High Temperature Chemical Vapor Deposition (Htcvd) Reactor Using Bcl3 and Nh3 as Precursors, N. COUDURIER, R. BOICHOT, F. MERCIER, **E. BLANQUET**, SIMaP CNRS/Grenoble INP/UJF, France, A. HENRY, Linköping University, IFM, Thin Film Physics Division, Sweden

FP16

Effect of Anodization Parameters on Ca-P Incorporated Nanotubes Properties, **P. SOARES**, Pontificia Universidade Católica do Paraná, Brazil, V. LESZCZAK, K. POPAT, Colorado State University, US

FP17

Current-Voltage Characteristics During High Power Impulse Magnetron Sputter Deposition of TiO_2, P.-H. LI, MingDao University, Taiwan, C. LIU, Fujian University of Technology, Fuzhou, China, J.-Y. JIAN, C.-M. YEH, C.L. CHANG, **W.-Y. WU**, MingDao University, Taiwan

FP18

Thickness Dependent Magnetic Properties of Co-sputter Deposited Ni-Mn-Al Heusler Alloy Hard Nanostructured Thin Films, A. MISHRA, R. CHANDRA, S. SRIVASTAVA, A. GEHLOT, P. DUBEY, D. KAUR, **S. CHAUHAN**, Indian Institute of Technology Roorkee, India

Applications, Manufacturing, and Equipment
Room: Town & Country and San Diego - Session GP

Symposium G Poster Session
5:00 pm

GP1

Fabrication and Characteristics of Ceramic/Ni-Cr-Mo Steel Coatings by Centrifugal Casting Process, H. KIM, Sejong University, Korea, K. OH, K. YI, S. KIM, S.M. Metal, Korea, **K. PARK**, Sejong University, Korea

GP2

Oxidation-induced Cu Coating on Steel Surface, N. LI, University of Science and Technology Liaoning, China, **W. SHA**, Queen's University Belfast, UK

GP3

Desk-top RF-DC Plasma Nitriding System for Automotive Steel Parts, **Y. SUGITA**, YS-Eletric Industry, Co. Ltd., Japan, T. AIZAWA, Shibaura Intitute of Technology, Japan, K. TSUKUI, E. NAKAYAMA, Yamanashi University, Japan

GP4

MicroporousN-doped Carbon Films Produced by Cold Atmospheric Plasma Jet and Compatibility with MC3T3-E1 Preosteoblasts, **L.M. LI**, X.M. ZHANG, M. ZHANG, P.H. LI, P.K. CHU, City University of Hong Kong, Hong Kong Special Administrative Region of China

Topical Symposia
Room: Town & Country and San Diego - Session TSP

Symposium TS Poster Session
5:00 pm

TSP-1

Characterization of 4H-SiC Grown by Thermal Evaporation System Using Single Boat, K. MAHMOOD, **M. ASGHAR**, The Islamia University of Bahawalpur, Pakistan, I. FERGUSON, R. TSU, University of North Carolina, US

TSP-2

Dye Sensitized Solar Cells of TiO_2 Nanotubes by Anodization with $TiCl_4$-ZnO Treatment, J.H. YANG, K.H. KIM, **H.W. CHOI**, Gachon University, Republic of Korea

TSP-3

Thermal Expansion and Elasticity of Metastable Cubic B1-AlN, **M. BARTOSIK**, Vienna University of Technology, Austria, D. HOLEC, Montanuniversität Leoben, Austria, M. TODT, Vienna University of Technology, Austria, J. TODT, Montanuniversität Leoben, Austria, F.G. RAMMERSTORFER, P.H. MAYRHOFER, Vienna University of Technology, Austria

TSP-4

The Synthesis of Ag/Pt Bimetallic Nanoparticles Supported on Carbon with Enhanced Electocatalytic Activity by Solution Plasma Process, **S.-M. KIM**, Korea Aerospace University, Republic of Korea, J.W. KIM, University of Incheon, Republic of Korea, S.-Y. LEE, Korea Aerospace University, Republic of Korea, J.J. LEE, Seoul National University, Republic of Korea, W.Y. JEUNG, Korean Institute of Science and Technology, Republic of Korea

TSP-5

Completely Topographically Corrected Scratch Test – Examples and How it has Been Done, **N. SCHWARZER**, N. BIERWISCH, Saxonian Institute of Surface Mechanics, Germany

TSP-7

Optical Properties of Multi layers MnO/Sb/MnO Thin Films Prepared by Electron-beam Evaporation Technique, **M. ALZAMIL**, King Saud University, Saudi Arabia

TSP-9

Reactor of Dielectric Barrier Discharge with Incidence in Liquid: One Efficient Tool for Extraction of Lignin, **F.S. MIRANDA**, F.L.C. LUCAS, E.D. SANTOS, University of Paraiba Valley (UNIVAP), Brazil, R.J. SILVA, Technological Institute of Aeronautics (ITA), Brazil, C. CARLI, S. RABELO, C. ROSSEL, J. PRADELLA, Brazilian Bioethanol Science and Technology Laboratory, Brazil, H.S. MACIEL, R.S. PESSOA, L.V. SANTOS, University of Paraiba Valley (UNIVAP), Brazil

TSP-10

Characteristics of Anticorrosion Layer of Silicon Oxide Films on Magnesium Alloys by Atmospheric Pressure Plasma Jet, **Y.L. KUO**, K.H. CHANG, J.Y. JIAN, National Taiwan University of Science and Technology (NTUST), Taiwan

TSP-11

Emerging Concepts for Large Scale Graphene Synthesis Towards Enhanced Electrochemical Applications, D. BROWNSON, C. BANKS, **P. KELLY**, Dalton Research Institute, Manchester Metropolitan University, UK

TSP-12

Fabrication of Core-shell Particles Having the Absorption-desorption Property for a Fluidized Bed Electrode, **E.H. KIM**, Y. JUNG, Changwon National University, Korea, J.-G. YEO, S.-C. YANG, J. CHOI, Korea Institute of Energy Research, Korea

TSP-13

Improving Oxidation Resistance and Fracture Strength of MgO-C Refractory Through Precursor Coating, **G.-H. CHO**, J. LI, E.H. KIM, Y. JUNG, Changwon National University, Republic of Korea, Y.-KI BYEUN, Technical Research Laboratories Pohang Research Lab, Republic of Korea

Friday Morning, May 2, 2014

	Coatings for Use at High Temperatures Room: Sunrise - Session A2-2 **Thermal and Environmental Barrier Coatings** **Moderators: K.A. Unocic**, Oak Ridge National Laboratory, US, **V. Maurel**, Mines-ParisTech, France, **K. Lee**, Rolls Royce, US	Hard Coatings and Vapor Deposition Technology Room: Golden West - Session B3 **Deposition Technologies for Diamond Like Coatings** **Moderators: K. Böbel**, Robert Bosch GmbH, Germany, **C. Engdahl**, Crystallume, US
8:00 am	**A2-2-1** Deposition and Properties of a High Temperature Thermal Barrier Coating Using The Solution Precursor Plasma Spray Process, **M. GELL**, E. JORDAN, J. ROTH, C. JIANG, University of Connecticut, US, J. WANG, B. NAIR, HiFunda LLC, US	**B3-1** The Chemical Functionalization of DLC to Create an Oleophobic and Hydrophobic Surface with High Thermal and Oxidative Stability, **D.A. SMITH**, SilcoTek Corporation, US
8:20 am	**A2-2-2** Feasability of Multilayer Sol-Gel Thermal Barrier Coating Sensor for Through-thickness Temperature Sensing and Interface Delamination Early Diagnostic, **E. COPIN**, T. SENTENAC, Y. LE MAOULT, Ecole Nationale Superieure des Mines - Albi, France, F. ANSART, CIRIMAT, University of Toulouse, France, P. LOURS, Ecole Nationale Superieure des Mines - Albi, France	**B3-2** Deposition of Diamond-like Carbon Films on Steel Surfaces by Enhanced Asymmetrical Bipolar Pulsed-DC PECVD Method and Acetylene as Precursor, G. CAPOTE, National University of Colombia, Colombia, E. CORAT, **V. TRAVA-AIROLDI**, Institute for Space Research, Brazil
8:40 am	**A2-2-3 Invited** Analysis of Possible Microstructures in Suspension Plasma Sprayed Deposits, **L. PAWLOWSKI**, P. SOKOLOWSKI, University of Limoges, France, S. KOZERSKI, Wroclaw University of Technology, Poland, A. DENOIRJEAN, University of Limoges, France	**B3-3 Invited** Developments of Amorphous Hydrogenated DLC Coatings for Automotive Applications, **M. KEUNECKE**, R. WITTORF, M. WEBER, I. BIALUCH, K. BEWILOGUA, G. BRAEUER, Fraunhofer Institute for Surface Engineering and Thin Films IST, Germany
9:00 am	Invited talk continued.	Invited talk continued.
9:20 am	**A2-2-5** Slurry Based Thermal Barrier Coatings with Quasi-foam Structures from Sintered Micro-sized Hollow Alumina Spheres, **V. KOLARIK**, M. JUEZ LORENZO, R. ROUSSEL, V. KUCHENREUTHER, Fraunhofer ICT, Germany	**B3-5** A MF-AC Enhanced PECVD Technology for High Rate Deposition of DLC, H. TAMAGAKI, J. HAGA, H. ITO, **A. UMEDA**, Kobe Steel, Ltd., Japan
9:40 am	**A2-2-6** Characterization of Plasma Electrolytic Oxidized Coatings on Hot-dip Aluminized Carbon Steel, **F. CHANG**, National Taiwan University of Science and Technology (NTUST), Taiwan, J.W. LEE, Ming Chi University of Technology, Taiwan, C.J. WANG, National Taiwan University of Science and Technology (NTUST), Taiwan	**B3-6** Modifications of Closed Drift Ion Source for Various Surface Treatments from Etching to Coating, **S. LEE**, K.-T. KIM, Y.-J. KANG, D.-G. KIM, J.-K. KIM, Korea Institute of Materials Science, Korea
10:00 am	**A2-2-7** The Influence of Temperature Gradients on the Interaction of Molten Silicates with Thermal Barrier Coatings, **R.W. JACKSON**, E. ZALESKI, M.R. BEGLEY, C.G. LEVI, University of California, Santa Barbara, US	**B3-7 Withdrawn** Plasma Beam Deposition of Amorphous Carbon, **M.F. WEILER**, CCR TECHNOLOGY GmbH, Germany
10:20 am	**A2-2-8** The Effect of Cycle Frequency, H_2O and CO_2 on TBC Lifetime with NiCoCrAlYHfSi Bond Coatings, **M. LANCE**, K.A. UNOCIC, J. HAYNES, B.A. PINT, Oak Ridge National Laboratory, US	Invited talk continued.
10:40 am	**A2-2-9** Failure Characteristics And Mechanisms Of Eb-Pvd Tbcs With Pt-Modified Nial Bond Coat, L. ZHOU, S. MUKHERJEE, **Y.H. SOHN**, University of Central Florida, US	
11:00 am	**A2-2-10** Time and Temperature Dependent Mechanical Properties of Superalloy Bond Coat at Nanometer Length Scale, **K. RZEPIEJEWSKA-MALYSKA**, J. VIEREGGE, O.L. WARREN, S.A.S. SYED, Hysitron, Inc., US	
11:20 am	**A2-2-11** Development and Performance Evaluations of HfO2-Si Based Bond Coat Systems for Advanced Environmental Barrier Coatings, **D. ZHU**, NASA Glenn Research Center, US	
11:40 am	**A2-2-12 Withdrawn** Evaluation Of Hot Corrosion Resistance On Inconel 718 Superalloys Of Thermal Barrier Coatings, **K.M. DOLEKER**, A.C. KARAOĞLANLI, Bartın University, Turkey	
	2015 ICMCTF **April 20-24, 2015**	**2015 Abstract Submission Deadline** **October 1, 2014**
	Thank You & See You Next Year Party **Trellis Courtyard near Pool** **12:30-1:30 pm**	**Awards Nominations Deadline** **October 1, 2014**

Friday Morning, May 2, 2014

	Hard Coatings and Vapor Deposition Technology Room: Royal Palm 1-3 - Session B4-5 **Properties and Characterization of Hard Coatings and Surfaces** **Moderators: C. Mulligan**, US Army ARDEC, Benet Laboratories, US, **J. Lin**, Southwest Research Institute, US, **U. Beck**, BAM Berlin, Germany	Hard Coatings and Vapor Deposition Technology Room: Royal Palm 4-6 - Session B7 **Computational Design and Experimental Development of Functional Thin Films** **Moderators: B. Alling**, Linköping University, Thin Film Physics Division, Sweden, **D. Holec**, Montanuniversität Leoben, Austria
8:00 am	**B4-5-1** Bias Effect on Structure and Mechanical Properties of Magnetron Sputtered Nanocrystalline Zirconium Tungsten Nitride Thin Films, **P. DUBEY**, R. CHANDRA, Indian Institute of Technology Roorkee, India	**B7-1 Invited** Ab-initio Simulation of Vacancy Formation in $Ti_{0.5}Al_{0.5}N$ Alloy: From the Diverse Local Environments Towards Self-diffusion, **F. TASNÁDI**, I.A. ABRIKOSOV, Linköping University, IFM, Sweden, M. ODÉN, Linköping University, IFM, Nanostructured Materials, Sweden
8:20 am	**B4-5-2** Structural, Mechanical and Electronic Properties of 3d Transition Metal Nitrides in Cubic Zincblende, Rocksalt and Cesium Chloride Structures: a First-Principles Investigation, Z. LIU, X. ZHOU, **S. KHARE**, University of Toledo, US, D. GALL, Rensselaer Polytechnic Institute, US	Invited talk continued.
8:40 am	**B4-5-3** Local Residual Stress Measurement on Amorphous Plasma-sprayed Single-splats, **M. SEBASTIANI**, University of Rome "Roma Tre", Italy, G. BOLELLI, L. LUSVARGHI, University of Modena and Reggio Emilia, Italy, E. BEMPORAD, University of Rome "Roma Tre", Italy	**B7-3** Room-Temperature Plasticity in ZrC: Role of Crystal Anisotropy, S. KIANI, **S. KODAMBAKA**, C. RATSCH, University of California, Los Angeles, US, A. MINOR, University of California, Berkeley; National Center for Electron Microscopy, Lawrence Berkeley National Laboratory, US, J.-M. YANG, University of California, Los Angeles, US
9:00 am	**B4-5-4** Oxidation Behavior of $TiC_{0.81}N_{0.48}$ Coating and $TiC_{0.61}N_{0.44}O_{0.15}$ Coating Deposited by Chemical Vapor Deposition, **L. ZHU**, Y.M. ZHANG, T. HU, Shanghai University, China, P. LEICHT, Y. LIU, Kennametal Incorporated, US	**B7-4** Ab Initio Guided Design of Corundum Type $(Al_{1-x-y}Cr_xM_y)_2O_3$ Thin Films, **C.M. KOLLER**, Vienna University of Technology, Austria, J. RAMM, Oerlikon Balzers Coating AG, Liechtenstein, S. KOLOZSVÁRI, Plansee Composite Materials GmbH, Germany, D. HOLEC, Montanuniversität Leoben, Austria, J. PAULITSCH, P.H. MAYRHOFER, Vienna University of Technology, Austria
9:20 am	**B4-5-5** Modulus and Compressive Stress Graded Ti-C Coating on Ti-6Al-4V Aerospace Alloy, **T.R. KAMALAKSHI HEMACHANDRAN**, M. RAO GOWRAVARAM, Indian Institute of Science, India	**B7-5 Invited** WITHDRAWN Accelerated Molecular Dynamics Simulation of Adatom Kinetics using SISYPHUS, **A. VAN DE WALLE**, Brown University, US, P. TIWARY, ETH Zurich, Switzerland
9:40 am	**B4-5-6** Analysis of the Coating Interface Mechanics, **C.Y. NIE**, L. GU, D. ZHENG, L. WANG, Harbin Institute of Technology, China	Invited talk continued.
10:00 am	**B4-5-7** Corrosion and Tribological Behaviour of Laser Surface Alloyed Aisi 1016 Mild Steel, **O. FATOBA**, Tshwane University of Technology, South Africa	**B7-7** Molecular Dynamics Study of the Growth of Various Crystalline Phases of Metal Oxides, **J. HOUSKA**, University of West Bohemia, Czech Republic, S. MRÁZ, J. SCHNEIDER, RWTH Aachen University, Germany
10:20 am		**B7-8** Lattice Ordering Effects on Toughness Enhancement in TiN and VN Thin Films Alloys, D. EDSTRÖM, D. SANGIOVANNI, **V. CHIRITA**, L. HULTMAN, Linköping University, IFM, Thin Film Physics Division, Sweden
10:40 am		**B7-9 Invited** A Computational Approach to Designing Boron Based Coatings, **H. EUCHNER**, J. PAULITSCH, P.H. MAYRHOFER, Vienna University of Technology, Austria
11:00 am		Invited talk continued.
11:20 am		**B7-11** Modeling the Thermo-Mechanical and Optical Properties of Solar Selective Coatings, **I. HERAS**, Abengoa, Spain
	2015 ICMCTF **April 20-24, 2015**	**2015 Abstract Submission Deadline** **October 1, 2014**
	Thank You & See You Next Year Party **Trellis Courtyard near Pool** **12:30-1:30 pm**	**Awards Nominations Deadline** **October 1, 2014**

Friday Morning, May 2, 2014

	Advanced Materials for Modern Device Applications **Room: Sunset - Session C2** **Novel Aspects in Thin Film Characterization and Data Modeling** **Moderators: J. Krueger**, BAM Berlin, Germany, **T. Hofmann**, University of Nebraska–Lincoln, US	**Applications, Manufacturing, and Equipment** **Room: Tiki - Session G6** **Advances in Industrial PVD & CVD Deposition Equipment** **Moderators: M. Ahlgren**, Sandvik Coromant, Swedin, **K. Bobzin**, RWTH Aachen University, Germany
8:00 am	**C2-1 Invited** Spectroscopic Ellipsometry Characterization in the Photovoltaic Device Configuration, **N.J. PODRAZA**, University of Toledo, US	**G6-1** Comparison of Plasma Characteristics of DC and Pulsed Arc Evaporation, **T. TAKAHASHI**, R. CREMER, KCS Europe GmbH, Germany, S. HIROTA, Kobe Steel Ltd., Japan
8:20 am	Invited talk continued.	**G6-2** Hybrid Coatings in Arc Systems: HI3 Process (HIPAC plus arc), Types of Nitriding Processes and DLC, **J. VETTER**, J. CRUMMENAUER, J. MUELLER, O. JARRY, Sulzer Metaplas GmbH, Germany
8:40 am	**C2-3** Broad Band Spectroscopic Ellipsometry Modelling of Metallic Structures using FDTD, **J.A. ZAPIEN**, Y. FOO, City University of Hong Kong, Hong Kong Special Administrative Region of China	**G6-3 Invited** Recent Developments in ALD Equipment and Processes, **M. RITALA**, University of Helsinki, Finland
9:00 am	**C2-4** Phase Stability and Intrinsic Growth Stresses in Ti/Nb Multilayered Thin Films, **L. WAN**, X.X. YU, G.B. THOMPSON, The University of Alabama, US	Invited talk continued.
9:20 am	**C2-5** Experimental and Simulation Studies of Compact Nitride Layers Growth During Plasma Nitriding of Pure Iron, **C. JIMENEZ**, C. LEÓN, J. OSEGUERA, F. CASTILLO, ITESM-CEM, Mexico	**G6-5** Integration of HiPIMS Equipment into an Industrial Coating Production for Cutting Tools, T. LEYENDECKER, O. LEMMER, W. KOELKER, **C. SCHIFFERS**, CemeCon AG, Germany
9:40 am	**C2-6 Invited** Metal-Dielectric Coatings and their Applications in Optical Instruments and Optical Microscopy - Optimizing Performance and New Developments, **H. NIEDERWALD**, Carl-Zeiss Jena GmbH, Germany	**G6-6** Replacement of Electroplating Produced in a Flexible Inline Production Platform, D. DRIESENAAR, **P. SEGERS**, J. LANDSBERGEN, I. KOLEV, J. CLABBERS, R. TIETEMA, T. KRUG, IHI Hauzer Techno Coating BV, Netherlands
10:00 am	Invited talk continued.	**G6-7** Mechanical and Tribological Property of Titanium Series Thick Coating Deposited by our Kobelco new PVD Machine, AIP-G60R, **S. TANIFUJI**, H. FUJII, H. NOMURA, Kobe Steel Ltd., Japan
	2015 ICMCTF **April 20-24, 2015**	**2015 Abstract Submission Deadline** **October 1, 2014**
	Thank You & See You Next Year Party **Trellis Courtyard near Pool** **12:30-1:30 pm**	**Awards Nominations Deadline** **October 1, 2014**

Topical Symposia
Room: California - Session TS6

Atmospheric Plasma Applications
Moderators: H. Barankova, Uppsala University, Sweden, **D. Dowling**, University College Dublin, Ireland

8:00 am	**TS6-1 Invited** Superhydrophobic Coating Deposition with Atmospheric rf Plasma, **S. KIM**, D. MARCHAND, Pennsylvania State University, US	
8:20 am	Invited talk continued.	
8:40 am	**TS6-3** Atmospheric Plasma Deposition of Thin Films for Aerospace Applications, **A.N. RANADE**, The Boeing Company, U.S.	
9:00 am	**TS6-4** Atmospheric Pressure Plasma Polymerization on PE to Increase Bone Cement Adhesion, **P. COOLS**, N. DE GEYTER, S. VAN VREKHEM, Ghent University, Belgium, A. VAN TONGEL, Ghent University Hospital, Belgium, P. DUBRUEL, Ghent University, Belgium, F. BARBERIS, Universita' degli Studi di Genova, Italy, R. MORENT, Ghent University, Belgium	
9:20 am	**TS6-5 Invited** Disinfection, Decontamination, and Nano-particle Production using a Pulsed Submerged Arc, N. PARKANSKY, **R.L. BOXMAN**, Tel Aviv University, Israel	
9:40 am	Invited talk continued.	
10:00 am	**TS6-7** Plasma Reforming of Ethanol, H. BARANKOVA, **L. BARDOS**, Uppsala University, Sweden	
10:20 am	**TS6-8** Growth of Multifunctional Nanocomposite Thin Films on Wood Substrates using Dielectric Barrier Discharges at Atmospheric-pressure, J. PROFILI, LAPLACE and U. Montréal, Canada, O. LEVASSEUR, **L. STAFFORD**, Université de Montréal, Canada, N. GHERARDI, CNRS-LAPLACE, Canada	
10:40 am	**TS6-9 Invited** Removal of Organic and Inorganic Coatings using Atmospheric Pressure Air Plasma, **P. YANCEY**, Atmospheric Plasma Solutions, Inc., US	
11:00 am	Invited talk continued.	
11:20 am	**TS6-11** Facile Synthesis of Pt-Pd Bimetallic Nanoparticles by Plasma Discharge in Liquid and their Electrocatalytic Activity Toward Methanol Oxidation in Alkaline Media, S.-M. KIM, A.-R. CHO, Korea Aerospace University, Korea, J.W. KIM, University of InCheon, Republic of Korea, **S.-Y. LEE**, Korea Aerospace University, Korea	
11:40 am	**TS6-12** An Atmospheric Pressure Inductively Coupled Plasma (AP-ICP) Torch for Anti-corrosive Silicon Carbide Coating of the Consumables for a 450 mm Wafer Etching Equipment, **Y. GLUKHOY**, A. RYABOY, T. KERZHNER, Nanocoating Plasma Systems, Inc., US	
	2015 ICMCTF **April 20-24, 2015**	**2015 Abstract Submission Deadline** **October 1, 2014**
	Thank You & See You Next Year Party **Trellis Courtyard near Pool** **12:30-1:30 pm**	**Awards Nominations Deadline** **October 1, 2014**

Monday Morning, April 28, 2014

Plenary Talk
Room: Town & Country - Session PL

Plenary Lecture

8:00am **PL1 Self-healing Materials: An Alternative Approach to Create more Durable/Reliable Materials and Products**, ***S. van der Zwaag*** *(s.vanderzwaag@tudelft.nl)*, TU Delft, Netherlands **INVITED**

From the start of civilisation mankind has tried to improve the performance and durability of the materials it uses. Over 20 centuries of dedicated materials development has led to today's wide range of materials with exceptional mechanical and other properties. To make our materials as reliable and durable as possibly, materials scientists have developed a wide range of microstructures, which ultimately all are based on a common underlying paradigm " the damage prevention concept'. Nature on the other hand seems to have 'realised' that the occurrence of damage is unavoidable and has developed many of its structural and functional materials on the basis of an alternative paradigm "the damage management concept", leading to materials which derive their high reliability from their autonomous healing capability.

In this lecture the concept of self healing in engineering and functional materials will be described and several concepts to create self healing materials, such as polymers, composites, metals, ceramics, concrete, asphalts and functional materials such as thermal interface materials, low friction coatings, thermal barrier coatings and thermal interface materials will be presented. While self healing behaviour has now been realised in almost all material classes and the first commercial products are about to enter the market, many more routes remain to be developed.

Hard Coatings and Vapor Deposition Technology
Room: Royal Palm 1-3 - Session B1-1

PVD Coatings and Technologies
Moderator: A.N. Ranade, The Boeing Company, S. Weißmantel, University of Applied Sciences Mittweida, J.W. Lee, Ming Chi University of Technology, Taiwan

10:00am **B1-1-1 Composition Control in Zr-Cu-Ni-Al Thin Film Metallic Glass for Improvement of Mechanical and Anti-microbial Properties**, ***J.L. Lee***, *K.C. Hsu, J.G. Duh (jgd@mx.nthu.edu.tw)*, National Tsing Hua University, Taiwan

This study focuses on the correlations among the compositions of Zr-Cu-Ni-Al thin film metallic glass (TFMG) and corresponding mechanical as well as anti-microbial properties. The TFMG was prepared by DC magnetron co-sputtering technique with Zr-Cu and Ni-Al targets. By adjusting working power and pressure, thin films with various constituents were fabricated. The chemical compositions of the Zr-Cu-Ni-Al thin films were analyzed by field emission electron probe micro-analyzer (FE-EPMA). The amorphous structures were verified by X-ray diffractometer (XRD). The hardness and elastic modulus were measured by nano-indention tester. The cross-sectional morphologies of the thin films were observed by field emission scanning electron microscope (FE-SEM). With the increasing Ni and Al content in (Zr5Cu5)100-2xNixAlx system, the hardness was improved up to 50% as compared to Zr-Cu TFMG. The strengthening mainly results from the atomic radii difference, and the enthalpy of mixing among mutual atomic bonding. In pursuit of high hardness, whether the coating still belongs to a metallic glass is critical. Differential scanning calorimetry (DSC) analysis further identifies the metallic glass characteristics of films with the formation of super-cooling regions. In addition, the property difference between (Zr5Cu5)100-2xNixAlx and (Zr4Cu6)100-2xNixAlx system were investigated.

Liquid culture methods and plate counting methods are used to assess the antimicrobial performance of specimens. The antimicrobial rate against Escherichia coli (E. coli) under Japanese Industrial Standard JIS Z2801: 2000 is over 95%. The results show that the surface of SS 304 stainless steel substrate can be modified by deposited Zr-Cu-Ni-Al TFMG, and their improved anti-microbial efficiency against E. coli is attributed to their amorphous rough surface, and released copper ion.

Finally a Zr-Cu-Ni-Al TFMG with appropriate composition to exhibit improved hardness, thermal stability, and antimicrobial ability was revealed and discussed.

10:20am **B1-1-2 Low-Temperature, High-Rate Growth of Dense, Hard and Stress-free Refractory Ceramic Alloy Coatings**, ***G. Greczynski*** *(grzgr@ifm.liu.se), J. Lu, J. Jensen*, Linköping University, IFM, Thin Film Physics Division, Sweden, *I. Petrov, J. Greene*, University of Illinois at Urbana-Champaign, US, *W. Kölker, S. Bolz, C. Schiffers, O. Lemmer*, CemeCon AG, Germany, *L. Hultman*, Linköping University, IFM, Thin Film Physics Division, Sweden

Growth of thin films by means of physical vapor deposition requires elevated substrate temperatures to ensure high adatom mobilities necessary for film densification. With no external heating applied during deposition resulting layers are underdense and exhibit poor mechanical properties. Bombardment of the growing film surface with gas ions accelerated in the intentionally applied electric field of the substrate helps to eliminate porosity through collisional increases in adatom mean free paths. [1] However, at higher incident ion energies, necessary to obtain densification, a steep price is extracted in the form of residual ion-induced compressive stress resulting from both recoil implantation of surface atoms and trapping of rare-gas ions in the lattice.

Here, we propose a new PVD method to grow dense, hard and stress-free thin films at low substrate temperature T_s, i.e., with no external heating applied. We use hybrid high-power pulsed and dc magnetron co-sputtering (HIPIMS and DCMS) [2,3] to grow $Ti_{1-x}Ta_xN$ alloys. The Ta target driven by HIPIMS serves as the pulsed source of energetic Ta^+/Ta^{2+} metal-ions, as determined by the *in-situ* ion mass spectrometry, while the Ti target operates in DCMS mode resulting in a continuous flux of metal atoms to sustain the high deposition rate. Substrate bias V_s is applied in pulses synchronized to the metal-ion phase of the HIPIMS discharge and the amplitude is varied from 20 to 280 V to investigate the effect of the bombarding Ta-ion energy on film properties. The densification of the magnetron sputtered film is achieved by pulsed bombardment with heavy Ta ions that are constituents of the alloy films and thus the excessive stresses are eliminated. The deposition rate is high (defined by the DCMS cathodes) and no external heating is used. We show that with as little as 8 mol% of TaN incorporated in the film, $Ti_{0.92}Ta_{0.08}N$ alloys with high hardness can be obtained with T_s not exceeding 130 °C during the 1 h-long deposition; XTEM and STEM images reveal that upon Ta ion irradiation, the intracolumnar porosity observed in the reference TiN layer is greatly reduced. The films hardness and modulus of elasticity increase from 7.8 and 211 GPa for the reference TiN film deposited at T_s < 120 °C to 24.1 and 360 GPa for $Ti_{0.92}Ta_{0.08}N$ layers prepared with V_s = 120 V.

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10:40am **B1-1-3 Estimating Metastable Phase Formation During Magnetron Sputtering**, ***K. Chang*** *(chang@mch.rwth-aachen.de), D. Music, D. Lange, M. to Baben, H. Bolvardi, J. Schneider*, RWTH Aachen University, Germany

Saunders and Miodownik [1] reported a model to predict metastable phase formation by estimating the migration distance of atoms. This model was critically appraised for the immiscible Cu–W system using both experimental and theoretical means. Cu–W thin films were synthesized by DC combinatorial magnetron sputtering. By applying X-ray diffraction, the phase formation was studied with respect to magnetron power density and substrate temperature. Then, a metastable Cu–W phase diagram was constructed. At 150 °C, it is observed that a two phase region containing bcc and fcc phases forms for Cu concentrations ranging from 73.6 and 82.4 at. %. This range broadens as the substrate temperature increases.

The random bcc and fcc Cu–W configurations were studied by *ab initio* calculations applying special quasirandom structures (SQS) and coherent potential approximation (CPA) approaches. The predicted lattice parameters and solubility limits are consistent with those determined by experiment.

[1] N. Saunders and A. Miodownik, J. Mater. Sci. **22** (1987) 629.

11:00am **B1-1-4 Microstructure and Superhardness Effects of VC/TiC Nanoscale Multilayer Films**, ***J.L. Yue*** *(jlyue2010@csu.edu.cn), J. Chen, X.C. Dong*, Central South University, China, *G.Y. Li*, Shanghai Jiaotong University, China

The nanoscale multilayer films have proven great potential for the development of novel thin film materials with tailored properties due to superhardness effect. In this work, a series of VC/TiC multilayers with various bilayer modulation periods were synthesized with VC and TiC target by magnetron sputtering. The microstructure and mechanical properties of the films have been studied by x-ray diffraction, energy dispersive x-ray spectrometry, high-resolution transmission electron microscopy and nanoindentation. The results reveal that VC/TiC multilayer films grow into coherent structure when their bilayer modulation period is below a critical thickness (5 nm). Correspondingly, the hardness and elastic modulus of the multilayers increases significantly and reaches the maximum value of 41.9 GPa and 326 GPa, respectively. With further increase in the modulation period, coherent structure of multilayers are destroyed, resulting in a remarkable decrease of hardness and elastic modulus. The superhardness effect of VC/TiC naomultilayers is related to the three directional strains generated from the coherent structure.

11:20am **B1-1-5 Recent Developments in Industrial Scale Pulsed Laser Deposition Technology for Thin Films**, ***J. Liimatainen***, *V. Kekkonen (ville.kekkonen@picodeon.com)*, Picodeon, Ltd., Finland **INVITED**

Despite its numerous advantages (flexibility, simple setup, coating quality), PLD is still very little utilized in real industrial coating and thin-film processes. The conventional PLD techniques, relying mainly on low repetition rate lasers and point sources, do not allow a large-scale or large-area coating with the high throughput, reliability, homogeneity, and reproducibility required in industrial processes.

Recently, thin-film coating technology has been developed which is based on ultra-short pulsed laser deposition (USPLD) enabled by the cutting edge, industrial laser technology utilized in machining. The industrial production capability and scalability of the technology is based on producing a line source of plasma instead of static point source of conventional PLD techniques. The technology is made possible by the high repetition rate and high average power of the new lasers combined with state-of-the-art, high-speed laser scanning technology. Together with the industrial approach

which includes roll-to-roll production, the advantages of cold ablation (high-quality plasma, controlled ablation, reduced amount of particles) form a strong basis for scalable, high production rate ultra short pulsed laser deposition coating for variety of materials. Now, this technology has been made available with equipment. Here, we demonstrate the results produced using the equipment and the development of special coatings, especially B-C-N materials and composites based on, DLC, oxides, and metals, with the main focus in applications requiring wear resistance, tribological properties, optical quality, and/or biocompatibility.

Hard Coatings and Vapor Deposition Technology
Room: Sunset - Session B5-1

Hard and Multifunctional Nano-Structured Coatings
Moderator: J. Paulitsch, Vienna University of Technology, Austria, J. Houska, University of West Bohemia

10:00am **B5-1-1 Hard Multifunctional Hf-B-Si-C Films Prepared by Pulsed Magnetron Sputtering**, ***P. Mares*** *(pmares@kfy.zcu.cz), J. Kohout, J. Vlcek, J. Houska, R. Cerstvy, P. Zeman*, University of West Bohemia, Czech Republic, *M. Zhang, J. Jiang, E. Meletis*, University of Texas at Arlington, US, *S. Zuzjakova*, University of West Bohemia, Czech Republic

Hf–B–Si–C films were deposited on silicon and glass substrates using pulsed magnetron co-sputtering of a single B_4C–Hf–Si target (at a fixed 15% Hf fraction and a varying 0-50% Si fraction in the target erosion area) in pure argon. We focus on the effect of the Si content. We found that the nanocolumnar Si-free Hf–B–C films exhibit a high hardness of 37 GPa and a high electrical conductivity (electrical resistivity of 1.8×10^{-6} Ωm). However, the high hardness of these films is accompanied by a high compressive stress of 4.9 GPa. The highly textured nanocolumnar Hf–B–Si–C films prepared at 1% Si fraction in the target erosion area exhibit a similar high hardness at a lower compressive stress of 1.8 GPa. A further increase in the Si fraction in the target erosion area to 7.5% results in a formation of nanocomposite Hf–B–Si–C films with a high hardness of 37 GPa, a low compressive stress of 0.9 GPa and significantly improved oxidation resistance in air (mass gain after annealing to 800 ºC is below 0.03 mg/cm^2). We obtained a relatively high H/E* ratio of around 0.15, indicating a high elastic strain to failure, for all these nanostructured HfB_2-based films. The highest oxidation resistance in air (almost no mass change after annealing up to 800 ºC) was achieved for the amorphous Hf–B–Si–C films prepared at 30% Si fraction in the target erosion area. All films exhibit very smooth defect-free surfaces with an average roughness below 1 nm. The films may be used as a new class of hard and electrically conductive protective coatings with a high oxidation resistance at elevated temperatures.

10:20am **B5-1-2 Influence of Hf on the Structure, Thermal Stability and Oxidation Resistance of Ti-Al-N Coatings**, *Y. Xu*, Central South University, China, *L. Chen*, Central South University and Zhuzhou Cemented Carbide Cutting Tools Co., LTD, China, ***Y. Du*** *(yongducalphad@gmail.com)*, Central South University, China, *F. Pei*, Central South University and Zhuzhou Cemented Carbide Cutting Tools Co., LTD, China, *Y. Peng*, Central South University, China

Alloying with transition metal (TM) elements into Ti-Al-N to improve its performance is attracting considerable interest. Here, we investigate the effect of Hf on structure, mechanical and thermal properties of Ti-Al-N coating with cubic structure. Alloying with 3 at.% Hf slightly promotes the spinodal decomposition of Ti-Al-N to form Al-depleted and Al-enriched domains during thermal annealing. According to TGA and DSC results, Hf-containing coating exhibits less oxidation below 1053 °C, which is attributed to the retarded transformation of anatase (a) TiO_2 to rutile (r) TiO_2. However, incorporation of Hf results in worse oxidation resistance above 1053 °C due to the deterioration of barrier effect of diffusion from large Hf atom. Ti-Al-Hf-N coatings onto Al_2O_3 substrates can retain most of dense unoxidized layer after oxidation at 850 °C for 10 h under synthetic air atmosphere and fully transform to oxides when oxidation temperature elevate to 950 °C. An oxidation of the coatings following the DSC curve during air up to 1100 °C shows that the oxide scales of Ti-Al-N and Ti-Al-Hf-N coatings are 3.45 and 3.87 μm, respectively.

The financial support from National Natural Science Foundation of China (grant nos. 51371201 and 51371199) and Zhuzhou cemented carbide cutting tools limited company of China is acknowledged.

10:40am **B5-1-3 Growth of Hard Amorphous Ti-B-Si-N Coatings by Cathodic Arc Evaporation**, ***H. Fager*** *(hanfa@ifm.liu.se)*, Thin Film Physics Division, IFM, Linköping University, Sweden, *J. Andersson*, Seco Tools AB, Swedon, *J. Lu, J. Jensen, L. Hultman*, Thin Film Physics Division, IFM, Linköping University, Sweden

Transition metal nitrides are used in many applications because of their high hardness, mechanical wear resistance, high thermal stability, and good oxidation resistance. For these materials, much research has concerned nanocrystalline films and nanocomposites. Especially in the development of hard ceramic coatings for wear-resistant applications, microstructural design has been of great importance, as has the correlation between microstructure and mechanical properties. Recently, we have directed focus to a less studied area: *amorphous* transition metal nitrides. We propose amorphous multicomponent transition metal nitrides for a new class of durable materials that could extend the range of possible applications, due to the material's homogeneous structure, lack of weak grain boundaries, and mixed character of bonding. We previously showed that the addition of Al and Si to TiN in $Ti_{1-x-y}Al_xSi_yN$ distorts nanocrystalline growth and promotes renucleation and an amorphous structure in cathodic arc evaporation [1]. We concluded that the coatings were amorphous when the Ti content 1-x-y<0.34. Isothermal annealing experiments showed that the amorphous coatings were thermally stable up to 900 °C and exhibited age hardening up to 1100°C with an increase in hardness from 19.4 GPa to 31.6 GPa. Here, we exchange Al for B and explore the $Ti_{1-x-y}B_xSi_yN$ system. B is a well-known grain refiner, and a good choice for promoting growth of amorphous phases, since it can be both three- and fourfold coordinated. Also, B-N bonds are stronger than Si-N ones, which is beneficial for hard coating applications. The coatings were grown onto cemented carbide substrates in an industrial scale cathodic arc evaporation system using Ti-Si and Ti-B cathodes in a pure N_2 atmosphere. Compositional analysis of the as-deposited films was performed by elastic recoil detection analysis, and the structural information and phase composition was gained by X-ray diffraction, and analytical transmission electron microscopy. Mechanical properties of the coatings are characterized by nanoindentation. We show that the structure of as-deposited films remain amorphous up to a Ti content of 0.63. The structure changes to nanocrystalline for Ti content 1-x-y>0.70. The hardness of the as-deposited amorphous coatings is 17.1-18.9 GPa depending on composition. In addition, we will present results for the phase composition, thermal stability, and crystallization behavior of the coatings, as well as from metal cutting tests.

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11:00am **B5-1-4 Structure, Oxidation Resistance and High Temperature Tribological Properties of CrTiAlN Coatings**, ***J. Lin*** *(jlin@swri.org), K. Coulter, P. Lee*, Southwest Research Institute, US, *W. Sproul*, Reactive Sputtering, Inc., US

CrTiAlN coatings with different Cr/Ti ratios have been reactive sputtered from a CrAl and a Ti target, which were powered by pulsed dc magnetron sputtering and deep oscillation high power pulsed magnetron sputtering (DOMS), respectively. DOMS is an alternative high power pulsed magnetron sputtering technique that uses large voltage oscillation packet to achieve high power pulses for sputtering. The coatings were deposited onto WC-Co, AISI 304 steel coupons, and Si wafers at room temperature using a -60 V dc negative substrate bias voltage. The microstructure, mechanical properties, and oxidation and tribological behavior at elevated temperatures of the CrTiAlN coatings were investigated and compared to the $Cr_{0.7}Al_{0.3}N$ baseline system.

By varying the Cr/Ti ratio, while maintaining the Al content in the metal lattice lower than 30 at.%, the CrTiAlN coatings exhibited a large variation in the hardness between 26 GPa to 38 GPa, which showed great improvement as compared to 30 GPa for the $Cr_{0.7}Al_{0.3}N$ coating. Appropriate addition of Ti into CrAlN coatings improved the oxidation resistance of the coatings. The onset oxidation temperature has been successfully delayed to 1000 ºC for the TiCrAlN coatings as compared to 800 ºC for the low Al concentrated $Cr_{0.7}Al_{0.3}N$ coating. However, excessive addition of Ti is detrimental to the oxidation resistance of the coatings. At the end of the study, high temperature wear resistance of the CrTiAlN coatings from 400 to 700 ºC in an ambient air will also be reported.

11:20am **B5-1-5 Growth of $AlYB_{14}$ Thin Films by HPPMS**, ***O. Hunold*** *(hunold@mch.rwth-aachen.de), D. Music, Y.-T. Chen, S. Mráz, J. Schneider*, RWTH Aachen University, Germany

Icosahedral boron-rich solids, containing B_{12} clusters, exhibit outstanding physical properties[1] such as high hardness, a Young's modulus above 500 GPa[2] and a melting point on the order of 2400 °C. Calculations[3,4] and experiments[5] have shown that these materials provide very favorable properties for wear resistant applications. Furthermore, spontaneous self-healing[1] has been reported after radiation induce vacancy formation. Among

others $AlYB_{14}$ (space group: *Imma*) belongs to this group of boron-rich solids. However, synthesizing crystalline XYB_{14}, where X and Y are metals, is challenging both with respect to the incorporation of impurities[5] and the required synthesis temperature: 1400 °C.[6]

The influence of the duty cycle $t_{on}/(t_{on}+t_{off})$ on the structure evolution of $AlYB_{14}$ was studied using high power magnetron sputtering (HPPMS). The film structure was analyzed by X-ray and electron diffraction. Depending on the duty cycle the formation of crystalline $AlYB_{14}$ was obtained at a temperature of 800 °C. Our data indicate that crystalline $AlYB_{14}$ grains grow within an amorphous matrix.

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Advanced Materials for Modern Device Applications
Room: Sunrise - Session C1

Recent Advances in Optical Thin Films and Nanomaterials

Moderator: J.H. Hsieh, Ming Chi University of Technology, L. Martinu, Polytechnique Montreal

10:00am **C1-1 Challenges and Perspectives of Optical Interference Coatings: FromTelecom and Space to Security and Consumer Electronics Applications**, ***R. Sargent*** *(robert.sargent@jdsu.com), J. Ockenfuss, D. Hendrix*, JDSU, US **INVITED**

Optical interference coatings find wide application in science and industry. It is hard to think of an optical instrument or system that does not benefit from their use, and many systems would not be possible without them.

The challenges of the optics and security industries are constantly driving better performance and the development of improved and new optical coating technologies. A few of the application areas and how they drive the technology include: **Space.** Applications for optical coatings in space include antireflective protective covers for solar cells, solar thermal control coatings, and filters for instrumentation. An enabling type of filter used in space-based sensors is the linear variable filter, or LVF. The spectral performance of this type of filter varies across one dimension, making it ideal for use with arrayed detectors such as CCDs. LVFs are also used in many ground-based devices such as miniature spectrometers. **Document Security**. The availability of color photocopying machines in the 1970s initiated a need for new anti-counterfeiting technologies for banknotes and secure documents. Beginning in the 1980s security devices based on optical interference have been employed since they shift in color as a document is tilted, an effect that cannot be readily duplicated by a photocopier. Challenges today include the creation of effects that are more eye-catching and even more difficult for counterfeiters to replicate. **Telecommunications**. The 1990s saw a major build-out of the fiber-optic telecommunications infrastructure. To bring the cost of the deployment down, signal streams were multiplexed by sending multiple laser wavelengths through each fiber. Optical filters were adopted for combining and separating the wavelengths, for correcting the wavelength-dependent amplification of optical amplifiers, and other uses. These requirements drove major improvements in optical coating technology during the mid-1990s through the early 2000s, and optical filters are still widely used in telecommunications today. **Consumer Electronics**. The processing of multiple devices at the wafer level in the field of electronics has a long history dating back to the 1960s. Until recently, however, sensors that employ filters and electronic detectors were constructed using costly unit-by-unit assembly methods. In the past few years processes have been developed which enable optical filters to be deposited directly onto semiconductor wafers, enabling the integration of detectors, filters, and circuitry at the wafer level. This advance has been driven by the need for inexpensive sensors for devices such as smart phones and tablet computers.

10:40am **C1-3 Assessment of the Mechanical Properties of Optical Coatings by *in situ* Real-time Approaches**, ***Schmitt, T.*** *Poirié, E. Bousser, L. Martinu, J.E. Klemberg-Sapieha (jsapieha@polymtl.ca)*, Polytechnique Montreal, Canada

Surfaces of optical devices such as touch screens, correction glasses, low emissivity or smart windows are exposed to everyday mechanical and tribological interactions. This clearly calls for the development of multi-functional films possessing controlled optical characteristics coupled with superior tribo-mechanical properties, and it also stimulates the development of new tools and methods for their assessment.

In this work we present three *in situ* real-time techniques that provide instantaneous information about the mechanical response of optical coatings exposed to different types of solicitations: a) Analysis of the dynamics of solid particle erosion of coatings deposited on a Quartz Crystal Microbalance; b) Evaluation of the mechanical stress to assess the contribution of each individual layer on the total stress, as well as the effect of environmental conditions; and c) *In situ* scratch and wear testing to study defect initiation, progression and propagation.

Using the above techniques, we show specific examples of the mechanical properties of optical films on glass and plastic substrates. We discuss how the combination of these techniques with other complementary characterization methods can provide a better understanding of the mechanisms governing the tribo-mechanical performance of optical coating systems.

11:00am **C1-4 Low Temperature Deposition of Thermochromic VO_2 Optical Coatings Using HiPIMS**, *S. Loquai, B. Baloukas, R. Vernhes, O. Zabeida,* ***J.E. Klemberg-Sapieha****, L. Martinu (lmartinu@polymtl.ca)*, Polytechnique Montreal, Canada

Vanadium dioxide (VO_2) is a well known thermochromic material of interest for applications in smart windows. However, the high deposition temperature, typically over 400°C, required to obtain the appropriate VO_2 crystalline phase represents one of the major challenges for its implementation on a large scale. In our previous work, we showed that high quality VO_2 films could be obtained by the HiPIMS deposition technique at a lower substrate temperature (300 ^{0}C) compared to DC or RF magnetron sputtering. In the present study, the HiPIMS process is further optimized through detailed pulse parameters management including pulse frequency and the instantaneous power. We correlate these parameters with the microstructure, crystallinity and composition of the VO_2 films, as well as with their thermochromic properties, namely the transition temperature, and the IR switching efficiency.

11:20am **C1-5 The Characteristics of Heavily Ga-doped ZnO Films with High Carrier Concentration for use in Plasmonics**, ***T. Yamamoto*** *(yamamoto.tetsuya@kochi-tech.ac.jp), H. Song, J. Nomoto, H. Makino*, Kochi University of Technology, Japan

We have been investigating the characteristics of heavily Ga-doped ZnO (GZO) films with carrier concentrations of 1.1 to 1.2×10^{21} cm^{-3}, which can be promising low-loss alternatives to metals in near-infrared (NIR) wavelength ranges for use in plasmonics. Plasmonics offers the potential to confine and guide light below the diffraction limit and promises a new generation of highly miniaturized photonic devices. Current plasmonic devices based on metals or metal alloys at telecommunication and optical frequencies face significant challenges due to losses encountered in the materials. We have deposited GZO films with various thicknesses in the range from 100 to 350 nm by ion-plating with dc arc discharge. Temperature of glass substrates was 200ºC. Hall effect measurement results of 105-nm-thick and 344-nm-thick GZO films show electrical resistivity of 2.5×10^{-4} Ωcm, carrier concentration of 1.08×10^{21} cm^{-3} and Hall mobility of 23 cm^2/Vs and electrical resistivity of 1.8×10^{-4} Ωcm, carrier concentration of 1.23×10^{21} cm^{-3} and Hall mobility of 29 cm^2/Vs, respectivley. Hall mobility monotonically increases with increasing thicknesses up to 344 nm, whereas carrier concentration changes a little. Analysis of spectroscopic ellipsometry measurement shows that 105-nm-thick and 344-nm-thick GZO films exhibit negative real permittivity that is an essential property of any plasmonic material at wavelenghth of more than 1256 nm and 1198 nm, respectively. Note that, for all the GZO films, we find that values of the imaginary part of the dielectric function, which describes the losses encountered in polarizing the films, were of less than 0.6 in the range of wavelength smaller than 1500 nm in the NIR wavelength region. Taking into account that just the losses are relevant in defining the quality factor of transformation optics (TO) devices and superlens, the GZO films can be a promising low-loss material for the plasmonics in the NIR wavelength region, and can work well at the telecommunication wavelength.

11:40am **C1-6 Smart Optical Coating Systems for Energy Efficient Building Envelopes**, ***C.M. Lampert*** *(cmlstar@sonic.net)*, Star Science, US
INVITED

This study investigates the role of coating processes in the glass industry to make functional coatings. One chief mature technology is pyrolytic deposition of chemistries to make Low-e or transparent conductive SnO_2. One of larger application for the coatings is for improved energy efficiency of building glazing. Low-e coatings are used for thermal infrared management and visible light control and solar control in building glazing. Highlights will include the current advances being made in CVD and PE-CVD to the application of functional surface coatings for glass. Variants of nanostructured metal oxides, such as TiO_2 can be surface modified to provide antireflection, self-cleaning surfaces, hydrophilic, hydrophobic and oleophobic properties. The foremost functional coating systems are electrochromic metal oxides and related electrically controllable switchable technology. Electrochromic materials consist of layered metal oxides in an electrolyte or solid ion conductor which have transport and charge storage characteristic similar to a battery structure. The structure consists of electrode/electrochromic/ion conductor/ion storage/electrode/glass in a thin film stack. Coloration of tungsten oxide ($WO_{\sim 3.0}$) films is achieved by both electron injection and ion intercalation. By surface nano-engineering various visible and near-infrared responses can be induced. The effect on microstructure and properties will be discussed. Performance gains from nano-engineered films will be detailed. The role of photovoltaic integrated glazing will be discussed for building integrated PV (BIPV). Included will be materials challenges, market and industry manufacturing issues, which control efficiency, yield and ultimate manufacturing cost. Keywords: Glass, Energy, Electrochromics, Low-e, Transparent conductors , BIPV

12:20pm **C1-8 Potential Impact of Ambient Gases and Oxygen Partial Pressure on Structural, Hydrophobic, Optical and Electrical Property of Nanostructured HfO_xN_y Film**, ***V. Dave***, Indian Institute of Technology Roorkee, India, *P.K. Mishra*, Ranchi University, India, *H.O. Gupta, R. Chandra (ramesfic@gmail.com)*, Indian Institute of Technology Roorkee, India

The outdoor glass insulators installed in the electrical power substation undergoes frequent surface flashover phenomenon due to atmospheric contamination. Synthesis of hydrophobic dielectric coating over the insulator surface is one such technique to overcome this problem. In this paper, we report the deposition of DC sputtered HfO_xN_y films over glass insulators. The coatings were developed in two different sputtering gas atmosphere namely Ar and He by varying oxygen partial pressure from 2.5% to 20% keeping nitrogen flow constant. The structural, hydrophobic, optical and electrical properties of the deposited films were characterized using XRD, AFM, EDS, contact angle goniometer, UV-vis-NIR spectrophotometer, impedance analyzer and four probe method. The average crystallite size and the deposition rate were higher for the films deposited in N_2+Ar atmosphere in comparison to the film deposited in N_2+He environment. The nano roughness of the samples estimated from the AFM micro graphs was correlated with the crystallite size and nitrogen content of the films. All the deposited samples were hydrophobic with highest contact angle of 94.3° for the film deposited at 2.5% oxygen partial pressure in Ar environment. The surface energy of the HfO_xN_y films was estimated from water contact angle using Wu and Owens methods. The deposited samples shows the optical transmission > 85%. The refractive index and the bandgap gap calculated from the optical records were significantly affected by the atomic mass of the sputtering gas. The electrical resistivity of the films was found out to be packing density dependent and shows a decreasing trend with the rise of O_2 partial pressure. The dielectric constant of the films was high in comparison to HfO_2 film and was thickness dependent.

Tribology & Mechanical Behavior of Coatings and Engineered Surfaces
Room: California - Session E1-1

Friction, Wear, and Lubrication: Effects and Modeling
Moderator: M. Chandross, Sandia National Laboratories, O.L. Eryilmaz, Argonne National Laboratory, K. Polychronopoulou, Khalifa University of Science, Technology & Research

10:00am **E1-1-1 Contact and Friction of Rough Adhesive Surfaces**, ***M. Robbins*** *(mr@jhu.edu)*, Johns Hopkins University, US, *L. Pastewka*, Fraunhofer IWM, Germany, *T. Sharp*, Johns Hopkins University, US
INVITED

Experimental surfaces typically have roughness on a wide range of length scales. This roughness greatly reduces the fraction of the area that is in intimate molecular contact and can contribute to friction and adhesion. The talk will first describe recent numerical calculations of elastic contact between rough surfaces with nominally flat or spherical geometries on large scales. An efficient Greens function approach allows calculations for systems with roughness on nanometer to micrometer scales to be performed with atomic resolution in the contact. Results for a wide range of geometries can be collapsed using simple scaling relations that depend on the root mean squared surface slope, sphere radius, elastic modulus, and work of adhesion. The scaling relations explain why adhesive interactions have little effect unless the surfaces are extremely smooth or soft. The talk will next consider how forces in the contact area give rise to friction. Friction shows strong scale effects and the partial slip assumed in many contact models is not found in contacts with dimensions of nanometers to micrometers.

10:40am **E1-1-3 Wear Phenomena of ta-C Under Ultra-low Friction Conditions**, ***S. Makowski*** *(stefan.makowski@iws.fraunhofer.de), V. Weihnacht, F. Schaller, A. Leson*, Fraunhofer IWS, Germany

Diamond-like carbon coatings offer a unique combination of high hardness, low friction and low tendency to stick. Among the diversity of DLC films, the hydrogen-free ta-C films are becoming more and more important. Besides superhardness this coating type shows ultra-low and super-low friction in combination with specific lubricant types. Several authors have been reported on extreme low friction of ta-C lubricated with glycerol and corresponding esters. In these reports, wear was not investigated in detail. However, recent investigations have shown relatively high wear of some ta-C coatings with fatty-acid based lubricants. Surprisingly, high wear and ultra-low friction occurred at the same time. Though all of the described ta-C coatings were similar by composition regarding sp3- and hydrogen content, different coating processes were used. These different processes, covering lab-scale to industry-scale technologies, could lead to different properties and cause the discrepancy in wear behavior under ultra-low or super-low friction.

In this study, the influence of sp3-content, intrinsic stress and particle density on the low-friction-high-wear phenomenom was systematically investigated measuring the wear and friction coefficients. Tribological testing was performed with an oscillating test rig, using glycerol and glycerol mono-oleate as lubricants to achieve the low friction state. A fully formulated engine oil was used for reference. The hybridization state and depth-resolved chemical composition of the tribolayer on the coating and counter part was studied using Raman spectroscopy, TEM, and NRA. The results are correlated and an attempt is made to describe the influence of specific ta-C coating properties on friction and wear.

11:00am **E1-1-4 Temperature-induced Low Friction of Sputtered Si-containing Amorphous Carbon Coatings**, ***O. Jantschner*** *(oliver.jantschner@unileoben.ac.at)*, Montanuniversität Leoben, Austria, *S. Field*, Teer Coatings Limited, Miba Coating Group, UK, *K. Zorn*, MIBA High Tech Coatings, Austria, *D. Music, J. Schneider*, RWTH Aachen University, Germany, *C. Mitterer*, Montanuniversität Leoben, Austria

This contribution presents a tribological study of magnetron sputtered amorphous carbon-based thin films containing Si (a-C:Si) compared to a common sputtered carbon thin film (a-C). Molecular dynamics simulations predict tetrahedral bonds between C and Si in the amorphous carbon matrix. Ball-on-disk-tests carried out at room temperature against Al_2O_3 revealed a coefficient of friction (COF) of 0.1 for both film types. Between 250 and 325°C, Si addition decreases the COF and the wear rate to < 0.05 and < $3*10^{-18}$ m^3/ N*laps, respectively. For comparison, the a-C reference shows a COF of 0.15 and a wear rate of $9*10^{-17}$ m^3/N*laps. This low friction behavior was further investigated by combining X-ray photoelectron spectroscopy, transmission electron microscopy and Fourier transform

infrared spectroscopy techniques of the wear tracks and the worn material on the counterbody. Besides friction-induced graphitization of the coating surface, a reaction layer based on Si-O compounds was formed, being responsible for the excellent thermal stability of a-C:Si coatings.

11:20am **E1-1-5 The Aging and Temperature effects of DLC Coatings**, ***H. Ronkainen*** *(helena.ronkainen@vtt.fi)*, VTT Technical Research Centre of Finland, *K. Holmberg*, VTT Technical Resesearch Centre of Finland, *A. Laukkanen*, VTT Technical Research Centre of Finland

Diamond-like carbon (DLC) films cover a wide range of different carbon based coatings, starting from soft hydrogenated films to extremely hard hydrogen-free films. Due to the varying characteristics of DLC coatings, they have differing tribological properties that influence on their performance and applicability. Coating properties, such as elasticity and fracture toughness, greatly influence on the practical performance of the coatings in real applications. An interesting aspect is also the influence of tempering or aging of the coating on the performance.

In order to study how aging influences the tribological performance of DLC coatings we have evaluated 20 years old DLC coatings and compared the results to earlier results reported. It seems that the effect on the wear resistance has not changed greatly. However, variation in the friction performance for the a-C:H type coatings was observed. When studying the temperature effects on a-C:H type DLC coatings similar type of effects were observed.

These aging and temperature effects were further elaborated by multi-scale modeling. In multiscale modelling the integrated approach combining material microstructural features modelled by molecular dynamic simulation (MDS) on nanoscale with FE modeling was applied. The tribological aspects of aging and elevated temperatures on DLC films will be reviewed with the validation of the models in different scaled and the arguments for aging mechanisms are presented.

11:40am **E1-1-6 Nanoscale Sliding Friction Phenomena at the Interface of Diamond-like Carbon and Tungsten**, ***P. Stoyanov*** *(pantcho.stoyanov@mail.mcgill.ca)*, Kennametal, Inc., US, *P. Romero*, *M. Dienwiebel*, *M. Moseler*, Fraunhofer-Institute for Mechanics of Materials IWM, Germany

Nowadays, it is widely accepted that nanoscale phenomena of sliding couples determine the friction and wear performance of a macroscopic system. Understanding these processes can lead to optimal tribological performance by developing novel materials and optimizing the sliding conditions (e.g. contact pressure, sliding velocity, etc.). However, studying these phenomena can be quite challenging due to the confined nature of the sliding interfaces and the dimensions of third bodies. In this study, macroscopic tribometry is linked with classical atomistic simulations in order to improve our understanding of the nanoscale interfacial processes during sliding of hydrogenated DLC (a-C:H) against a metal (W) in dry and lubricated conditions. Experimentally, using an on-line tribometer, wear and roughness measurements are performed after each sliding cycle, which are then correlated to the frictional resistance. *Ex situ* analysis is also performed on the worn surfaces (i.e. plates and counterfaces) using X-ray photoelectron spectroscopy (XPS), Auger Electron Spectroscopy (AES), and cross-sectional transmission electron microscopy (TEM) imaging of the near-surface region. Then, in order to elucidate the atomistic level processes which contribute to the observed microstructural evolution in the experiments, classical molecular dynamics are performed employing a bond order potential for the Tungsten-Carbon-Hydrogen system. Macroscopic tribometry shows that dry sliding of a-C:H against W results in higher frictional resistance and significantly more material transfer compared to lubricated conditions. Similarly, the molecular dynamic simulations exhibit higher average shear stresses and clear material transfer for dry conditions compared to simulations with hexadecane as a lubricant. In the lubricated simulations the lower shear stress and the absence of a material transfer is attributed to hexadecane monolayers that are partially tethered to the a-C:H surface and that significantly reduce adhesion and mechanical mixing between the sliding partners.

Keywords: Mechanical Mixing, Third-body, Transferfilm, Diamond-like carbon, Hexadecane, Molecular Dynamics

12:00pm **E1-1-7 Scratch Testing for Diamond-like Coatings Evaluation at Micro and Nano-scale**, *F.L.C. Lucas*, University of Paraiba Valley IP&D/UNIVAP, São Jose dos Campos - SP, Brazil, *S.F. Fissmer*, Technologic Institute of Aeronautics, ITA/CTA, São Jose dos Campos - SP, Brazil, ***L.V. Santos*** *(lvs.lucia@gmail.com)*, University of Paraiba Valley IP&D/UNIVAP, São Jose dos Campos - SP, Brazil, *D.S. Silva*, Institute of Chemistry, University of Campinas - UNICAMP, Campinas SP, Brazil, *C.A.R. Costa*, *E.M. Lanzoni*, *F. Galembeck*, National Nanotechnology Laboratory at the National Center for Energy and Materials Research, Campinas SP, Brazil

The first scratch method was Mohs scale; it has been used to characterize the scratch resistance of various minerals through the ability of a harder material to scratch a softer material. It was created in 1812 by the German geologist and mineralogist Friedrich Mohs. Now a day the Scratch Testing in micro scale is run out with constant, progressive or with increment load. The track is monitored with optical microscopy and acoustic sensor to evaluate the failure, the first failure is named critical load CL [1]. In nanoscale the scratch test is run out with constant normal load applied with a pyramidal diamond tip connected at atomic force microscopy.

In this paper we present the scratch test results in micro and nano scale from Silver diamond coatings (DLAg). The scratch test in micro scale was run out in progressive normal load with an acoustic Emission (AE) sensor connected with Rockwell C tip. The critical load sound was simultaneously measured to confirm the failure in scratch test. The failure was evaluated with an optical microscope. The load at which such failure of the coating occurred was plotted as a function of time.

In nano-scale the scratch test was run out in the same silver diamond coatings (DLSi) and it was used in constant normal load applied under diamond corner of a cube tip connected at atomic force microscopy. The scratch was performed to analyze the depth profile and the grain morphology in the track. Also was used as a supplementary analyzes Kelvin probe force microscopy (KPFM), also known as surface potential microscopy. It is a noncontact variant of atomic force microscopy (AFM). The KPFM was used to analyze the track surface potential and the results showed information about the surface composition and electronic state of the local structures on the surface track and some grains self-healing the track.

[1] - ASTM Standard G171 (03) – Standard Test Method for Scratch Hardness of Materials Using a Diamond Stylus.

12:20pm **E1-1-8 Failure Mechanisms of DLC Coated Ti-6Al-4V and CoCr Biomedical Materials under Cyclic High Combined Contact Stresses**, ***Y. Chen***, *X. Nie (xnie@uwindsor.ca)*, University of Windsor, Canada

Titanium alloys and Co-Cr based alloys are very promising materials for the femoral components of total hip and knee replacements. The metallic joint replacement components should have some common features, including not only high static and dynamic fatigue strength and biocompatibility bust also high corrosion and wear resistance. In this study, pin-on-disc and cyclic impact-sliding wear test methods were used to study tribological behaviour of both DLC coated and uncoated Ti-6Al-4V and ASTM F-75 CoCr bio-materials. The tests were carried out in both ambient dry and Hank's balanced salt solution (HBSS). The potentiodynamic polarization test was also conducted which showed that uncoated Ti-6Al-4V and CoCr substrates had excellent corrosion resistance in the HBSS environment. Pin-on-disc test results indicated that the HBSS provided a lubricate effect with less concern of corrosion in the pure sliding condition and during the impact-sliding wear tests. The CoCr substrate was superior to Ti alloy substrate in the cyclic impact-sliding tests at both dry and HBSS test conditions,. The lubricating effect also appeared for both DLC-coated substrates. The DLC coating performed better on CoCr than on Ti alloy in both test environments, which matched the behaviours of uncoated substrates. The phenomena were discussed with consideration of a stronger strain-induced work hardening effect of CoCr substrate.

New Horizons in Coatings and Thin Films
Room: Royal Palm 4-6 - Session F5

Coatings for Compliant Substrates
Moderator: N.R. Moody, Sandia National Laboratories

10:00am **F5-1 Electromechanical Properties of ZNO:Al Thin Films on Polymer Substrates for Optoelectronics Applications**, ***D. Mohammed***, University of Birmingham, UK, *R. Waddingham, A. Flewitt*, University of Cambridge, UK, *S. Kukureka (s.n.kukureka@bham.ac.uk)*, University of Birmingham, UK

Highly-transparent, conducting Al-doped ZnO films have been widely used as transparent electrodes for optoelectronic applications including flat-panel displays, solar cells and thin film transistors (TFT). The advantages of such films in various display technologies include high visible transparency and electrical conduction and they are low cost compared with indium tin oxide (ITO). Investigations of electromechanical properties for Al-doped ZnO films are still relatively limited. However flexible optoelectronic device, in particular rollable electronics, will involve various mechanical deformations such as stretching, bending and twisting depending on their application as well as during fabrication and handling processes. Therefore, we deposited Al-doped ZnO films using RF magnetron sputtering on polyethylene naphthalate (PEN) and polyethylene terephthalate (PET) substrates and investigated their mechanical properties using uniaxial tensile fragmentation, monotonic bending and twisting tests, coupled with in-situ optical microscopy. Changes in electrical resistance were monitored *in situ*. Also SEM and AFM were used to provide surface characterisation of the mechanically-tested samples. In addition, the effects of acrylic acid on the electromechanical properties of ZnO:AL /PENand ZnO:AL/PET systems were investigated under uniaxial tension, monotonic bending and twisting, in order to evaluate the stability of ZnO:Al in contact with pressure sensitive acrylic acid adhesives, which are employed in the fabrication of flexible electronics devices. Cracking and buckling delimitation failure modes were observed for all samples investigated at critical strains. Fracture behaviour of the Al-doped ZnO films was examined to further understand the failure mechanisms, which depend on the applied stress conditions. Then, a comparison of the properties of ZnO:AL/polymer systems and ITO/polymer system was performed. The results such as values of crack onset strain, critical radius of curvature and stress corrosion of films can help the understanding of such systems and aid the design of more reliable optoelectronic devices.

10:20am **F5-2 Low Temperature Titanium Dioxide Diffusion Barrier Layers on PEN Using Spatial Atomic Layer Deposition**, ***M. Aghaee*** *(morteza.aghaee@lut.fi)*, *P. Maydannik*, Lappeenranta University of Technology, Finland, *P. Johansson*, Tampere University of Technology, Finland, *K. Lahtinen, D. Cameron*, Lappeenranta University of Technology, Finland, *J. Kuusipalo*, Tampere University of Technology, Finland

High performance diffusion barriers against water vapour are essential for many applications in flexible optoelectronics such as OLEDs. Spatial atomic layer deposition (SALD) is one technique which has been shown to produce high quality barriers in a roll-to-roll process using aluminium oxide layers [i] [#_edn1] . Titanium dioxide is a material which should have higher stability against long-term degradation than aluminium oxide because of its greater chemical inertness. For high throughput low temperature deposition, high vapour pressure, highly reactive precursors are necessary. Titanium chloride is typically used but has the disadvantage of some chlorine incorporation in the film and also the formation of corrosive byproducts. Titanium tetraisopropoxide (TTIP) is an alternative titanium precursor as it has a high vapour pressure at room temperature compared to other titanium metal organics.

As an initial step before SALD of TiO_2 deposition, a study of conventional ALD has been carried out using TTIP and water, ozone or an oxygen plasma precursors to determine the basic process parameters and barrier properties with polyethylene naphthalate (PEN) as substrate material. Deposition took place at temperatures in the range 80-120^{o}C. The highest growth rate (0.055 nm/cycle) and highest refractive index (2.35) films were obtained using plasma oxidation. Water and ozone oxidation gave growth rates of 0.048 and 0.012 nm/cycle and refractive indices of 2.04 and 1.8 respectively. The water vapour transmission rates were approximately 1×10^{-3} g.m^{-2}.day^{-1} in tropical measuring conditions (38°C, 90% RH) for a film thickness of 45-50 nm.

Based on these results, a low pressure SALD process was carried out using a Beneq TFS200R system. Results will be presented of the performance of the SALD process in terms of speed, growth per cycle, etc. and the properties of the deposited layers will be described.

[i] [#_ednref1] Roll-to-roll ALD process for flexible electronics encapsulation applications

P. S. Maydannik, T. O. Kaariainen, K. Lahtinen, D. C. Cameron, M. Soderlund, P.Soininen, P. Johansson and J. Kuusipalo, submitted for publication

10:40am **F5-3 Stretch to the Limit: Ductility of Thin Metal Films on Polymer and Elastomer Substrates**, ***T. Li*** *(LiT@umd.edu)*, University of Maryland, US **INVITED**

Flexible electronics is an emerging technology with an array of potential applications such as paper-like displays, printable thin-film solar cells, and electronic sensitive skins. Thin metal films deposited on polymer substrates are often used as conductors and interconnects in flexible electronics. Unlike conventional electronic devices, flexible devices are often subject to large deformation (stretches, bending and twists). The mechanical failure of the polymer-supported metal conductors under large deformation poses significant challenge to the functional reliability of flexible electronics. Existing theoretical studies often assume plane strain condition of the deformation of these polymer-supported metal conductors. In reality, however, flexible devices are often subject to large and complicated deformation. For example, the electronic sensitive skins covering the elbow of a robot experience large bi-axial stretches. To decipher the failure mechanisms of polymer-supported metal conductors under various biaxial loading conditions (i.e., different ratios of tensile strains in two in-plane directions), we perform bifurcation analysis to determine the critical tensile strain above which necking sets in the metal conductors. We consider two representative material combinations, namely, thin metal conductors on stiff plastic substrates, and thin metal conductors on compliant elastomer substrates. Also emerging from the analysis is the orientation of the necking respect to the tensile loading directions. The results quantitatively correlate the critical necking limit strain as well as the necking orientation with the mechanical properties and the thickness of the metal conductor and the polymer/elastomer substrate. These results offer understandings on the deformability of polymer-supported metal conductors in flexible electronics; therefore shed light on optimizing the material selection and structural design of deformable metal conductors to achieve better mechanical reliability of flexible electronics.

11:20am **F5-5 Small Diameter Circular Ion Sources for Surface Engineering of Polymers**, ***F. Papa*** *(frank.papa@gencoa.com)*, Gencoa Ltd., US, *D. Monaghan, V. Bellido-Gonzalez, R. Brown, A. Azzopardi, L. Sorzabal-Bellido*, Gencoa Ltd., UK

Linear Ion sources have been used for more than 15 years as a means to plasma treat surfaces either before, during or after coating. The goals of such treatments are to improve adhesion/activate surfaces, densify coatings and to texture surfaces. Coatings can also be deposited via PACVD methods. Such linear ion sources are generally used in large area web or glass coaters, making process development costly and difficult. In order to accelerate process development, a new small diameter circular ion source has been developed. This source has similar characteristics to linear sources making processes easy to upscale to larger linear systems. Results of plasma etching, DLC deposition and surface nanotexturing on several polymer substrates will be presented.

11:40am **F5-6 Mechanical Design of Organic Light Emitting Diodes on Polymer Substrates**, ***S.J. Bull*** *(steve.bull@ncl.ac.uk)*, Newcastle University, UK

In many current applications coatings are being developed which do not exist in bulk form and cannot be examined by conventional mechanical tests. This raises problems in the mechanical design of devices based on such materials as no property data is available to include in design calculations. One particular example is the semiconducting layers in organic light emitting diodes (OLEDs) which may consist of evaporated films of organic molecules. The elastic properties of these coatings are often essential for design of devices, particularly if they are deposited on compliant substrates which allow bending during manufacture or service (e.g. in flexible electronics). Whereas it is possible to make good measurements of elastic properties on stiff substrates such as silicon there are serious issues with the reliability of data from coatings on compliant substrates such as the PET used for plastic electronics. This presentation will outline the development of a simple analytic model of the extraction of the contact modulus of a coating from nanoindentation data obtained from a coating/substrate system and analyse the reliability of the data produced. The data will then be used to optimise the design of a multilayer OLED on a compliant substrate subject to bending through the development os an analytic bending model.

12:00pm **F5-7 On the Response of Ti-6Al-4V and Ti-6Al-7Nb Alloys to a Nitron-100 Treatment**, *J.C. Avelar-Batista Wilson (junia.avelar-batista@tecvac.com), **S. Banfield**, J. Housden,* Tecvac Ltd, UK, *C. Olivero, P. Chapon*, Horiba Jobin Yvon S.A.S., France

Titanium alloys have been widely used in automotive, biomedical and aerospace industries due to their high strength-to-weight ratio, outstanding corrosion resistance and biocompatibility. Although alpha-beta alloys such as Ti-6Al-4V (workhorse of aerospace industry) and Ti-6Al-7Nb (much used for surgical implants) exhibit a good combination of mechanical properties, their tribological properties are still limited as they tend to seize and gall when in contact with other surfaces. In this paper, the response of Ti-6Al-4V and Ti-6Al-7Nb alpha-beta alloys to a Nitron-100 treatment is investigated. This treatment, which enhances the load-bearing capacity of titanium alloys, consists of two sequential processes: plasma nitriding using a glow discharge under triode configuration and deposition of a TiN coating. Scanning electron microscopy (SEM), optical surface profilometry, Knoop microhardness measurements and glow discharge optical emission spectroscopy (GDOES) were used to characterise both titanium alloy materials prior to and after the Nitron-100 treatment. Although the Nitron-100 treatment significantly improved the load-bearing capacity of both alloys, the Ti-6Al-7Nb alloy exhibited a superior hardening response under identical processing conditions. This could be attributed to its high niobium content, a strong nitride-forming element.

12:20pm **F5-8 A Comparison of Nanoindentation Pile-up in Bulk Materials and Thin Films**, ***N. Moharrami*** *(noushin.moharrami@ncl.ac.uk), S.J. Bull*, Newcastle University, UK

During nanoindentation testing there are many issues that need to be considered if high quality data is to be obtained when testing both bulk and thin film materials. For soft materials, one of the main issues in determining mechanical properties based on the Oliver and Pharr method is the accuracy of the determined contact area due to the pile-up around the indenter leading to a significant increase in the contact area. During nanoindentation tests for both thin films and bulk materials, the deformation mechanisms, and therefore the governing dislocation nucleation and propagation events, are complex and hence the volume of the pile-up is not always proportional to the indentation load and its shape can vary. Therefore accurate measurement of the Young's modulus and hardness requires the determination of the contact area using another technique such as atomic force microscopy (AFM) or scanning electron microscopy (SEM) images.

In this study, AFM images made by the indenter tip after the main indentation cycle was complete were analysed to measure the pile-up heights and widths obtained in bulk materials (copper, gold and aluminium) and the results were compared to those from their respective thin films under similar indentation conditions. It was observed that the amount of pile-up that appeared in the thin films was considerably higher than in the bulk materials. Thin films with low hardness values deposited on harder substrates show a different plastic response under the indenter. During the indentation tests, the harder substrate does not deform to the same extent as the softer deposited coating and consequently it has an extreme effect on the degree of pile-up formation for the thin film.

Applications, Manufacturing, and Equipment
Room: Tiki - Session G4

Coatings for Machining Advanced Materials and for use in Advanced Manufacturing Methods

Moderator: D. Kurapov, Oerlikon Balzers Coating AG, R. Cremer, KCS Europe GmbH, Germany

10:00am **G4-1 Nobel Wear Resistant Coating System for AHSS Stamping Die**, ***K. Yamamoto*** *(yamamoto.kenji1@kobelco.com), K. Ozaki,* Kobe Steel Ltd., Japan, *T. Kashi,* Nippon Koshuha Steel Co., Ltd., Japan, *H. Yamashita*, Kams Co. Ltd., Japan

Stamping dies used for AHSS (Advanced High Strength Steel) component production are conventionally coated by carbide coatings such as TiC or VC by thermal process for wear protection. As the strength of the steel increased, it becomes evident that wear and tear of dies with conventional surface treatment proceeds rapidly more than expected. An in-depth failure analysis of a worn die revealed that significant surface oxidation was taking place for conventional carbide coating. This indicated that surface temperature of the stamping mold was increased due to friction generated heat even it was a cold stamping process. Based on this failure analysis, a new coating for was developed for exclusively dies and molds for cold stamping. The new coating has a two layer structure; an inter-layer which increase the adhesion strength and resistance to external stress, and a top layer which is highly oxidation and wear resistant TiAlN based coating. Whole coating system is deposited by arc ion plating process at enough low temperature so virtually there is no dimensional change before-and after the deposition. A high temperature wear test was conducted to simulate oxidation wear process during the stamping process and found that severe oxidation and even oxygen diffusion up to several hundreds of nanometers was observed for VC coating deposited by thermal diffusion process. Whereas only very thin (ca. 10nm) oxide layer was observed in top layer of the developed coating. This difference in oxidation behavior affects wear amount of the coating and VC coating showed 2 to 3 times larger. Other critical properties of the developed coating such as mechanical property, adhesion and load bearing capability will be reported. Finally, it is noteworthy that the developed coating is now widely used for mass-production stamping dies for AHSS more than 500MPa and die life improvement factors are in general 2 to 3, 10 times at best.

10:20am **G4-2 Development of (Cr,Al)ON Coatings using Middle Frequency Magnetron Sputtering and Investigations on Tribological Behavior against Polymers**, *K. Bobzin, N. Bagcivan,* ***T. Brögelmann*** *(broegelmann@iot.rwth-aachen.de)*, Surface Engineering Institute - RWTH Aachen University, Germany

Plastics processing is an enormous and expanding commercial sector since the worldwide manufacturing of plastics products breaks through the 280 mio. tons mark in 2011. Injection molding and extrusion are common techniques for efficient mass production of plastics components with high shape accuracy and high surface quality for a broad variety of applications. In the framework of a world affected by globalization, it is fundamental to develop a sustainable production strategy to assure the production in high-wage countries. The cost-effective manufacturing of individualized optical products with improved functionality by reducing the number of process steps and shortening the cycle times offers a promising approach to meet the challenges of production in a globalized world but places high demands on molding processes. Adhesive and abrasive wear as well as corrosion taking place during the production of plastics products and high deforming forces lead to the necessity of developing new material concepts. Ternary nitride hard coatings deposited by PVD (Physical Vapor Deposition) find widespread application as hard protective coatings against wear and corrosion due to their outstanding tribological, mechanical and chemical properties. Besides ternary nitrides, quaternary chromium based oxy-nitride coating systems as $(Cr_xAl_{1-x})ON$ have gained much attention revealing high potential for decreasing adhesion and deforming forces between PVD coated tool and plastics melt during the production, e. g. of optical components or microstructered parts. The present work deals with the development of chromium based oxy-nitride hard coatings $(Cr_xAl_{1-x})ON$ on stainless tool steel ASTM 420 (X42Cr13, 1.2083) using middle frequency (mf) pulsed magnetron sputtering (MS) PVD technology. The aluminum content of the $(Cr_xAl_{1-x})ON$ coatings was varied in the range of 5 at.-% and 80 at.-%. By means of optical emission spectroscopy (OES) the deposition process was monitored regarding Cr/Cr^+ and Al/Al^+ ratios and the working points were varied via oxygen gas flow. Morphology, mechanical properties, phase and chemical composition were analyzed. Adhesion behavior between $(Cr_xAl_{1-x})ON$ coatings towards polymers by high temperature contact angle measurements revealed a significant impact of the coatings' chemical composition. Tribological model tests in a pin-on-disk-tribometer verified a positive influence of $(Cr_xAl_{1-x})ON$ coatings on the adhesion behavior towards polymers which is directly linked to lowering of deforming forces. This makes $(Cr_xAl_{1-x})ON$ coatings a promising candidate for the production of optical components or microstructured parts by injection molding or extrusion.

10:40am **G4-3 Tailoring Wear Resistant PVD Coatings for Metal Cutting Applications**, ***E. Göthelid*** *(emmanuelle.gothelid@sandvik.com)*, Sandvik Coromant, Sweden **INVITED**

Manufacturing industry is craving for more productivity, versatility and reliability while machining more demanding materials. The challenge faced by tool manufacturers is thus to deliver products with longer tool life, and predictable performances, which requires a deep understanding of the wear mechanisms involved: abrasive, adhesive, chemical or thermomechanical. Each of the wear mechanisms results in specific wear types (flank wear, crater wear, thermal crack to cite a few) which, when combined, may results in sporadic and catastrophic failure of the tool.

In this work, the resistance of different PVD coatings to specific wear types has been systematically studied, and related to the physical properties of the films (composition, nano-hardness, E module, crytal structure, architecture, etc). This knowledge can then be applied to tailor coating solutions for specific applications. Examples to illustrate this work will be given.

11:20am **G4-5 Investigation of Suitability of CVD Diamond Thick Film Tool Coatings for High Performance Cutting of Ti6Al4V Super Alloys**, ***F. Degen*** *(florian.degen@ipt.fraunhofer.de), F. Klocke, T. Bergs, M. Busch*, Fraunhofer Institute for Production Technology IPT, Germany

Coatings are used in metal cutting since many years. Due to tool coatings the tool service life can be increased significantly. Thus, nowadays most cutting tools are coated. The problem hereby is that the thickness of the coatings is limited to only several micro meters. Thicker coatings affect the sharpness of the cutting edge negatively and favor spalling of the bonding. Therefore, the favorable effect of the bond is lost as soon as the bond is breached, for example due to tool wear.

In the past years many tool manufacturers are offering novel so called thick film bonded tools (TFC tools). These are tools where a very thick bond (300 – 1000 µm) usually made of diamond is produced by CVD on a wafer first, is cut afterwards into small inserts and then brazed on the tip of the tool. The advantage of this novel kind of bond using for cutting tools is that the favorable effect of the bond is not gone when tool wear occurs. Furthermore, due to the large thickness it is possible to machine the bonds in a final step to sharpen the tool edge. Against the background that the bond is made completely out of diamond and no bond phase is existent, like in PCD, diamond thick film tools are much more resistant towards abrasive wear. Thus, the tool life should be significantly higher compared to common TiN coated cemented carbides. However, as diamond turns into graphite at 700°C the suitability of such tools in high performance cutting is questionable. It is unknown if diamond thick film tools are able to substitute TiN coated cemented carbides. Therefore it is investigated in this paper if TFC tools are suitable for high performance cutting of Ti6Al4V super alloys. Experiments were conducted to compare the tool life of TFC tools with common TiN coated cemented carbide tools. Besides this it is investigated which effect the thermal load has on the wear resistance of the diamond coating. This was done by using different kind of cooling strategies and cooling pressures (1 bar flood cooling - 80 bar direct injection cooling). Investigations show that TFC tools have a significantly higher tool life than common TiN coated cemented carbide tools. But, investigations also show that a sufficient high pressure cooling is required. Otherwise thermal loads become too high and cause early tool/ bond failure.

11:40am **G4-6 Technology Trends in Coated Cemented Carbides for High Demanding Applications CVD, PVD, Cutting Tool**, ***C. Czettl*** *(christoph.czettl@ceratizit.com), M. Pohler*, CERATIZIT Austria GmbH, Austria **INVITED**

The development of hard coatings for cutting applications starting with the early CVD TiC coatings to the nowadays used multilayer CVD and PVD coating systems will be reviewed. Especially in high demanding cutting applications, solutions for difficult to cut materials like high alloyed steels or titanium alloys are needed. A detailed understanding is indispensable to increase the performance of tool systems regarding wear resistivity and toughness by fine tuning of material properties. Not only carbide and coating are of major importance, also the tool system has a high impact on the performance and productivity. An example of the automotive industry will demonstrate this effect in the crankshaft milling process. The optimized interaction of tool system, geometry, carbide and coating is necessary to fulfil the needs of future challenges in metal cutting operations.

Hard Coatings and Vapor Deposition Technology
Room: Royal Palm 1-3 - Session B1-2

PVD Coatings and Technologies
Moderator: A.N. Ranade, The Boeing Company, S. Weißmantel, University of Applied Sciences Mittweida, J.W. Lee, Ming Chi University of Technology, Taiwan

1:30pm **B1-2-1 High-temperature Sputter Deposition of $Ti_{1-x}Al_xN$/TiN Multilayer Coatings on Powder-metallurgical High-speed Steels**, *T. Weirather, K. Chladil,* Montanuniversität Leoben, Austria, *B. Sartory,* Materials Center Leoben Forschung GmbH, Austria, *D. Caliskanoglu,* Böhler Edelstahl GmbH & Co KG, Austria, *R. Cremer,* KCS Europe GmbH, Germany, *W. Kölker,* CemeCon AG, Germany, ***C. Mitterer*** *(christian.mitterer@unileoben.ac.at)*, Montanuniversität Leoben, Austria

Although spinodal decomposition of metastable cubic $Ti_{1-x}Al_xN$-based hard coatings and the underlying mechanisms have been extensively explored, the effect of high deposition temperatures is essentially unknown. It is thus the aim of this work to elucidate structure, properties, thermal stability and wear performance of $Ti_{1-x}Al_xN$/TiN multilayer coatings sputter deposited on powder-metallurgical high-speed steels at substrate temperatures of up to 575°C. Sharper domain boundaries and multilayer interfaces yield increased hardness in the as-deposited state, while the detrimental formation of wurtzite AlN during vacuum annealing is retarded by 50°C according to Rietveld refinement of X-ray patterns. Tribological tests at room temperature and up to 650°C corroborate the high potential of increased coating temperatures, while demonstrating the crucial importance of using a substrate material with adequate hot hardness. Cutting tests verify the high temperature deposition approach to show an increase in tool performance of ~40 %.

1:50pm **B1-2-2 Wear Protective Coating for Cutting Tools Applications Deposited by S3p™**, ***D. Kurapov*** *(denis.kurapov@oerlikon.com), S. Krassnitzer, T. Bachmann, J. Hagmann, W. Kalss, M. Arndt, H. Rudigier*, Oerlikon Balzers Coating AG, Liechtenstein

In this work wear protective coatings for cutting tool applications were produced by novel S3p™ deposition method. S3p™ technology enables scalability of the pulse power density and pulse length. The coating growth was studied with respect to the pulse parameters. The chemical composition of the coatings was investigated by means of energy dispersive X-ray spectroscopy (EDX). The evolution of the growth morphology and crystallographic structure as a function of plasma characteristic was studied by scanning electron microscopy (SEM) and X-ray diffraction (XRD), respectively. The elastic modulus of the coatings was measured by nanoindentation method. The applied pulse power density and pulse length were found to be crucial parameter influencing the phase composition and properties of the coatings. The correlation between coating growth conditions and the cutting performance of the coatings is discussed.

2:10pm **B1-2-3 Internal Oxidation of Nanolaminated Coatings**, ***Y.I. Chen*** *(yichen@mail.ntou.edu.tw)*, National Taiwan Ocean University, Taiwan **INVITED**

Nanolaminated coatings, consisting of alternating gradient concentration, were prepared using co-sputtering deposition by exposing the substrates alternatively under sputter sources. After annealing in oxygen containing atmospheres, internal oxidation has been observed for the nanolaminated coatings, resulting into the formation of an oxidized laminated structure, which consisted of alternating oxygen-rich and deficient layers stacked adjacent to the surface. The forming mechanism for crystalline coatings was proposed as follows: (1) one of the elements should be relatively noble, such as Ru; (2) the coatings show an orientated columnar structure in the as-deposited state, and the elements stack on the substrate with an alternating gradient concentration; and (3) the inward diffusion of oxygen is faster than the outward diffusion of the coating constituents. In this study, thermodynamic and kinetic considerations were examined. Internal oxidation of ternary alloy coatings, Ta–Ru–Zr, was investigated**.**

2:50pm **B1-2-5 Ion Energy Distributions in DC Arc Plasma from Compound Cathodes**, *I. Zhirkov (igozh@ifm.liu.se), O. Vozniy,* ***J. Rosen***, Thin Film Physics Division, IFM, Linköping University, Sweden

Arc deposition from compound cathodes is today a common method for synthesis of a wide range of functional multi-element coatings. It is known, that the kinetic ion energy is a crucial plasma parameter for the structural evolution of the film. Therefore, an increased understanding of the plasma generation from compound cathodes is highly motivated. In this work, unfiltered DC arc plasma from Ti-C, Ti-Al, and Ti-Si cathodes were characterized with respect to charge-state-resolved ion energy (velocity). We found that the most likely ion velocity is independent on mass, and hence the same for all ion species and ion charge states originating from the same cathode. Therefore, measured difference in kinetic energies can be inferred to the difference in ion mass, as $E=mv^2/2$. It was also discovered that plasma generated from the cathodes with increased concentrations of C and Si resulted in more energetic ions. This effect may be explained by the "Cohesive energy rule", where single-element (C) and binary ($Ti_{1-x}C_x$, $Ti_{1-y}Si_y$) phases of higher cohesive energy generally result in increasing ion energies. The collected results are consistent with a gas-dynamic mechanisms of ion acceleration based on pressure gradients, and suggest that the addition of C, and Si into Ti cathodes increase the pressure in the arc spots which in turn lead to increased ion velocities/energies. This is supported by an obtained most likely ion velocity of 1.47, 1.76, and 1.81 ($\cdot 10^4$ m/s) for ions from Ti, $Ti_{0.75}C_{0.25}$, $Ti_{0.75}Si_{0.25}$, respectively. For Ti ions this correspond to an ion energy of 53.8 eV, 77.1 eV and 81.5 eV, respectively.

3:10pm **B1-2-6 Filtered Cathodic Vacuum Arc Processes for Nano-scale Layering of Wear-resistant Structure on High Speed Steel Tools**, ***A. Vereschaka*** *(ecotech@rambler.ru), M. Volosova, S. Grigoriev, A. Vereschaka*, Moscow State University of Technology (MSUT "STANKIN"), Russian Federation, *A. Batako*, Liverpool John Moores University, UK

This paper presents a development of filtered cathodic vacuum arc formation processes of nano-scale wear-resistant structures to increase life span of high speed steel cutting tools. An attempt is made to increase the efficiency of complex-profile tools made of high speed steel (HSS). This is achieved by depositing wear-resistant complexes (WRC) on the cutting tools using combined catholic vacuum arc deposition processes with filtration of steam-ion flow in a single technological cycle. The wear-resistant coatings have four-component architecture. This includes a thermo-stabilizing layer, which increases the thermal stability of HSS against high temperature creep and thermoplastic deformation at cutting temperatures. This leads to more stable and enduring work of the nano-dispersed multilayer coating, which consists of adhesive underlayer, intermediate and outer layers. This work investigates into the influence of process parameters on the formation of the nano-scale structure of wear-resistant complex coatings and their properties. This allowed defining the optimal conditions for WRC formation, under which the maximum increase of tool life was observed for different cutting regimes. It was found that the tool life of different types of HSS tools coated with the newly developed WRC significantly exceeded the life span of both commercially available uncoated and coated HSS tools.

3:30pm **B1-2-7 Structure and Corrosion Properties of TiN Films Deposited by Combined HIPIMS-DCMS Process**, ***P.Eh. Hovsepian*** *(p.hovsepian@shu.ac.uk), A.A. Sugumaran, A.P. Ehiasarian*, Sheffield Hallam University, UK

TiN films were deposited using four cathode coating system equipped with power supplies for High Power Impulse Magnetron Sputtering (HIPIMS) and power supplies for Direct Current Magnetron Sputtering (DCMS). In this study, the coatings were produced using different combinations of HIPIMS and standard magnetron sputtering sources. Increasing the number of HIPIMS sources involved in the combined process proved to be an effective tool to manipulate the ionisation degree in the plasma. Optical emission spectroscopy revealed that the intensity ratio of Ti^{1+}:Ti^0 in the plasma increased with increasing the number of HIPIMS sources involved in the process from 0.09 to 1.93 for pure DCMS and pure HIPIMS respectively.

TiN coatings phase composition, microstructure texture as well as residual stress, and corrosion properties were studied by number of surface analyses techniques such as X-Ray Diffraction (XRD), Fracture Cross Sectional Scanning Electron Microscopy, (XSEM), Transmission Electron Microscopy, (TEM) as well as RAMAN spectroscopy.

It was revealed that in mixed HIPIMS - DCMS processes the residual stress can be controlled in vide range from -0.21 GPa to -11.35 GPa by smart selection of the degree of HIPIMS utilisation, strength of the electromagnetic field of the unbalancing coils of the machine as well as the bias voltage applied to the substrate.

XSEM analyses revealed that the fracture morphology changes from open columnar to dense almost glassy morphology when the number of HIPIMS sources in the process increases due to the higher ionisation and therefore

higher mobility of the condensing species. Furthermore, higher ionisation with HIPIMS dominated processes leads to change in preferred film orientation from (111) to (200).

Significant improvement in corrosion performance was achieved by increasing the number of the HIPIMS sources involved in the process. Raman spectroscopy was used to analyse the nature of the corrosion products as well as to estimate the extent of the corrosion damage. When polarised around E_{corr} values (-1 V to + 200 mV), pure DCMS and 1 HIPIMS + 3 DCMS coatings exhibited iron and chromium oxide (Fe_2O_3, Cr_2O_3) peaks at ~495 cm-1 and ~ 550 cm-1 in the spectra indicating that the corrosion has reached the substrate. No corrosion products were found in the above potential range for 2 HIPIMS + 2 DCMS and pure HIPIMS coatings demonstrating the advantages of the denser structures.

Mixing HIPIMS with DCMS is also seen as an effective tool for improving the productivity of the deposition process.

3:50pm **B1-2-8 Ternary Carbonitride Coatings deposited by High Power Impulse Magnetron Sputtering**, ***T. Hirte*** *(tina.hirte@de.bosch.com), R. Feuerfeil, V. Perez-Solorzano Borragan,* Robert Bosch GmbH, Germany, *M. Scherge,* Fraunhofer Institute for Mechanics of Materials, IWM, Germany

Many recent studies have been investigating ternary carbonitrides including metals or metalloids (like TiCN, NbCN and BCN) for their potential as wear resistant coatings in several applications. The adjustability of their properties, such as hardness, coefficient of friction, wear resistance, and temperature stability is especially promising. Different deposition methods are used to grow thin films for wear protection purposes and it is agreed that structure has a strong influence on their mechanical and chemical properties.

The short pulses with very high power density applied in High Power Impulse Magnetron Sputtering (HiPIMS) result in a higher ionization rate of the sputtered material compared to conventional DC magnetron sputtering. Therefore, HiPIMS technology can have a beneficial influence on the film structure and provides a promising approach to tailor the properties of ternary coating systems.

This work focuses on the influence of chamber pressure and nitrogen to argon ratio during the deposition of ternary carbonitride coatings on their composition and structure. The films were grown on high speed steel and silicon substrates with DC-MS and HiPIMS and were characterized using X-ray photoelectron spectroscopy and X-ray diffraction. Topography and morphology were examined by scanning electron microscopy. Furthermore, hardness and adhesion were measured using nano indentation and Rockwell indentation and the correlation with the structure was investigated. The differences in composition, structure and hardness we observed between DC-MS and HiPIMS sputtered coatings are discussed within this publication.

4:10pm **B1-2-9 Laser Assisted and Arc Technologies for Hard Carbon Film Deposition – An Overview from the Beginning up to the Industrial Application**, ***H.J. Scheibe*** *(hans-joachim.scheibe@iws.fraunhofer.de),* Fraunhofer Institute for Material and Beam Technology IWS, Germany **INVITED**

Pulsed laser assisted and arc methods are preferentialy applied for the generation of a fully ionized plasma with high kinetic ion energy from a solid target material. These are necessary conditions for the deposition of dense hard films with a good adherence to the substrate material, especially for hard amorphous carbon films.

An overview will be given about the development of both technologies during the last 20 years from basic processes in the laboratory scale to the industrial applicable deposition source. Just as well the combination of both technologies in form of the laser assisted pulsed arc deposition process (Laser-Arc) will be presented. The advantages of this combination are presented with respect of introduction for high volume coating of parts and tools.

Mainly advantages of the Laser-Arc technology are to have a very controlled pulsed arc deposition technology with a high deposition rate (2 µm/h twofold rotating axes of a planetary). By the laser controlling of pulsed arc evaporation a longtime using of the applied rotating graphite cathodes is guaranteed and ta-C films with a thickness up to 10 microns can be deposited. By integration of a filter unit for separation of particles from the carbon plasma, an improved ta-C film quality can be obtained, regarding their roughness, hardness and Young´s modulus with an acceptable loss of the deposition rate.

The nature of the Laser-Arc-Module system is, that this carbon ion source can be integrated in commercial available coating machines, independently of producer.

4:50pm **B1-2-11 Super-hard Tetrahedral Amorphous Carbon Films (ta-C) with Low Internal Stress -The Potential of the Pulsed Laser Deposition Technique**, ***K. Guenther*** *(guenthe2@hs-mittweida.de),* University of Applied Sciences Mittweida, Germany, *V. Weihnacht,* Fraunhofer IWS, Germany, *S. Weißmantel*, University of Applied Sciences Mittweida, Germany

Super hard tetrahedral amorphous carbon (ta-C) films have been deposited by: 1) pulsed laser deposition (PLD) using an excimer laser (248 nm wavelength) 2) PLD in combination with laser pulse stress relaxation (PLD – LSR) 3) pulsed laser arc method (ARC) and 4) filtered pulsed laser arc method (fARC). The aim was a comparative study of growth and properties of ta-C films produced by these various production methods. Therefore, ta-C films with the same thickness of 2 µm have been deposited onto polished steel, tungsten carbide and silicon substrates using these different methods. The films were characterized with regard to their morphology, adhesion and hardness by scanning electron microscopy (SEM), scratch testing and nanoindentation, respectively. Both the ARC and PLD methods have in common that large particles (droplets) are incorporated into the films. Our investigations by SEM show that both the size and the number of the droplets are lower for PLD or PLD-LSR films in comparison to ARC films. We will also show how the number of droplets can be reduced by using fARC instead of ARC and will compare the surface roughness of all the films. There are also differences in the film properties. Scratch tests show critical loads of ta-C films on steel substrates between 11 N and 27 N and on tungsten carbide substrates between 30 N and 35 N. The ta-C films produced by PLD and especially by PLD-LSR show clearly different behavior in film failure in the scratch in comparison with the ARC ta-C films, which will be discussed in terms of number and size of droplets, film stress and hardness. Furthermore, hardness measurements will show, that it is possible to produce with all methods equal hardness between 10 GPa and 60 GPa, which can be adjusted by using different deposition parameters. By using the ARC and fARC method it is possible to produce ta-C layers with internal stresses between 1-3 GPa for industrial applications. By using PLD the internal stress is with up to 8-10 GPa higher. This can be reduced near to 0 GPa by using PLD-LSR. The deposition rate of industrial ARC amounts to about 3.6 µm/(h.m2). The plasma filter has a transparency of about 50%, i.e. the deposition rate for fARC is reduced to about 1.8 µm/(h.m2). In comparison, both PLD methods allow at the moment deposition rates up to 0.9 µm/(h. m²). It is shown, that all 4 methods are appropriate to produce the ta-C layers for wear protection of different kinds of tools and sliding components.

5:10pm **B1-2-12 Structure and Properties of Nitride Coatings, Prepared by PIII&D Using Multicomponent As-cast TiAl-based Cathodes**, *V. Belous, V. Vasyliev, A. Luchaninov, V. Marinin, E. Reshetnyak, V. Strel'nitskij,* National Science Center "Kharkov Institute of Physics and Technology", Ukraine, *S. Goltvyanytsya,* ***V. Goltvyanytsya*** *(vladtnt@gmail.com),* Real Ltd., Ukraine

Doping the TiN and TiAlN coatings with small amounts of Y, Hf, Nb, B, V, Cr and Si and other elements that are traditionally added to the heat-resistant alloys can significantly improve their oxidation and wear resistance. It enables to develop new multicomponent nanostructured coatings used for protection of tools and machine components that undergo extreme environmental conditions. The goal of the present work was to obtain and to study the composition, structure and mechanical properties of multicomponent nitride coatings prepared by PIII&D using filtered vacuum-arc plasma source and as-cast TiAl-based cathodes with additions of Cr, Si, Y, Re, Ni, Mo, Fe.

Cathodes were produced by vacuum-arc remelting in an argon atmosphere (by Real Ltd., Zaporozhye, Ukraine).

Nitride coatings with thickness of 6-8 µm were deposited on the stainless steel substrates from vacuum-arc plasma source using straight filter. As plasma gas a mixture of nitrogen with a small amount of argon was used. The partial pressure of nitrogen in the chamber was 0.1-0.2 Pa. During the deposition the pulsed potential of negative polarity was applied to the substrate with the following parameters: the amplitude in the range of -1,5-2,5 kV, the pulse duration 5 µs and the repetition frequency – 24 kHz.

The elemental and phase composition, texture and substructure characteristics of the coatings were controlled by X-ray diffraction (XRD) and X-ray fluorescence analysis (XRA). The hardness (H) and Young's modulus (E) of the coatings were measured with a G200 nanoindenter in CSM mode.

A nitride with cubic lattice of NaCl was revealed in all studied coatings. All investigated coatings had relatively high hardness in the range of 23-32 GPa and Young's modulus of 340-390 GPa.

The influence of the cathode and the gas phase elemental composition and deposition parameters on the elemental composition of the coatings, its substructure characteristics and wear resistance were analyzed.

Hard Coatings and Vapor Deposition Technology
Room: Sunset - Session B5-2

Hard and Multifunctional Nanostructured Coatings
Moderator: J. Paulitsch, Vienna University of Technology, Austria, J. Houska, University of West Bohemia

1:30pm **B5-2-1 The Selection of Interfaces for Achieving Super- and Ultrahardness**, ***S. Veprek*** *(stan.veprek@lrz.tum.de)*, Technical University Munich, Germany, *V. Ivashchenko*, Institute of Problems of Material Science, NAS of Ukraine, Ukraine, *M. Veprek-Heijman*, Technical University Munich, Germany

Based on a combination of thermodynamics and first-principles quantum molecular dynamics (QMD) calculations, we shall discuss the prospects of a variety of one monolayer thick (1 ML) interfacial XY-layers (XY = SiNx, BN, AlN and SiC) for achieving super- and ultrahardness in fcc-TiN/XY heterostructures and nanocomposites. In the past we have shown that superhardness of ≥ 65 GPa can be achieved in long-term stable quasi-binary nc-TiN/Si3N4 nanocomposites, and ultrahardness of 80 to ≥ 100 GPa in quasi-ternary nc-TiN/Si3N4/TiSi2 systems only when the oxygen impurities are sufficiently low, in the range of few 100 ppm. The present work deals with clean systems essentially free of impurities. We present new results regarding the dynamic stability of different SiNx interfacial layers in the TiN/SiNx system, which is immiscible and forms a semi-coherent interface. The possible hardness enhancement in the TiN/BN system, which is from thermodynamical point of view also immiscible, is limited due to the strongly incoherent nature of the TiN/BN interface and, as shown by the QMD calculation, by the inherent dynamic instability of the interfacial BN layer which transforms into a highly disordered h-BN-like phase already at 0 K. The hardness enhancement reported for the nc-TiN/BN nanocomposites is therefore more probably due to the refinement of the TiN crystallite size to about 10 nm (the "strongest size") and not to a semicoherent interfacial layer strengthened by valence charge transfer like in the TiN/SiNx system. QMD calculations show that the AlN interfacial layer in the TiN/1 ML AlN/TiN is dynamically stable within the whole temperature range of 0 to 1400 K considered. However, thermodynamic considerations suggest that, although the heterostructures with 1-2 ML AlN have been shown to possess a relatively high stability, the formation of nc-TiN/AlN nanocomposites with thermal stability comparable to the nc-TiN/Si3N4 system seems to be questionable because of the relatively low positive mixing enthalpy (i.e. low de-mixing energy) of the TiAlN solid solution. The interfacial SiC layer in the fcc-TiN/1 ML SiC/TiN heterostructures is, according to the QMD calculations, stable only up to about 600 K above which it transforms into strongly distorted 3C-SiC phase. Moreover, the formation of nc-TiN/SiC nanocomposites is unlikely because, from the thermodynamical point of view, the solid solution TiN(1-x)Cx should form, particularly at a higher temperature. These combined thermodynamical, DFT and QMD calculations allow to identify the TmN/XY systems which are promising candidates for new superhard nanocomposites and rule out those which are less or not suitable.

1:50pm **B5-2-2 Comparison of TiSiN and TiSiVN Films Deposited by DC and HIPIMS Reactive Magnetron Sputtering Techniques**, *F. Fernandes*, University of Coimbra, Portugal, *T. Polcar*, University of Southampton, UK, ***A. Cavaleiro*** *(albano.cavaleiro@dem.uc.pt)*, University of Coimbra, Portugal

TiSiN hard coatings are well established in commercial tribological applications due to their excellent oxidation, and extremely high hardness. The aim of this investigation was to compare the properties of TiSiN films deposited by DC reactive magnetron sputtering and high power impulse magnetron sputtering (HIPIMS). HIPIMS could remedy the drawbacks of standard DC process such as: lower film density, high number of voids and defects, and issues related to the nanocomposite structure formation. Further, the effect of V incorporation in the TiSiN films was also considered. The idea was to take advantage of the lubricious properties of V rich oxides to decrease the friction coefficient of TiSiN films. The structure, mechanical properties, oxidation resistance and tribological behaviour of DC and HIPIMS deposited films were characterized by nanoidentation, X-ray diffraction, scanning electron microscopy, thermo gravimetric analysis (TGA) and pin-on-disc tests. In the range of Si contents studied (up to 12 at.%), all the coatings presented an fcc NaCl-type structure characteristic of TiN phase. Improvement of the mechanical properties was achieved with HIPIMS deposition. Hardness and Young modulus of coatings are not changed with increasing V content. V incorporation successfully reduced the friction coefficient and consequently the wear volume loss of films. Scanning electron microscopy and Raman spectroscopy showed that V_2O_5 phase is the responsible for this performance. HIPIMS improved the wear performance of deposited coatings although no significant changes were observed in the friction behaviour.

2:10pm **B5-2-3 Structure and Properties of Novel Al-based PVD Nanostructured/Amorphous Coatings**, ***J. Lawal***, *A. Leyland (a.leyland@sheffield.ac.uk)*, *A. Matthews*, University of Sheffield, UK

The primary motive for most new PVD nanostructured coating development has been to enhance the tribological properties of engineering components. However, there are many applications in which there is a simultaneous requirement to accommodate abrasion, erosion, corrosive environment, and provide other functional properties such as lubricity, antibacterial properties, sensing or actuating capability – or to adapt to fluctuating conditions. As well as the potential to improve both wear and corrosion properties of engineering components, nanostructured PVD coatings (where combinations of ceramic, metallic, crystalline, and amorphous phases can be generated) have unrivalled design flexibility to develop multifunctional capabilities. Such coatings can exhibit unusual combinations of high hardness, long elastic strain to failure, strong resistance to crack formation and/or propagation – and often exhibit surprisingly good corrosion resistance, especially in terms of pitting.

In this research, the tribological and corrosion behaviour of some novel Al-based multi-element metal-alloy PVD coatings were studied. The coatings were deposited on austenitic stainless steel and low alloy steel, materials which are in widespread use, yet tend to exhibit poor tribological properties and poor corrosion properties respectively. These coatings have the potential to provide alternatives to electroplated cadmium, IVD-aluminium, electroplated hard chromium, electroless nickel and other 'traditional' coatings used in aerospace, automotive and other engineering applications – where environmental legislation is restricting the use of many of the toxic materials and processes required to deposit and functionalise them. We demonstrate that metallic PVD nanostructured/amorphous coatings with multifunctional and adaptive properties could be developed to suit a range of technically challenging environments.

The characteristics of the coating-substrate systems were studied using a reciprocating-sliding ball-on-plate test and a microabrasion wear test. SEM, and EDX were conducted to check the composition and measure the thickness of the coatings. XRD and TEM investigations provide more detailed explanations for the unusual properties of these coatings. Hardnesses and elastic modulii were also determined. The reactive addition of nitrogen to the multi-element metal-alloy films is shown to have a significant influence on the wear behaviour of the system. Open circuit potential scans and potentiodynamic polarisation measurements were used to investigate the pitting potential, passivation and sacrificial corrosion behaviour of the coatings in a 3.5 wt. % NaCl environment.

2:30pm **B5-2-4 The Modifying Effect of Cu and Ni on Nanostructuring and Properties of ARC - PVD Coatings Based on Titanium Nitride**, ***D.S. Belov*** *(d.belov@email.com)*, *I.V. Blinkov*, *A.O. Volkhonskiy*, National University of Science and Technology "MISIS", Russian Federation

Metal-ceramic TiN-Cu (TiN-Ni) coatings with metal content from 0 to 20 % synthesized by the methods of the filtered vacuum arc deposition of carbide tools. Addition of metals into the coating leads to the reduction of nitride phase crystalline grain size from 100 to 20 nm. Besides, enhancement of metal content in the coating up to 3-5 % results in the increase of the coating hardness from 20-22 (typical for TiN) to 45-50 GPa and friction coefficient from 0,65 (typical for a hard alloy) to 0,45. Further enhancement of metals content up to 20 %, attended by the reduction of nitride phase crystalline grain size, displays the decrease of hardness to 15-19 GPa related to the impact of soft ductile metal and emerging coating porosity. Adhesive/cohesive properties of coatings were investigated. It is established that the coatings were destructed according to the cohesion mechanism. The critical loads characterizing the emergence of the first cracks in the coatings and the complete abrasion of the coating to the substrate (L and L) were determined, which reached 45 and 80 N, respectively. The formed coatings display thermal stability of their structure and composition up to 800 °C. Hard-alloys cutting tool developed with the coatings showed more than five-fold and three-fold increase in resistance in continuous and interrupted cutting steels , respectively.

2:50pm **B5-2-5 Low Temperature Synthesis of Mo_2BC Thin Films**, ***H. Bolvardi*** *(bolvardi@mch.rwth-aachen.de)*, *J. Emmerlich*, *S. Mráz*, RWTH Aachen University, Germany, *M. Arndt*, *H. Rudigier*, OC Oerlikon Balzers AG, Liechtenstein, *J. Schneider*, RWTH Aachen University, Germany

Emmerlich et al. [J. Phys. D: Appl. Phys. 2009, p42] reported the formation of Mo_2BC coatings at a substrate temperature of 900 °C by combinatorial magnetron sputtering. This synthesis temperature limits the choice of substrate materials severely. Here, utilizing high power pulsed magnetron sputtering (HPPMS), the synthesis temperature was reduced to 380 °C, while the measured elastic modulus and lattice parameters of the

asdeposited films are consistent with ab-initio data. Since the crystallization of amorphous Mo_2BC powder was observed at 820 °C the HPPMS plasma was analyzed to identify the cause of the significantly reduced synthesis temperature. The measured ion current at the substrate and the ion energy distributions are consistent with the notion that energetic ion bombardment of film forming ions as well as Ar+ during HPPMS enables surface diffusion and, hence, causes the substantial decrease of the formation temperature of crystalline Mo_2BC to 380 °C reported here. Thus, low temperature synthesis of Mo_2BC is surface diffusion controlled. The synthesis strategy reported here greatly expands the range of technologically interesting substrate materials for application.

3:10pm **B5-2-6 Nanostructured Coatings with Adaptive Friction and Thermal Properties**, ***A.A. Voevodin*** *(Andrey.Voevodin@us.af.mil)*, Air Force Research Laboratory, US, *C. Muratore*, University of Dayton, US, *J.J. Hu, J. Gengler*, Air Force Research Laboratory, US, *D. Stone, S.M. Aouadi*, University of North Texas, US, *O. Jantschner, C. Mitterer, R. Rachbauer*, Montanuniversität Leoben, Austria, *P.H. Mayrhofer*, Vienna University of Technology, Austria, *D. Music, J. Schneider*, RWTH Aachen University, Germany **INVITED**

This presentation provides a review of adaptive surface materials and thin film technologies that were recently explored to impart adaptive behavior for mechanical contacts. Two main functions are considered for the surface adaptation which are most practically important for a multitude of mechanical contacts operating at high loads, speeds, and temperatures: i) adaptive tribological behavior with an emphasis on reduced friction and wear through sliding surface chameleon self-adaptation; ii) adaptive heat transport regulation at contact interfaces with an emphasis on surface engineering (texture, morphology, inclusions) to control heat flow at interfaces and mitigate thermal spikes. The focus is placed toward adaptive behavior at high temperatures in air, as this is one of the most challenging environments due to accelerated oxidation in addition to structural evolution processes. Examples include: multilayered oxide and nitride coatings with inclusions of noble metals for controlled surface diffusion and regulation of surface friction and thermal conductivity; transition metal nitride coatings with inclusions of silver for the formation of lubricating ternary oxides with a low shear strength; hard oxide coatings with vanadium additions to induce low melting point oxides for liquid lubrication and heat spike mitigation; age-hardened nitride coatings with thermal conductivity adaptation through structural evolutions; intrinsically nano-laminated complex carbides with low shear planes for friction reduction; and nano-laminated transition metal dichalcogenides with anisotropic thermal properties for heat redirection. While some of these concepts are experimentally verified and used in real-life applications, many are yet in an early design and development stages. The conclusions outline challenges and possible directions toward future developments in nanostructured coatings with adaptive behavior.

3:50pm **B5-2-8 Synthesis and Characterization of Multifunctional Me-B-C (Me = Cr, Nb, Mo) Thin Films Deposited by DC Magnetron Sputtering**, ***P. Malinovskis***, *N. Nedfors, U. Jansson (ulf.jansson@kemi.uu.se)*, Uppsala University, Angstrom Laboratory, Sweden, *J. Lu, P. Eklund, L. Hultman*, Linköping University, IFM, Thin Film Physics Division, Sweden

Ceramic Me-B-C thin films are interesting because of their multifunctional properties, such as high hardness, chemical inertness, conductivity and temperature resistance. The microstructure and thereby the properties are strongly dependent on elemental composition and type of transition metal Me. A basic understanding of how these parameters affect the film structure makes it possible to tailor the properties. We have investigated the influence of composition on Me-B-C (Me= Cr, Nb, Mo) thin films deposited by DC magnetron sputtering, at temperatures 300 - 500 °C, using MeB_2/C or Me/B_4C/C target combinations. The microstructure has been characterized using XRD (X-ray diffraction), XPS (X-ray photoelectron spectroscopy) and TEM (transmission electron microscopy).

In Cr-B-C and Nb-B-C films, carbon (C) forms a solid solution in substoichiometric MeB_2 phase at low carbon C contents. As more C is added the crystallinity is reduced. For the Cr-B-C films a completely amorphous structure is formed in the range of 20-30 at.% C while a nanocomposite structure with nanocrystalline boride grains is maintained for Nb-B-C films above 35% of C. In both systems, XRD suggest a solid solubility of C into the boride grains. XRD and TEM studies of the amorphous Cr-B-C films show that they are nanocomposites with two separate amorphous phases. In contrast, the Mo-B-C films exhibit a uniform amorphous structure. The hardness and elastic modulus was strongly dependent on the choice of metal, carbon content and degree of crystallinity. In general, the hardness was reduced with increasing C content and reduced crystallinity. The more crystalline Nb-B-C films exhibited the highest hardness (20-40 GPa) while the amorphous Cr-B-C films were less hard (17-25 GPa). Furthermore, the addition of C had a strong influence on the tribological properties. The addition of 36 at.% C to CrB_{2-x} films (at relative humidity 50%) reduces the coefficient of friction by a factor of three. XPS and Raman spectroscopy suggests that formation of graphitic carbon and possibly BO_x is responsible for this behavior. The general trends in mechanical and tribological properties will be discussed based on the stability of binary borides and carbides.

4:10pm **B5-2-9 High Temperature Properties of Hexagonal Structured ZrAlN Thin Films**, ***L. Rogström*** *(linro@ifm.liu.se)*, *N. Norrby*, Linköping University, IFM, Nanostructured Materials, Sweden, *M. Ahlgren*, Sandvik Coromant, Sweden, *N. Schell*, Helmholtz-Zentrum Geesthacht, Germany, *J. Birch*, Linköping University, IFM, Thin Film Physics Division, Sweden, *M. Odén*, Linköping University, IFM, Nanostructured Materials, Sweden

Ternary aluminum nitride alloys are commonly used as hard coatings for wear resistant applications. Coating materials such as TiAlN are known for high hardness even after being exposed to high temperatures. The good mechanical properties at high temperatures are an effect of spinodal decomposition of the unstable cubic (c) TiAlN phase leading to formation of nanostructured domains of TiN and AlN. For ZrAlN coatings, the larger miscibility gap between ZrN and AlN hinders the formation of a c-ZrAlN phase for AlN-contents larger than ~35 at.%. High Al-content ZrAlN coatings instead exhibits a hexagonal (h) structure in which nano-sized ZrN and AlN domains form during annealing at temperatures above 900 °C resulting in age hardening of the coating [1].

In this work, we study the decomposition paths of h-ZrAlN coatings and its effect on the coating's mechanical properties. h-$Zr_{1-x}Al_xN$ coatings with 0.46>x>0.71 were grown on WC-Co substrates by cathodic arc evaporation. For AlN contents between 0.51 and 0.71 the coatings have a single phase hexagonal structure with a strong 002 preferred growth orientation. Simultaneous *in-situ* small angle and wide angle scattering during annealing show that decomposition of the h-ZrAlN phase begins at temperatures around 750 °C and that the temperature at which decomposition is initiated is independent on chemical composition of the coating. The wide angle scattering results reveal that the c-ZrN formed is aligned with the 111 direction parallel to the h-(Zr)AlN 002 direction. From the small angle scattering results, the coatings are observed to form a layered structure during annealing. The layer period depends on chemical composition of the coating and increases from 1.7 nm for x=0.51 to 2.5 nm for x=0.71 while the periodicity is not changing with annealing temperature or time. The hardness of the coatings ranges between 22 and 26 GPa where the highest hardness is found for the highest Al-content coating (x=0.71). After 2 h annealing at 1100 °C, the hardness has increased from 22 to 26 GPa for the coating with x=0.51 while for the coating with x=0.71 the hardness of the annealed coating is stable at 26 GPa. The increased or retained hardness of the annealed coatings is assigned to the nanoscale layering formed during decomposition of the h-ZrAlN phase.

[1] L. Rogström, M.P. Johansson, N. Ghafoor, L. Hultman, M. Odén, J. Vac. Sci. Technol. A 30 (2012) 031504.

4:30pm **B5-2-10 Multi-Scale Mechanical Properties of Nanocrystalline Coatings Revealed by Micro- and Nano-Mechanical Tests**, ***J. Zálešák*** *(jakub.zalesak@gmail.com)*, Erich Schmid Institute, Austrian Academy of Sciences, Austria, *M. Bartosik, P.H. Mayrhofer*, Vienna University of Technology, Austria, *J. Keckes*, Montanuniversität Leoben, Austria

Hard nanocrystalline coatings prepared by magnetron sputtering possess complex gradients of residual stresses, phases, and microstructures. Hardness and elastic modulus characterization performed by nano-indentation provides volume-averaged quantities which do not reveal the mechanical response and function of individual coating components, regions, and/or intrinsic gradients. The presented approach is a step towards the characterization of thickness- and direction-dependent coating mechanical properties at the micro- and sub-micro-meter scale performed on compact coatings as well as on isolated coating segments. For the detailed studies we have selected TiAlN and CrN/AlN multilayer coatings as model systems. Coating cantilevers with the sizes in the range of 0.1-4 µm prepared using focused ion-beam milling are tested using in-situ micro- and pico-indentation in scanning and transmission electron microscopes, respectively. The results reveal the integral elastic and fracture properties of the coatings as well as the mechanical response of selected coating regions. The approach allows the identification of features, which provide an increase in the toughness and elastic moduli or deteriorate the coating mechanical behaviour.

Coatings for Biomedical and Healthcare Applications
Room: Sunrise - Session D1

Surface Functionalization, Drug Delivery, and Anti-microbial Coatings

Moderator: S. Rodil Posada, Universidad Nacional Autonoma de Mexico, Mexico, D.V. Shtansky, National University of Science and Technology "MISIS"

1:30pm **D1-1 Wetting and Biocompatible Properties of Oxygen Plasma Treatment on Diamond-like Carbon Thin Films**, ***C. Jongwannasiri*** *(s3124601@sstu.nit.ac.jp),* Nippon Institute of Technology, Japan, *A. Khantachawana*, King Mongkut's University of Technology Thonburi, Thailand, *S. Watanabe*, Nippon Institute of Technology, Japan

Titanium and titanium alloys have found several applications in the biomedical field due to their unique biocompatibility. However, there are problems associated with these materials in applications in which there is direct contact with blood, for instance, thrombogenesis and protein adsorption. Surface modification is one of the effective methods used to improve the performance of titanium and titanium alloys in these circumstances. In this study, oxygen (O_2) plasma treatment on diamond-like carbon (DLC) film surfaces is studied, taking into account the wetting and biocompatible properties. All the films were prepared on silicon (100) wafers and nickel-titanium by a plasma-based ion implantation (PBII) technique using acetylene (C_2H_2) as plasma source. The as-deposited DLC films were then treated with O_2 plasma using various radio frequency (RF) powers and treatment times in order to characterize the wettability and biocompatibility, compared to as-deposited DLC, fluorinated diamond-like carbon (F-DLC), titanium alloys and polymers. The thickness and structure of the films were evaluated using stylus profilometer and Raman spectroscopy. The wettability was assessed using a contact angle meter. The friction coefficient was measured using ball-on-disk friction testing. Cytotoxicity tests were performed using MTT assay and dyed fluorescence. The results indicate the O_2 plasma treatment on DLC film surfaces influenced to thickness change, but unaffected to structure of the films with various RF powers and treatment times. These films present their hydrophilic surfaces due to a low contact angle and high surface energy. Further, O_2 plasma treatment on DLC film surfaces exhibits low friction coefficient and less cytotoxicity on their surfaces. It is concluded that O_2 plasma treatment can be used to make hydrophilic DLC, making it a favorable wetting surface and improving the biocompatibility for biomedical applications.

1:50pm **D1-2 Preparation and Assessment of Bone Morphogenetic Proteins Immobilized Titanium Dioxide on Titanium Surface for Bone Implant**, ***H.W. Shu***, Feng Chia University, Taiwan, *H.T. Chen (cjchung@ctust.edu.tw),* China Medical University Hospital, Taiwan, *C.J. Chung*, Central Taiwan University of Science and Technology, Taiwan, *J.L. He*, Feng Chia University, Taiwan

The increasing demand of high performance medical implants for improving living quality of human beings has led very rapid growth and development of medical implant products. Characterized by their light-weight and bio-inertness to living bone, titanium alloys are widely used as implant material for dental and orthopedic applications. Research works on the improved osseointegration capability and the reduced healing time of such implants still persist, particularly those works on developing a bioactive ceramic layer followed by attaching bone cell favoring reagents.

By considering micro-arc oxidation (MAO) technique to grow bioactive ceramic layer over titanium surface, it provides a wide range of benefits for implant purposes, porous structure (acting as scaffold) and strong film adhesion (avoiding delaminating during service) in particular. The aim of this study is to fabricate a biocompatible titanium dioxide (TiO_2) coating over the titanium metal via MAO technique, followed by covalently grafting bone morphogenetic proteins (BMP-2/BMP-7). The experimental results revealed that the MAO coatings are porous structure which facilitate hydroxylation of TiO_2 coating to presumably absorb and anchor protein molecules, and then Ca^{2+} and PO_4^{3-} to form apatite. The *in-vitro* test suggested that it favors oesteoblast cell growth over the protein grafted TiO_2 surface of the titanium substrate.

Keywords: titanium; micro-arc oxidation (MAO); titanium dioxide (TiO_2); covalently grafting; bone morphogenetic protein (BMP).

2:10pm **D1-3 Biofilm formation and consequences in dental implants: New insights**, ***A. Almaguer-Flores*** *(argelia.almaguer@mac.com),* Universidad Nacional Autónoma de México, Mexico **INVITED**

Biofilms are fascinating and complex structures that nowadays are recognize that constitute the predominant mode of growth of many bacterial species. A biofilm is an assemblage structure of microbial cells irreversibly associated with a surface and enclosed in a matrix of primarily polysaccharide material, this structure provides protection to the microbial communities from predation, toxic substances such as antibiotics and physical perturbation. Biofilms have the potential to cause device-related and other chronic bacterial infections that have gradually come to predominate in modern medicine causing harm to millions of humans annually. The difficulty of eradicating biofilm bacteria with classic systemic antibiotic treatments is a prime concern of medicine because the bacteria in a biofilm can be up to a thousand times less susceptible to antimicrobial stress than their freely suspended counterparts. Oral biofilms are important due to their relationship with two of the most important diseases that can be present in the oral cavity; gingivitis and periodontitis. These diseases are the pathological manifestation of the host response against the bacterial challenge from the dental biofilm that colonize the dental surface. The term peri-implantitis describe a destructive inflammatory process affecting the soft and hard tissues around osseointegrated implants, leading to the formation of a peri-implant pocket and loss of supporting bone, this infection is caused by a biofilm and it is well known that bacterial adhesion on implant surfaces has a strong influence on healing and long-term outcome of dental implants. The first indication of the specific role of bacteria in peri-implant infections was originated from microscopic analysis of samples taken from failing implants that shown an abundance of motile rods, fusiform bacteria and spirochetes, whereas samples from successful implants contained only a small number of coccoid cells and very few rods. These findings revealed a site-specific disease process with microorganisms associated in patterns known from chronic periodontitis of natural teeth. The formation, properties and composition of oral biofilms an also some factors that can influence biofilm formation on a biomaterial surface, like chemical composition, surface energy, hydrophilicity and topography will be discussed. Finally, it is pointed out the importance of the understanding of the mechanisms of biofilm formation on different biomaterial surfaces in order to control and prevent the formation of this structure and to assure the long-term successful life of biomedical devices like dental implants.

2:50pm **D1-5 Medical Coating Innovations: Antimicrobial PVD Coatings**, ***C. Acikgoz*** *(canet.acikgoz@oerlikon.com), C. Pinero, V. Derflinger, A. Janssen, H. Rudigier*, Oerlikon Balzers Coating AG, Liechtenstein

The modification of implant surfaces with antimicrobial properties has an important route to solve problems, such as infections and fouling, in biomedical applications and healthcare. A number of strategies have been applied for the modification of surfaces to inhibit bacterial adhesion and growth. Due to the increasing problems with multi-resistant microorganisms, especially in hospital environments, numerous efforts have been taken to fabricate surfaces to possess or release an antimicrobial agent, e.g. silver, copper etc. Silver ions are very efficient at killing bacteria, and in contrast to antibiotics they are effective against a number of different bacterial strains, owing to their several mechanisms of action. Therefore, Oerlikon Balzers has developed new antimicrobial silver doped titanium nitride (TiN-Ag) and chromium nitride (CrN-Ag) coatings for orthopaedic and medical devices. The use of silver as an additional phase in a nitride matrix provides additional wear resistance due to its tribological properties. Nevertheless, the incorporation of silver into the coatings for use in implant and medical devices must be adjusted to ensure a good balance between tribological and biomaterial properties. The characterization of the properties of these materials as extensively as possible can give us an opportunity to improve their properties for a founded choice of application.

TiN-Ag and CrN-Ag coatings were developed by a combined arc/sputter process. The coatings were characterised using transmission electron microscopy (TEM), energy-dispersive X-ray spectroscopy (EDX) and X-ray diffractometry (XRD). The formation of island shaped agglomerations having grain sizes of about 8-10 nm x 3-4 nm in TiN-Ag coating containing 2,5 at% of silver was observed. Ag release properties were assessed in NaNO3 buffer and the maximum concentration of Ag released from the coatings was determined. The antibacterial properties of the TiN-Ag and CrN-Ag surfaces against *S. aureus* were determined by plate count technique, a test method based on ASTM E-2180 standards. Both surfaces showed a reduction compared with controls of 3 logs in bacterial adhesion. In order to verify the applicability of the coated samples as biomaterials, samples were assayed in terms of their effect on fibroblast cells and the coated surfaces did not affect the cell functionality.

References:

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2. Ewald A. BioMedical Engineering OnLine, 2006, 5, 22.

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3:10pm **D1-6 Surface Modification of Biodegradable Magnesium Alloys *via* Plasma-based Methods**, ***G.S. Wu*** *(guosonwu@cityu.edu.hk)*, *P.K. Chu*, City University of Hong Kong, Hong Kong Special Administrative Region of China

Recently, magnesium alloys are considered revolutionary metallic biomaterials due to their biodegradability and Young's modulus being similar to that of human bone. However, their applications are hampered by poor corrosion resistance as well as low wear resistance. Plasma-based surface modification techniques including sputtering, filtered cathodic vacuum arc, and ion implantation are useful and environmentally friendly compared to most chemical methods. We have applied these technologies to modify the surface properties of magnesium alloys to meet actual requiements. A metallic interlayer is usually prepared to improve the adhesion between the insulating ceramic coating and magnesium substrate. However, it also provides the possibility of galvanic corrosion in aqueous enviroments *via* the defects such as pores and cracks in the coatings. Ion implantation involves a process in which ions are accelerated and impinge into the surface. Different from surface coatings, an ion-implanted layer does not have an abrupt interface and layer delamination is thereby not a serious issue. Samples with a complex shape can also be processed easily with a more advanced technique termed plasma immersion ion implantation (PIII). In this talk, recent work related to magnesium research conducted in our laboratory is described and reviewed.

3:30pm **D1-7 Corrosion Resistance, Anti-microbial Properties of Cu-Zr-Ag-Al Thin Film Metallic Glass with Various Cu/Zr Ratio in PBS Solution**, ***K.C. Hsu***, *J.G. Duh (jgd@mx.nthu.edu.tw)*, National Tsing Hua University, Taiwan

This study focuses on the effect of different Cu/Zr ratios in Cu-Zr-Ag-Al thin film metallic glass (TFMG) on corrosion, mechanical and anti-microbial properties. The thin films were prepared by DC magnetron sputtering with different ratios of Cu-Zr targets and a Ag-Al target. The chemical composition of the thin films was determined by field emission electron probe micro-analyzer (FE-EPMA). The morphology of cross section of thin films was examined by field emission scanning electron microscope (FE-SEM). The amorphous state was analyzed by X-ray diffractometer (XRD). The mechanical properties including hardness and elastic modulus were verified by nano-indention tester. Differential scanning calorimetry (DSC) is applied to evaluate if the thin films have glass transition temperature (Tg) and crystalline temperature (Tx), which is the thermal characteristic of metallic glass. The electrochemical corrosion behavior was investigated in 3 wt.% NaCl solution and PBS solution, which is a type of simulated body fluid (SBF), and is used in anti-microbial experiment to cultivate bacteria. Liquid culture methods and plate counting methods are used to determined the anti-microbial performance of thin films. With increasing Cu/Zr ratio, corrosion potential was improved up to 30%. It is also revealed that with small amount of Ag adding in Cu-Zr-Ag-Al system, anti-microbial efficiency against E. coli is significantly improved. Finally, the appropriate composition with better corrosion resistance, mechanical and anti-microbial properties can be controlled and achieved.

3:50pm **D1-8 Comparison of anti-HER2 Immobilization Using Three Different Techniques on Al-AlN-Al Thin Films**, ***M. Hernández***, *I. González*, *H. García*, *J. Oseguera (joseguer@itesm.mx)*, ITESM-CEM, Mexico

Al-AlN-Al thin films were deposited by RF reactive magnetron sputtering on silicon wafers (111). A comparison among three different methods for antibody immobilization relevant for surface modification for surface acoustic wave resonators was done. Antibodies against HER2 (anti-HER2), a fundamental protein marker in breast cancer diagnostics, were used as a model for identification of the protein. The evaluated techniques were (i) direct immobilization (random immobilization); (ii) alginate (ionic immobilization) and (iii) protein G (oriented immobilization). Standardized detection capabilities were detected by ELISA (enzyme-linked immunosorbent assay), revealing substantial results for every technique. As a result, immobilization using protein G was more efficient; although immobilization using alginate presented lower detection sensibility, it is a more affordable technique.

4:10pm **D1-9 Formation and Characterization of Nanostructured Bioactive Apatite Coating on TiVAl Alloys**, *Y. Greish, A. Al Shamsi, A. Ayesh*, United Arab Emirates University (UAEU), UAE, ***K. Polychronopoulou*** *(kyriaki.polychrono@kustar.ac.ae)*, Khalifa University, UAE

Bioinert alloys such as 316L stainless steel, Ti and TiVAl alloys have been extensively studied. Attempts to develop a bioactive coating onto them have been made. In the current study, a sputtering technique has been used to develop a bone-like apatite layer on the surfaces of TiVAl alloys with different degrees of surface roughness. Coatings were evaluated for their structure, morphology ad durability in simulated body fluid media. Results showed the formation of a stable, homogeneous, and nanostructured apatite layer with interconnected porosity, which make them potential for further evaluations for total bone replacement applications.

Tribology & Mechanical Behavior of Coatings and Engineered Surfaces
Room: California - Session E2-1

Mechanical Properties and Adhesion

Moderator: J. Michler, EMPA (Swiss Federal Laboratories for Materials Science and Technology), R. Chromik, McGill University, D.F. Bahr, Purdue University

1:30pm **E2-1-1 Thin Film Adhesion can be Measured From The Morphology of Telephone Cord Buckles**, *J.-Y. Faou*, *S. Grachev*, CNRS/Saint-Gobain, France, *G. Parry*, Grenoble INP-CNRS-UJF, France, ***E. Barthel*** *(etienne.barthel@saint-gobain.com)*, CNRS/Saint-Gobain, France **INVITED**

Thin films with large compressive residual stresses and low adhesion are prone to buckling and delamination. This is both a significant technical issue, with relevance to thin film stability, and an interesting academic problem where non-linear plate deformation couples to adhesion. This coupling produces intriguing patterns such as telephone cords, which are still ill-understood.

We have carried out an experimental study of buckle formation on a model system: the film is a Molybdenum overlayer with thickness ranging between 50 and 300 nm, while compressive biaxial stress (up to nearly 3 Gpa) is adjusted through the deposition conditions [1]. In addition a thin silver film (usually 10 nm) is deposited directly on the substrate, below the Mo layer: in this way a low and reproducible adhesion develops. With this system, we have obtained a wide range of buckling conditions. Beyond telephone cords we have also met with less ubiquitous morphologies, such as branching buckles. We have systematically explored the phase diagram of morphologies as a function of stress and thickness. To help understand these results, we have also modeled the formation of the buckles. Geometrical non-linearities of film buckling are taken into account within a Finite Element model, and film adhesion is included as a cohesive zone. We show that consistent predictions of the buckle morphologies are obtained provided the mode mixity dependence of interfacial toughness is included [2]. We have also demonstrated numerically that the period of the telephone cord buckle is directly connected to the mode I critical energy release rate GIc, and give some experimental evidence that in practice thin film adhesion energies can be measured quite accurately based on this observation [3].

[1] “Stress tuning in sputter-deposited MoOx films”, FAOU J.-Y. et al. Thin Solid Films 527 (2013) 222-226

[2] “How does adhesion induce the formation of telephone cord buckles ?” FAOU J.-Y et al. Phys. Rev. Lett. 108 (2012) 116102

[3] "Thin film adhesion energy measurement from telephone cord buckle wavelength" FAOU J.-Y et al., in preparation.

2:10pm **E2-1-3 Interface Delamination Study of Diamond-Coated Carbide Tools Considering Coating Fractures**, *P. Lu*, The University of Alabama, US, *X. Xiao*, Research & Development Center,General Motors Corporation, US, ***K. Chou*** *(kchou@eng.ua.edu)*, The University of Alabama, US

Interface delaminations and coating cracks are the major failure modes of diamond-coated carbide tools in machining. To study any influence to each other between the two failure modes, micro-scratch testing on diamond-coated carbide tools was conducted with normal and tangential forces as well as acoustic emission signals recorded to detect coating delaminations and crack initiations. Scratched samples were observed by optical microscopy after testing to determine the associated critical load of delaminations and cracking initiations. In addition, a 3D finite element

model was developed to simulate the scratch process using cohesive elements and the extended finite element method (XFEM) for delamination and coating fracture behaviors. The cohesive elements are based on a bilinear traction-separation cohesive zone model. XFEM is applied to model crack behavior in diamond coatings with a damage criterion of maximum principal stress.

The results indicate that the critical load for coating crack initiations increases almost linearly with the increased coating thickness, while decreases linearly with the increase of coating elastic modulus. Moreover, the interface fracture energy has a negligible effect on the critical load for coating crack initiations, so does coating cracking on the critical load for coating delaminations, indicating the two failure modes are almost uncoupled. From the simulations and experiments, it is estimated that the coating fracture energy of the samples tested in this research is from 140 to 252 J/m^2, and the interface fracture energy is from 87 to 192 J/m^2.

2:30pm **E2-1-4 Grain Structure Effect on the Stochastic Distribution of Local Adhesion Strength at Metal/Dielectric Layer Interface in Copper Wiring Systems**, ***N. Shishido*** *(shishido.nobuyuki@nitech.ac.jp)*, *C. Chen, S. Kamiya, K. Koiwa,* Nagoya Institute of Technology, Japan, *M. Omiya,* Keio University, Japan, *H. Sato, M. Nishida,* Nagoya Institute of Technology, Japan, *T. Nakamura, T. Suzuki,* Fujitsu Laboratories Limited, Japan, *T. Nokuo, T. Suzuki,* JEOL, Japan

Copper wiring systems of semiconductor devices has a risk of mechanical fracture along with the trend of further integration and miniaturization, because of many weak interfaces stacked to compose multilayered copper/dielectric systems [1]. Local adhesion strength of those interfaces would vary significantly, depending on material structures [2]. In fact, a recent study indicated that the fracture energy of the interface between a Cu line and a barrier layer was affected by both barrier composition and Cu electroplating purity, and that impurities were segregated to grain boundaries and triple points [3]. In addition, it was also reported that local material structure of copper influences the local adhesion strength [4]. These investigations suggest that grain structure of Cu line play a significant role to fluctuate local strength. For the case of micro-scale systems, the distribution of the strength is essential to statistically estimate the fracture risk of the systems because there must be the expected scatter of local strength, leading to weak spots from which cracks may extend.

In this paper, stochastic distribution of local adhesion strength at copper/dielectric interface was estimated by the new technique developed by the authors, which utilizes the FIB-SEM system with a nano-indenter [4]. Specimens including the copper/dielectric interface which is well known as the weakest interface in semiconductor devices, were fabricated by FIB as blocks of dielectric layer. Fracture loads obtained by the experiment with the nano-indenter under SEM observation were compared with interface crack extension simulation to determine the strength [5]. Furthermore, not only the strength but also the crystallographic information of copper line was obtained by using an electron back-scattering diffraction (EBSD) analysis. The correlation between the strength distribution and the grain structure was discussed, especially the impact of the grain boundary density on the scatter range of the evaluated strength. The result of examination above suggests that grain boundary weakens local adhesion strength and is the key factor to arise large scatter range of the strength in micro-scale systems.

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2:50pm **E2-1-5 Evaluation of Scratch Adhesion Resistance on Boride Coatings Formed on the Surface of AISI 304 Steel**, *G. Rodríguez-Castro,* ***L.F. Jiménez-Tinoco***, Instituto Politecnico Nacional, Mexico, *J.V. Méndez-Méndez, I. Arzate-Vázquez,* Instituto Politecnico Nacional, CNMN, Mexico, *J. Martínez-Trinidad, I. Campos-Silva (icampos@ipn.mx)*, Instituto Politecnico Nacional, Mexico

Boriding is a thermochemical surface treatment, whereby boron is diffused into, and combines with, the substrate material forming a single or double phase boride coating at the surface. The boriding of ferrous materials results in the formation of the Fe_2B coating or double-coating (FeB/Fe_2B) with definite composition. Unfortunately, the presence of a FeB/Fe_2B coating is not desirable in industrial applications due to the difference between the thermal expansion values of both coatings. This results in cracking and spalling at the FeB/Fe_2B interface, and reduces the mechanical properties of the borided steel.

One of the basic properties of a functional coating-substrate compound is a sufficient adhesion of the coating on the substrate. The basic idea of coatings – having special properties on a substrate surface that cannot be reached by the base material itself – is necessarily dependent on the adhesion between substrate and coating. The test procedure that is best known and most used for adhesion measuring of hard coatings on steel substrates is the scratch test.

In this study, the scratch adhesion-resistance of FeB/Fe_2B coatings developed on the surface of AISI 304 steel was estimated. First, the boriding of the AISI 304 steel was conducted by the powder-pack method at a temperature of 1223 K in the range of exposure times of 2-10 h. In addition, Berkovich depth-sensing indentation tests were carried out along the depth of the boride coatings using a constant indentation load of 50 mN, in which the state of residual stresses on the boride coatings was evaluated as a function of the boriding exposure times. The AISI 304 borided steels were scratched on a commercial scratch tester (Revetest, CSM Instruments), with a 200 μm-Rockwell C diamond indenter using an incremental loads from 1 to 90 N for the set of experimental parameters of the boriding process. After the scratch tests, the samples were analyzed using a JEOL JSM-7800F scanning electron microscope to identify the damage mechanisms at work on the borided steels.

From the Berkovich indentation tests, the compressive residual stresses on the FeB coating were 0.5 to 1.5 GPa under the applied set of boriding conditions, while on the Fe_2B coating the residual stresses increased to values around 2.7 GPa.

From the resulting scratch tracks on the surface of the borided steels, critical loads (L_C) of 35 and 43 N were established for the exposure times of 2 and 6 h with the presence of chipping failure, in comparison with the value of 27 N obtained for the exposure time of 10 h with the presence of spalling failure on the surface of the AISI 304 borided steel.

3:10pm **E2-1-6 Incoherent Interface Effect in the Mechanical Properties of Cu/W and Zr/Nb Nanomultilayers**, ***E. Frutos Torres*** *(frutoemi@fel.cvut.cz)*, Czech Technical University in Prague, Czech Republic, *M. Callisti*, University of Southampton, UK, *M. Karlik*, Czech Technical University in Prague, Czech Republic, *T. Polcar*, University of Southampton, UK

Nanoscale metallic multilayer systems (NMM) attract attention due to their unique mechanical properties and, particularly, high tolerance to radiation damage. Specific interfaces can accommodate significant amount of implanted He atoms and prevent formation of helium bubbles, which compromise mechanical properties. On the order of a few to tens of nanometers, it is possible to find yield strength values above 1 GPa and Young's modulus values around 100-150 GPa.

Magnetron sputtered nanoscale metallic multilayer systems of Cu/W and Zr/Nb with three different layer thicknesses (5/5, 15/15 and 30/30) and a total thickness 1 micron were deposited on silicon wafer. Structure was studied by XRD and by TEM investigation of multilayer cross-section. In case of Cu/W multilayer, the grain size was significantly lower for tungsten grains compared to that of copper; in fact, grain size of copper was often higher that the thickness of corresponding layer. Kurdjumov-Sachs interface <110> Cu // <111> W was the major interface; however, there were differences between W-Cu and Cu-W interfaces. The latter was represented in some localized spots by an amorphous, 2-4 nm thick layer, whereas the former was fully crystalline. Zr/Nb multilayer showed Pitsch-Schrader orientation relationship: <110> Zr// <110> Nb; moreover, XRD spectra suggested superlattice. Nanoindentation tests showed high hardness and Young's modulus dependence on layer thicknesses for both studied systems. Maximum values were around (5; 108 GPa) and (6; 130 GPa) for Zr/Nb (15/15) and Cu/W (15/15), respectively. We correlated mechanical response of the multilayers with the microstructure. Moreover, fracture toughness of these multilayers was correlated with the plastic deformation volume below indenter tip, which was estimated using different approaches.

3:30pm **E2-1-7 Interface Toughness Optimization of Metal/Oxide Interfaces for Functional Coatings**, ***J. Zechner*** *(johannes.zechner@empa.ch), C. Frantz, R. Koodakal, L. Philippe, J. Michler*, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland

The coating/substrate interface is a common source of mechanical failure in many coated materials, e.g. tools, microelectronic devices or architectural glazing. Therefore, the characterization and optimization of the interface toughness is an important topic in thin films technology. In the current work two different experimental setups are explored to assess the interface fracture toughness of thin films: a macroscopic double cantilever beam and a microcantilever fracture toughness test. The double cantilever beam setup was combined with post-mortem glow discharge optical emission spectroscopy to identify the crack path within a multilayer stack and the micro-cantilever tests were performed inside an electron microscope to follow the crack path in-situ. Advantages and disadvantages of both techniques in terms of practicability, notching strategies etc. will be presented.

A study of the interface toughness of two industrially applied coating systems, one multilayer structure deposited by sputtering and one coating produced by electrodeposition, both containing functional thin films, will also be presented. Thin nanostructured oxide films are introduced into these coatings and the influence of these layers, their structure, thickness and roughness on the interface toughness are examined. The results of the fracture mechanics experiments indicate that the introduction of oxide interlayers has a positive effect on the adhesion of the investigated systems. Furthermore, it is shown how the variations in oxide film properties can be used to optimize the interface and coating properties.

3:50pm **E2-1-8 Using Nanoindentation to Assess Fracture Toughness and Interface Adhesion of Thin Coating**, ***J. Chen*** *(Jinju.chen@ncl.ac.uk)*, Newcastle University, UK **INVITED**

The fundamental properties which often dictate the performance of ceramic coatings are coating toughness and their adhesion to the substrate. There are many methods to measure these key mechanical properties. The choice of methods is dependent on many factors such as the mechanical properties of coating and substrate, the interface properties, the microstructure of the coating/substrate system, residual stress, coating thickness and the intended applications. With the advent of miniature systems and very thin functional coatings, there is a need for assessing coating toughness and adhesion at nanoscale or submicroscale. In this case, the conventional methods may be inappropriate. Nanoindentation techniques have the widest range of applicability in thin coatings but it is necessary to analyse the failure mechanisms before choosing an appropriate model to extract coating toughness and adhesion. This paper will illustrate the failure mechanisms and evaluate the associated mechanical models at various testing conditions.

4:30pm **E2-1-10 Yb:fiber Laser Surface Texturing of Stainless Steel Substrate, with MCrAlY Deposition and CO_2 Laser Treatment**, ***V. Teleginski***, *D. Chagas*, Instituto Tecnológico de Aeronáutica (ITA), Brazil, *J.C. Santos, J. Azevedo, G. Vasconcelos (getuliovas@gmail.com)*, Instituto de Estudos Avançados (IEAv), Brazil

As aircraft and thermoelectric turbine blades work in aggressive environments (high temperatures and pressures), they are exposed to oxidation reactions. Ceramic coatings are employed to avoid this effect in the metallic substrate and at the same time, increase the turbine work temperature (improving its performance). A bond coat (BC) base of particulate material of Ni-Cr powders is necessary to assure a good adhesion and gradual decrease in thermal expansion coefficient between the metallic substrate and the ceramic top coating. One of the most important parameters of such coatings is the adhesion strength. This research aims the study the influence of the laser texturing on the deposition process of particulate materials of MCrAlY (BC) in AISI 316 stainless steel substrate. The laser texturing was done on the stainless steel surface by an Yb-fiber laser beam (IPG YLR-2000S; 2000 Watts) and further the BC powder was pre-deposited by a sedimentation technique and irradiated by a CO_2 laser beam (Synrad – J48-5W, 50 Watts) . The focus of this work was to evaluate the resulting interface and adhesion strength. For this propose, characterizations were made using the techniques of optical microscopy, scanning electron microscopy, energy dispersive spectroscopy, X-ray diffraction, adhesion tests, roughness and hardness measurements. The laser treatment of the MCrAlY bond coat with a Gaussian CO_2 laser beam showed to be efficient to form a homogenous dense layer, without cracks or pronounced imperfections. The picks formed due to the laser surface texturing increased the metallic substrate surface energy. This energy is released during the CO2 laser treatment, when melting occurs. The melted powder of MCrAlY is possibly mixed with the melted substrate, leading to a metallurgical bonding between the substrate and the coating.

4:50pm **E2-1-11 Design and Evaluation of a Novel Testing Method for Surfaces Subjected to Combined Impact and Sliding or Rolling Loads**, ***P. Epaminonda***, *C. Rebholz (claus@ucy.ac.cy)*, University of Cyprus, Cyprus

There are a large number of factors involved in wear processes (e.g. mechanical, physical and chemical properties, surface topography, loading), making the precise theoretical and quantitative approach of wear a challenge even for "simple" tribo-systems. Many of these factors are hard to measure, may vary with time and space, and there is not yet a general theory available of how to link the basic properties with the tribological response. Several well established testing methods (e.g. pin-on-disk, fretting and impact tests) have been widely used to study treated surfaces and coatings on various substrates. However, many of these existing techniques have limitations in their ability to characterize materials, since they mainly focus on a single mode of loading and wear (e.g. only impact or sliding).

In this study, the design and evaluation of a new Dynamic Impact and Sliding Test (DIST)/Dynamic Impact and Rolling Test (DIRT) for the tribo-mechanical evaluation of surfaces under complex loading conditions is presented, where the surfaces are simultaneously subjected to impact and sliding or rolling loads. Such modes exist in many critical applications, from biomedical (e.g. hip/knee implants) to automotive applications (e.g. diesel injectors, engine valves, cam shafts), in cutting tools, general machine parts and systems, etc. Expected benefits include the time and cost effective evaluation of various surfaces and the better understanding of their peculiarities under such multi-mode loading conditions. Some of the unique design characteristics of the DIST/DIRT (e.g. combined impact and sliding or rolling testing; wear area in a single point; pre-setting of desired maximum wear depth possible; evaluation of materials' properties and behavior in a single run) and the evaluation method are presented and discussed.

5:10pm **E2-1-12 Prevention of Ice and Snow Accumulation in Cold Environments**, ***R. Fillion***, *A.R. Riahi (ariahi@uwindsor.ca), A. Edrisy*, University of Windsor, Canada

An important issue that can be addressed on wind turbines, solar panels, or satellite dishes during cold winters is related to the icing and snow accumulation. Ability to minimize the snow and ice accumulation on these surfaces will have significant environmental and economical benefits. In this study, the hydrophobic coatings of polymethylmethacrylate (by dip coating), and polyhedral oligomeric silsesquioxane were applied on glass and aluminum surfaces. Subsequently, the contact angle of water and the tilt angle necessary for sliding of water droplet were measured. A laboratory scale simulator was set up to conduct the adhesion tests at -15 ℃. A nozzle was placed 200 mm above the sample holder to spray vapor, cold mist, and water on the substrate at different speeds. Two thermocouples with 0.5 mm diameter were installed on the nozzle and the sample to measure the temperature of the spraying water or vapor and the sample. All the setup was placed in an atmospheric controlled chamber. The adhesion strengthof the depositions to the substrate was measured using a centrifuge system. Due to the sensitivity of the adhesion strength to temperature, the measurements were conducted in situ. Disturbing waves with suitable energy were also applied to transfer shocking pulses to the precipitates and break the adhesion bond between the hydrophobic coating and water depositions (e.g. glaze, rim, hoarfrost, snow). The energy and specifications of such waves was calculated to to be enough to break the adhesion bond between the water deposit and hydrophobic coating, and not be harmful to the structure of substrate.

New Horizons in Coatings and Thin Films
Room: Royal Palm 4-6 - Session F1

Nanomaterials, Nanofabrication, and Diagnostics
Moderator: Y. Yamada-Takamura, Japan Advanced Institute of Science and Technology, C. Ciobanu, Colorado School of Mines

1:30pm **F1-1 In Situ Diagnostics during Plasma Synthesis and Passivation of Group IV Nanocrystals**, ***S. Agarwal*** *(sagarwal@mines.edu)*, Colorado School of Mines, US **INVITED**

There has been an increased interest in group IV nanoparticles (NPs) for a variety of applications including photovoltaics, lithium ion batteries, and bio-imaging. The properties of these quantum-confined NPs are governed by their size as well as the surface passivating layer. Si NPs, 3-7 nm in size, were synthesized in a tubular, capacitively-coupled, radio-frequency SiH_4/Ar plasma at pressures ranging from 5-8 Torr. The H-terminated surface of the as-synthesized Si NPs is highly reactive, and requires surface passivation to prevent oxidation. We have developed a single-step synthesis and in-flight surface passivation technique wherein we use a dual-plasma setup, which consists of a second capacitively-coupled C_2H_2 plasma, downstream from the SiH_4/Ar synthesis plasma. The Si NPs can be coated with amorphous carbon (*a*-C) to obtain core-shell nanostructures, which a thin SiC interface between Si and *a*-C. These core-shell NPs are transported by flow into a surface analysis chamber, which is equipped with *in situ* attenuated total reflection Fourier transform infrared and photoluminescence spectroscopy setups to determine the surface composition and the optical band gap of the NPs, respectively. The NPs are also extensively characterized using *ex situ* x-ray diffraction, Raman spectroscopy, and transmission electron microscopy (TEM). The thickness of the coating determined from TEM is ~2-4 nm. We have also studied the effect of varying the C_2H_2 plasma parameters on the structure and composition of the *a*-C coating and the SiC interface This plasma synthesis and passivation method has been extended to other group IV NPs such as Ge, which are less likely to have a carbide interface.

2:10pm **F1-3 Synthesis Of Copper Oxide Nanomaterials For Solar Cell Applications**, ***A. Bhaumik***, *K. Ghosh (KartikGhosh@missouristate.edu)*, Missouri State University, US

Copper oxide nanoparticles are increasingly used in various applications such as solar energy transformation, magnetic phase transitions, gas sensors, catalysts, superconductors, and nanomedicines. The worldwide quest for a clean, renewable and economical source of energy has encouraged an extensive research in the field of solar cells. Solar cell technology, as a sustainable source of energy, has enjoyed a tremendous growth in recent years and production of solar cells increases at an annual average of ~ 40% [1].Copper oxide compounds as a p-type semi-conductors provide a unique possibility to tune the optical and electronic properties from insulating to metallic conduction, from band gap energies of 2.1ev to the infrared at 1.4ev, i.e. right into the middle of the maximum efficiency for solar-cell applications. With the decrease of the crystallite size of the copper oxide particles to the nanoparticles range, it exhibits unique physical and chemical properties from those of their bulk materials and thereby enhances its performance in the currently existing applications. Metal oxide nanoparticles have special physiochemical properties arising from the quantum size effect and a high specific surface area which may be different from their bulk counterparts [2]. It is well-known that inorganic nanocrystals are a benchmark model for nanotechnology, given that the tunability of optical properties and stabilization of specific phases are uniquely possible at the nanoscale .

We have easily prepared nanoparticles of copper oxides by a cost effective hydrothermal process using coppersulphate penthydrate as the precursor. The shape and size as well as the phase of the copper oxide can be engineered by altering the pH, reaction temperature, and time. The following SEM Images are taken for copper oxides formed at different reaction temperatures and time, using different bases (NaOH and NH_4OH).Different morphology of nanostructures are visualized like pollen grains, flakes and rods. The structural, phase identification, molecular vibrational modes, optical properties and morphology was determined by using XRD, Raman Spectroscopy, PL,UV-Visible spectroscopy and SEM.

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[1] A.Jager-Waldau, Solar Energy, **667**, 77 (2004)

[2] A Chowdhuri, V Gupta and K Sreenivas, "Response speed of SnO2-based H2S gas sensors with CuO Nanoparticles", Applied physics Lett. **84**, 1180 (2004)

2:30pm **F1-4 Synthesis by Reactive Magnetron Sputtering and Characterization of Nanostructured n-type and p-type Semiconductor Coatings as Dodecane Sensors**, ***M. Arab Pour Yazdi*** *(mohammad.arab-pour-yazdi@utbm.fr)*, *A. Taguett*, IRTES-LERMPS-UTBM, France, *J. Sanchez*, UMR CNRS 6249, Université de Franche Comté, France, *E. Monsifrot*, SARL DEPHIS, France, *P. Briois*, IRTES-LERMPS-UTBM, France, *F. Berger*, UMR CNRS 6249, Université de Franche Comté, France, *A. Billard*, IRTES-LERMPS-UTBM, France

In recent years, there has been considerable interest paid to semiconductor oxides to replace noble metals (Pt, Pd, ...) for gas sensor applications [1-2]. Zinc oxide (ZnO) as a n-type semiconductor and lanthanum cobalt based oxides ($LaCoO_3$) as a p-type semiconductor have attracted the interest of many scientists and have been the subject of intensive investigations as gas sensors mainly because of their high electrical conductivity, excellent catalytic activity and chemical stability.

In principle, electrical conductivity of a p-type semiconductor increases (or decreases) when oxidizing (or reducing) gases are adsorbed on their surface (the opposite for n-type semiconductors).The performance of the active layers in a number of modern devices and especially as gas sensors is strongly linked to their specific surface area that can be tuned by controlling their morphologies.

In this paper, we investigate the feasibility of ZnO and double substituted lanthanum cobalt ($La_{1-x-y}Sr_xAg_yCoO_{3-\alpha}$)coatings with different morphologies (dense, nano-tree and nano-wire) by reactive magnetron sputtering. After a short description of the experimental devices used for the deposition stage and the hydrocarbon sensing bench, a first part will be dedicated to the chemical, microstructural and structural characterization (SEM, XRD,…) of coatings in relation with their deposition parameters. Finally, the performance as dodecane-sensors of these coatings will be discussed depending on dodecane concentrations and sensitive surface's temperature and they will be compared together.

2:50pm **F1-5 Improved Dielectric and Magnetic Properties in Hexagonal-$YMn_{1-x}Fe_xO_3$ (x=0, 0.1) Thin Films Deposited by Pulsed Laser Deposition**, ***S. Chauhan***, *R. Chandra (ramesfic@gmail.com)*, *P. Dubey*, *S. Srivastava*, *A.S. Rajput*, Indian Institute of Technology Roorkee, India

We report the synthesis of hexagonal-$YMn_{1-x}Fe_xO_3$ (x=0, 0.1) thin films deposited on (111)Pt/(0001)sapphire and (111)Pt/(111)MgO substrates by pulsed laser deposition. X-ray diffraction confirms the c-axis orientation of the deposited thin films. The thickness of the films obtained from X-ray reflectivity measurement is found to be around 200 nm. The stoichiometric composition of the thin films is confirmed by energy dispersive X-ray spectroscopy. The dielectric and magnetic properties of the as-deposited films were studied. The dielectric response with temperature indicates an anomaly in the dielectric constant ε and loss tangent tan δ in the vicinity of 150 K, well above the bulk Neel temperature T_N~70 K. This anomaly in ε and tan δ is ascribed to the strain resulting from the lattice mismatch between substrate and $YMn_{1-x}Fe_xO_3$ (x=0, 0.1) thin films. The magnetization hysteresis loops indicate high coercivity in $YMn_{0.9}Fe_{0.1}O_3$ as compared to $YMnO_3$ thin film. Our results indicate that it is possible to enhance the multiferroic properties by Fe-substitution in $YMnO_3$ thin films.

3:10pm **F1-6 Formation of Metallic Glass Nanowires by Gas Atomization**, ***K. Nakayama*** *(kojisn@wpi-aimr.tohoku.ac.jp)*, Tohoku University, Japan **INVITED**

Metallic glasses have exciting potential for structural, chemical, and magnetic applications with the sizes ranging from micrometer to centimeter, but the fabrication and characterization down to nanoscale remains an important challenge. Progress has been hindered by the lack of bottom-up methodologies to produce amorphous nanostructures. We showed the self-organized amorphous nanowires that are formed on the fracture surfaces of bulk metallic glasses [1]. However, it is difficult to control their morphologies because they were formed during the instantaneous fracture process. Recently, the gas atomization, which is a conventional technique in powder metallurgy, is adapted for the formation of metallic glass nanofibers. This approach is able to produce a large quantity of the nanowires with the diameters of 50-2000 nm in range. Experiments performed with different conditions and alloy compositions confirm that the key mechanism of the nanowire formation is the spinnability that increases exponentially when the melt stream is supercooled from the liquid state [2].

[1] K. S. Nakayama *et al.*, Nano Lett. 8, 516 (2008).

[2] K. S. Nakayama *et al.*, Nano Lett. **12**, 2404 (2012).

3:50pm **F1-8 Namomechanical Properties of Platinum Thin Films Synthesized by Atomic Layer Deposition**, *M.A. Mamun*, *D. Gu*, *H. Baumgart*, *A.A. Elmustafa (aelmusta@odu.edu)*, ***D. Nminibapiel***, Old Dominion University, US

The nanomechanical properties of Pt thin films grown on Si (100) using atomic layer deposition (ALD) were investigated using nanoindentation. Recently, atomic layer deposition (ALD) has successfully demonstrated the capability to deposit ultrathin films of platinum (Pt). Using methylcyclopentadienyltrimethylplatinum ($MeCpPtMe_3$) as chemical platinum precursor and oxygen (O_2) as the oxidizing agent, the ALD synthesis of Pt can be achieved with high conformity and excellent film uniformity. The ALD process window for Pt films was experimentally established in the temperature range between 270-320 ºC, where the sheet conductance was constant over that temperature range, indicating stable ALD Pt film growth rate. ALD growth of Pt films exhibits very poor nucleation and adhesion characteristics on bare Si surfaces when the native oxide was removed by 2% HF etch. Pt adhesion improves for thermally oxidized Si wafers and for Si wafers covered with native oxide. Thin films and coatings of the noble metal platinum (Pt) find numerous applications in microelectronics and catalysis due to their excellent electrical properties and chemical stability. For example, platinum is used as electrode at high temperature in oxidative and reductive environments and Platinum is applicable as a gate metal with high-k dielectrics in metal-oxide-semiconductor field effect transistors (MOSFETs) because of its high work function. Furthermore Pt is also widely used in fuel cells due to its high catalytic activity and in chemical engineering Pt coatings are utilized as catalyst to enhance a multitude of chemical reactions. Aside from the jewelry industry major applications of Pt films are found in the automotive industry, where it is used in catalytic converters for emission control and in spark plug coatings. Three Pt films deposited with 800, 900, and 1000 ALD cycles were tested for the structural and mechanical properties. Additionally, the 900 ALD cycles sample was further annealed at 450 °C in forming gas for grain boundary passivation for 30 minutes. Cross-sectional transmission electron microscopy (TEM), X-ray diffraction (XRD), and atomic force microscopy (AFM) were employed to characterize the films' surface structure and morphology. Nanoindentation technique was used to evaluate the hardness and modulus of the Pt films of various film

thicknesses. The results indicate that the films depict comparable hardness and modulus results, however the 800 and 1000 ALD cycles films experienced significant amount of pile-up whereas the 900 ALD cycles forming gas annealed sample resulted in a small pile-up.

4:10pm **F1-9 Improving Electrochemical Performance of Silicon Based Anodes by Forming a Well-Aligned CuSi Helices via an Oblique Angle Co-deposition Method for LIB**, *B.D. Polat (b.denizpolat@gmail.com)*, Istanbul Technical University, Turkey, *L. Eryilmaz, R. Erck*, Argonne National Laboratory, US, ***O. Keles***, Istanbul Technical University, Turkey, *A. Erdemir, K. Amine*, Argonne National Laboratory, US

In this work, we deposited well-aligned CuSi helices on Cu substrates via an oblique angle ion-beam deposition technique. The electrochemical performance of these helices is compared with that of the non-aligned columnar CuSi thin films. Galvanostatic half-cell measurements showed that the well-aligned Cu-Si helices based thin film anodes exhibited much longer cycle lives with a moderate capacity due to the particularities in its structure and its morphology: The structural analysis revealed that depending on the differences in thin film nucleation and growth mechanisms, helical shaped thin films exhibited higher amounts of nano-sized and amorphous particles in them, which may have improved the cycleability of the anodes. Moreover, the morphological observation showed the importance of the helices formation in the thin film anode performance. Such a helical shaped thin film relaxes the stresses that may otherwise develop along the electrode and enhances the cyclic properties of these anodes because they increase the contact area of the thin film with Li, decrease the polarization and enhance the mechanical tolerance against the volumetric changes due to the homogenously distributed nanosized interspaces available among them.

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4:30pm **F1-10 Relaxation Phenomena and Modeling Processes in Lithium Heptagermanate Li2Ge7O15 Crystals**, ***Y. Obaidat*** *(obaidatukrain@yahoo.com)*, King Khalid University, Saudi Arabia

During the last decades ferroelectrics crystals attract researchers' attention in the field of fundamental solid state physics and applied material science [1,2]. The presence of phase transition stipulates high receptivity of ferroelectrics to the action of external fields, that makes them perspective for the use in micro-electromechanical systems, pyroelectric receivers, optical modulators, devices for recording and information storage. Research of processes of ionic conductivity testifies to possibility of application of ferroelectrics and related materials in the autonomous sources of electric current [3-5].

Dielectrics with high ionic conductivity are marked by the specific lines of crystalline structure. For migration of ions the presence in the structure of channels of conductivity is necessary, those vacant positions are connected for charge carriers. The structure of crystals of system Li_2O-GeO_2, which are perspective for creating new superionic materials, meets this condition. In particular, framework of grates of weakly polar ferroelectricity of lithium heptagermanate $Li_2Ge_7O_{15}$ is formed from germanium-oxygen polyhedral and contained through channels [7-10], in which cations Li^+ are located. It is possible to expect that mobility of ions lithium to a great extent determines electric properties of $Li_2Ge_7O_{15}$ crystals [11-14].

It is known, that introduction of admixtures substantially affects the processes of electric polarization and charge transfer in dielectric crystals. Therefore alloying crystals of lithium heptagermanate can be offered as a method of control after ionic payment in the processes of polarization and conductivity. We will also mark very small spontaneous electric polarization of crystals $Li_2Ge_7O_{15}$, which allows assuming the presence of anomalous physical properties in nearby critical point.

Scientific and practical interest to the study of processes of electric polarization and charge transfer in ferroelectrics determines actuality of research of electric properties nominally clean and doped crystals $Li_2Ge_7O_{15}$.

4:50pm **F1-11 The Synthesis and Optoelectronic Properties of Fluorinated Vanadium Oxide Nanowires**, ***K.Y. Pan***, National Tsing Hua University, Taiwan, *K.C. Chen, H.C. Shih (hcshih@mx.nthu.edu.tw)*, Chinese Culture University, Taiwan

Fluorinated vanadium oxide nanowires have been successfully fabricated by thermal evaporation and plasma-enhanced chemical vapor deposition (PECVD) in sequence. The conditions of CF_4 plasma treatment on the surface of V_2O_5 nanowires are 20 and 40 seconds. The physical analysis of V_2O_5 and F-doped V_2O_5 nanowires were verified by scanning electron microscope (SEM), transmission electron microscope (TEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). The fluorine concentrations of V_2O_5 nanowires with various CF_4 plasma treatment times of 0, 20, 40 seconds are calculated to be 0, 3.7 and 5.6 atom %, respectively. In terms of optoelectronic properties, the I-V curves under ultra-violet (UV) light were measured. The electrical resistance of V_2O_5 nanowires with various CF_4 plasma treatment times of 0, 20, 40 seconds are 8.1×10^7, 6.1×10^5 and 2.7×10^5 Ω, respectively. The photocurrent of V_2O_5 nanowires with various CF_4 plasma treatment times of 0, 20, 40 seconds are 6.0×10^{-3}, 3.5×10^{-2} and 2.1×10^{-2} A/cm^2, respectively. The outstanding characteristics of fluorinated V_2O_5 nanowires are highly promising in nanoelectronics , especially in UV photodetectors.

Applications, Manufacturing, and Equipment
Room: Tiki - Session G2

Additive Manufacturing
Moderator: D. Pappas, EP Technologies, LLC, X. Nie, University of Windsor

1:30pm **G2-1 Thin Films in a Thick 3D Printed World: How Thin Film will Enable 3D Printing.**, ***K. Church*** *(khc@sciperio.com)*, nScrypt Inc., US **INVITED**

3D printing is gaining momentum and has garnered significant attention. The real impact of 3D printing and the timing of this is yet to be determined, but for certain, the concept of digital printing 3D objects with advanced function is desirable and meaningful. The vision to one day print a smart phone without the restraints of the given shape and dimensions or to print an Unmanned Aerial Vehicle that is electrically, optically and mechanically functional is not challenging to imagine. The challenging part is in the details. How do billions of transistors become part of a structure without wire bonds or solder? How do specialized optics form to complex 3D structures and still focus and selectively choose wavelengths? How will heterogeneous materials integrate into monolithic random 3D shapes and maintain structural integrity over varying temperatures and humidity? The answer is similar to what the answer is for many current products, controlled thin film interfaces. Fast processors inset within a 3D structure could be thinned for flexible or shape forming, but connecting to the bond pads will be the critical interface and thin film has proven the solution for this. The thickness of dielectric stacks are driven by wavelength and this is a thin film regime. Disparate materials joined can create issues with adhesion and compatibility and thin film and nano texturing have proven effective in these areas. 3D printing is predicted to be the anchor for digital manufacturing which in turn has been dubbed the third industrial revolution. There will be no 3D printing revolution without solving the same issues that currently press state of the art manufacturing, control in the micron and submicron regime. Using standard solutions will be viable, however standard processes will need to adapt. The application of thin films for 3D and in existing 3D printing equipment will be challenging, but necessary.

2:10pm **G2-3 Barium Hexaferrite, Yttrium Iron Garnet and ZnS/Diamond Composite Thick Films Formed by the Aerosol Deposition Method**, ***C. Eddy, Jr.*** *(charles.eddy@nrl.navy.mil)*, U.S. Naval Research Laboratory, US, *S. Johnson*, American Association for Engineering Education, US, *S.-F. Cheng, M.-J. Pan, F. Kub*, U.S. Naval Research Laboratory, US

The deposition of thick films of nano-crystalline barium hexaferrite ($BaFe_{12}O_{19}$) (BaM) and Yttrium Iron Garnet

($Y_3Fe_5O_{12}$) (YIG) for application in high power passive rf electronic components and ZnS/Diamond composites for IR transparent protective coatings by the aerosol deposition method (ADM) is presented.

The advantages of the ADM include the ability to form dense ceramic films up to hundreds of microns thick at room temperature and at a high deposition rate on a variety of substrates. Deposition is achieved by creating

a pressure gradient that accelerates particles in an aerosol to a velocity up to 400 m/s. Upon impact with the target the particles fracture and embed [1]. Continual deposition forms the thick compacted film.

BaM and YIG films are characterized for their microstructural, morphological and magnetic properties by scanning electron microscopy, profilometry, and vibrating sample magnetometry, respectively. For BaM, magnetic saturation of the film is 80 % of the bulk value of 68 emu/g, but a significant increase in coercive field suggests significant particle fracturing. All samples have a squareness value near ½ indicating randomized orientation of the magnetization. YIG and BaM film stripes of 10 mm in length deposited for 5 minutes resulted in an approximately 200 micron thick film or a deposition rate of 40 microns/min.

In contrast to this high deposition rate, deposition from a mixture of ZnS/diamond onto sapphire results in linear trend from sputter erosion of the substrate at 100% diamond to formation of a film with increasing fractions of ZnS. The crossover from abrasion to film formation occurs at about 50 – 60 % ZnS and a mixture of 80% ZnS and diamond forms a well-adhered film of about 0.6 microns thickness at 0.12 microns/min. Fourier Transform Infrared Spectroscopy transmission measurements of these films indicate good transparency in the far infrared making the system a promising candidate for infrared window protective coatings.

[1] J. Akedo, *J. Thermal Spray Technol.***17** (2), 181 (2008).

2:30pm **G2-4 Laser Consolidation – Converting 3D Design to Net-shape Functional Metallic Components**, ***L. Xue*** *(lijue.xue@nrc.gc.ca)*, National Research Council, Canada **INVITED**

Laser consolidation (LC) is a novel computer-aided manufacturing process being developed by the National Research Council Canada (NRC) at its London facility. This additive manufacturing process produces net-shape functional metallic parts layer-by-layer directly from a CAD model by using a laser beam to melt the injected powder and re-solidifying it onto the substrate or previous layer. As an alternative to the conventional machining process, this novel manufacturing process builds net-shape functional parts or features on an existing part by adding instead of removing material. In this presentation, laser consolidation of various high performance materials (such as Ni-alloys, Ti-alloys, Al-alloys, tool steels, etc.) will be discussed, including their microstructure, mechanical and other properties. The examples will be given on laser consolidation to build complex functional components for potential aerospace, automotive and other applications.

3:10pm **G2-6 Protective Coatings of Ultra High Toughness – Ceramic-based Composite Inspired from Natural Armors**, ***T.H. Hsu***, *P.Y. Chen (poyuchen1025@gmail.com)*, National Tsing Hua University, Taiwan

Nature armors, such as abalone nacre and crustacean exoskeleton are hierarchically-structured multilayer composites of inorganic minerals and organic proteins which possess excellent mechanical properties and superior toughness. The organic and inorganic interfaces resist or deflect crack propagation and prevent the composites from catastrophic failure. Ceramic-based protective coatings with high hardness, wear and corrosion resistance have been extensively investigated and applied widely in the area of constructional instruments. However, their brittle mechanical behavior and poor toughness limit the commercial applications. Mimicking the exocuticle and endocuticle in crab exoskeletons, a functional graded composite of harder outer layers and tougher inner layers was designed and synthesized, resulting in a hybrid coating with both good abrasion resistance and high impact toughness. By combining a hybrid coating system of reactive RF sputtering and pulsed laser deposition, multilayer coatings with various thickness, organic/inorganic ratio and surface roughness were synthesized. The fatigue behavior with different thickness ratio and hardness of outer and inner layer has been discussed. Microstructural features were characterized by scanning electron microscope (SEM) and atomic force microscope (AFM). Nano-indentation and nano-scratch tests were conducted to evaluate the mechanical performance of multilayer films. The fracture toughness was determined by an energy-based method to eliminate the influence of substrates. The impact resistance of protective coatings can be measured by thin film impact test, which applies dynamic loads on specimens. The graded microstructure can significantly enhance the damage tolerance of periodic impact. Toughening mechanisms at the organic/inorganic interfaces were elucidated, which may lead to optimal designs for multifunctional protective coatings. This research is funded by the National Science Council, Taiwan (NSC-100-2218-E-007-016-MY3).

3:30pm **G2-7 3D Printing (aka Additive Manufacturing): From Prototypes to Uniquely Designed Production Parts**, ***R. Wicker*** *(rwicker@utep.edu)*, University of Texas at El Paso, US **INVITED**

Since the commercial introduction of Additive Manufacturing (AM) technologies more than two decades ago, considerable advancements in processing speed, accuracy, resolution and capacity have been achieved and the available AM materials have expanded considerably, enabling customized end-use products to be directly manufactured for a range of applications. Many AM technologies have been released that use different processes for fabricating the individual layers from a variety of liquid, solid, and powder-based materials ranging from photoreactive polymers to metals. In 2000, the University of Texas at El Paso identified AM as an emerging technology and invested strategically in establishing the W.M. Keck Center for 3D Innovation (Keck Center). The Keck Center has grown to occupy over 13,000 sq. feet (1200 sq. meters) with nearly 50 commercial and experimental AM machines. One particular focus of Keck Center research is on developing the methods and systems required to have spatial control over material placement and structure creation, leading to, for example, the realization of complex 3D devices that integrate electronics and thus intelligence within mechanical structures as well as 3D spatially complex bioactive, implantable, tissue engineered constructs. There are myriad issues associated with combining multiple materials to create functional products – from the deposition and processing of different materials to the combined performance of the materials in the resulting product. These efforts have resulted in demonstrations of multi-material, multi-functional products that were fabricated using multiple technologies operating in integrated manufacturing environments at different levels of automation, and although these product demonstrations exemplify the potential for AM to transform the human condition, significant progress is still required to make this future a reality.

Hard Coatings and Vapor Deposition Technology
Room: Royal Palm 1-3 - Session B1-3

PVD Coatings and Technologies

Moderator: A.N. Ranade, The Boeing Company, S. Weißmantel, University of Applied Sciences Mittweida, J.W. Lee, Ming Chi University of Technology, Taiwan

8:00am **B1-3-1 Properties of Composite ZrO_2-Al_2O_3 Coatings Deposited by Pulsed-DC Magnetron Sputtering and Filtered Vacuum Arc Techniques**, ***I. Zukerman*** *(Idozukerman@gmail.com)*, NRC-Negev, Israel, *A. Raveh*, Advanced Coatings Center, Rotem Industries Ltd, Israel, *R.L. Boxman*, Tel Aviv University, Israel, *J.E. Klemberg-Sapieha, L. Martinu*, École Polytechnique de Montréal, Canada

The composition, microstructure, residual stress and hardness of ZrO_2-Al_2O_3 coatings deposited by pulsed-DC magnetron sputtering (PDCMS) were compared to those prepared by the filtered vacuum arc (FVAD) technique. The coatings were obtained on Si and WC substrates at various substrate temperatures (T_s = 300-850 K), substrate bias (V_b, between floating and -200 V), and Zr:Al power source ratio.

The PDCMS deposition rate was ~10 nm/min, while that of FVAD was higher, 100-200 nm/min as a function of V_b and T_s. By controlling the Zr:Al power source ratio, the PDCMS coatings were deposited over a broad range of compositions, i.e. Zr:Al ratio from 9:1 up to 1:9. However, due to arc stability limitations, the Zr:Al ratio of the FVAD coatings varied between 1:1 and 5:1. It was found that PCDMS coatings deposited with a Zr:Al ratio of 1:9 to 3:7 exhibits a composite structure with a stabilized ZrO_2 crystalline phase and an amorphous Al_2O_3 phase, while those deposited at a higher Zr:Al ratio had an amorphous (X-ray amorphous) structure. Similar results were observed for FVAD depositions, namely crystalline structure for Zr:Al = 5:1 and amorphous for 1:1. XRD analysis indicated that PDCMS coatings had stabilized cubic-ZrO_2 structures as T_s increased, or tetragonal-ZrO_2 as V_b increased. The structure of the FVAD coatings could not be determined because the diffraction patterns were very broad.

The substrate temperature and bias were the main parameters controlling the coating hardness. Coatings deposited on un-heated substrate and at floating potential had low hardness, <10 GPa, using both PDCMS and FVAD. However, increasing T_s to 650 K increased the hardness to 16±1 GPa (Zr:Al = 5:1) for both PDCMS and FVAD coatings. In the FVAD layers, a further increase of T_s to 770 K raised the hardness to 22±1 GPa and reached a maximum value of 26±1 GPa for V_b = -100 V. The same maximum value was observed on PDCMS coatings deposited under V_b = -150 V on an un-heated substrate. The PDCMS coatings prepared at floating potential and T_s = 650 K had low residual stress (between -0.15 Gpa (compressive) and +0.2 Gpa (tensile)) depending on the Zr:Al ratio,. At higher V_b, the compressive stress increased up to -1.3 Gpa. The homogeneity of the FVAD coatings was very low and therefore their stress could not be determined. The differences in the coating properties deposited by PDCMS and by FVAD techniques are due to their differing deposition rates and ionization degrees.

8:20am **B1-3-2 Cutting Performance Comparison of Thick PVD Nitride Coating and CVD Oxide Coating in High Speed Turning of Cast Iron**, ***M. Abe*** *(abe.maiko@kobelco.com), K. Yamamoto, S. Tanifuji*, Kobe Steel Ltd., Japan

Thick Al2O3 coating deposited by thermal CVD is still dominantly used for high speed turning of cast iron, mainly because of superior stability at high temperature. There are some concerns about thermal CVD process, however, such as safety issue coming from somewhat hazardous gaseous sources. PVD process has advantages over CVD process in terms of easy operation and variety of coating material. Generally, hard coatings deposited by PVD process with highly ionized plasma are characterized by high degree of compressive stress and due to this stress, maximum coating thickness is usually limited less than 10 microns or even 5 microns on the sharp cutting edge. This has been made PVD coating not suitable for applications where certain coating thickness is mandatory.

Kobe Steel has developed a new type of arc cathode which is able to control the residual stress in a wide range and this made it possible to produce thick coating without chipping or delamination from the substrate.

Evaluation of cutting performance was done by turning test using WC-Co insert (ISO SNMA) PVD coated thick TiAlN and commercially available CVD coated TiCN/Al2O3 coatings were used as references. . In addition, two types of thick PVD TiAlN coatings were used: monolayer and bias multilayer. Regarding the cutting conditions, cutting speed is 300 m/min., feed is 0.25mm/rev., depth of cut is 2mm, and work-piece is ductile cast iron (AISI 80-55-06).

From the comparison of flank wear width, PVD coatings showed improved tool life by optimizing coating conditions. Especially, bias multilayered TiAlN achieved longer tool life than CVD coating: CVD coating almost reached the tool life (as defined 300 microns of flank wear) after 2700 m of cutting length, whereas flank wear width was much smaller for PVD coating. Crater wear depth of CVD coating reached 16mm after cutting of 2700 m, but PVD coating showed only 4 microns of crater wear, which proves good wear resistance.

Additional cutting tests result using different coating systems and discussion on the effect of coating properties such as hardness, oxidation resistance and residual stress of coating, and substrate material on wear mechanism will be presented.

8:40am **B1-3-3 The Structure and Composition Analyses of Tungsten Oxides Thin Film by PVD Process**, *C. Li (cli10@yahoo.com)*, National Central University, Taiwan, *J.H. Hsieh*, Ming Chi Institute of Technology, Taiwan, ***B.Q. Huang***, National Central University, Taiwan

Tungsten oxide (WO_3) is electrochromic under chemical insertion of metallic cations. This unique electro-optical property is due to the change of tungsten valance states from VI to V or IV to V. Such switch of multiple states enables tungsten oxide to be transparent or opaque according to the compositions and structures of W(IV), W(V) and W(VI). Since (WO_3) is mostly monoclinic in the temperature from 17 to 330 °C, it is very interesting to understand the underlying mechanism of valance-state change during the chemical insertions; as such electro-chemical changes are very useful for many practical applications, for instance, the vision shielding or detective sensors. In this study, the tungsten oxide thin film was prepared by DC reactive sputtering using physical vapor deposition. The chamber is monitored by the optical emission spectrometer and mass spectrometer for the plasma field. After deposition, the films' thickness and average deposition rates are measured by surface profiler. The structure, elemental and chemical compositions of films are assessed by the XRD, EDS, XPS, Raman spectrometer, and ellipsometry. For the electrochromic measure, a UV-Vis-NIR spectroscopy is employed to quantify the optical transmission under different deposition conditions as well as after the chemical insertion process. A correlation between the control parameters of sputtering process and structures, properties of films shall be carefully examined to understand the forming mechanisms of films. This correlation provides a possible way of optimizing the sputtering conditions to fabricate appropriate tungsten oxide thin films for different applications.

9:00am **B1-3-4 Plasma-activated High-rate Deposition of Titanium Dioxide Coatings by Electron Beam, Spotless Arc and Dual Crucible Technology**, ***C. Metzner***, *B. Scheffel (bert.scheffel@fep.fraunhofer.de), G. Mattausch, Th. Modes*, Fraunhofer FEP, Germany

Spotless arc Activated Deposition (SAD) combines electron beam high-rate evaporation using an axial electron beam gun and a spotless arc discharge burning in the metal vapor of a hot evaporating cathode. The SAD process is suitable for the evaporation of high-melting metals such as titanium, zirconium or tantalum, provides a high deposition rate of up to 2000 nm/s and enables a reactive mode of operation for the deposition of oxides, nitrides or other compounds with a deposition rate between 20 and 100 nm/s.

The limitation of the long-term stability of the SAD process that was caused by coatings deposited at the anode equipment could be overcome by introducing a dual crucible technology. Whereas evaporating metal in the first crucible acts as cathode, evaporating material in the second crucible forms the anode of the arc discharge. Both plasma electrodes evaporate and are in contact with vapor and reactive gas so that the plasma process is no longer disturbed by the coating of electrodes.

The challenging process conditions typical for plasma-activated high-rate electron beam evaporation have triggered substantial equipment innovations concerning the electron beam guns, the high-voltage power supplies and the control systems, too. As an enabling tool for advanced coating processes, a new class of high-power (up to 300 kW) electron beam modules was developed. They excel in improved dynamic pressure decoupling stages between electron beam gun and deposition chamber (coating pressure up 30 Pa), enhanced acceleration voltage (up to 80 kV), and availability of high-dynamic beam scanning systems (up to ± 45° x 10 kHz) as well as mid-frequency power supplies (with arc recovery time in the 1 to 10 ms range).

The main process parameters and discharge characteristics were studied for the evaporation of pure titanium and reactive processing in oxygen atmosphere in order to deposit titanium dioxide coatings on steel strip. Dense titanium dioxide layers were deposited with a high refractive index

between 2.3 and 2.5, measured by ellipsometry . This relatively high refractive index allows to create coatings with strong color effects based on thin film interference. At elevated temperatures crystalline titanium dioxide thin films, especially layers with predominantly anatase phase, were deposited. These layers exhibit super-hydrophilic properties and photo-catalytic activities after exposition to ultraviolet light.

9:20am **B1-3-5 An Investigation Into the Improvement of the Corrosion Behaviour of PVD Coatings**, ***JL. Daure***, *KT. Voisey (katy.voisey@nottingham.ac.uk), PH. Shipway*, University of Nottingham, UK, *DA. Stewart*, Rolls-Royce plc, UK

Physical vapour deposition (PVD) coatings can be readily applied to complex systems, they are very thin coatings, often around 5 microns in thickness. The aim of this work is to investigate the effect of coating architecture on corrosion behaviour of scratch resistant PVD coatings.

The coatings include single and multilayered systems. It was found that the thinner the multilayers the better the scratch resistance of the coating, however the coatings were seen to contain growth defects which expose the substrate to corrosive media and reduce the corrosion resistance of the coating. These defects decrease the corrosion resistance of the coatings. Growth defects typically occur during coating deposition, all coatings contain a degree of microporosity making them susceptible to corrosion however PVD coatings contain microporosity as well as growth defects, these growth defects can cause local loss of adhesion, higher friction, voids, act like stress raisers and pitting corrosion.

In order to improve the tribological properties of PVD coatings it is important to minimise the density of these defects, many attempts have been made to reduce these defects but they have yet to be fully eliminated so corrosion resistance is still limited by defects. These growth defects are non-uniformly distributed throughout the coating, their form, size and density depend on the deposition time, deposition techniques, deposition parameters, substrate position in the vacuum chamber, substrate orientation and rotation mode, and the surface conditions of the substrate

These growth defects are caused by various factors including substrate surface irregularities such as pits and asperities, foreign particles such as dust, debris or residues from grinding, blasting and polishing, or by the deposition process: depending on the deposition conditions microdroplets can form and fall onto the surface.

In order to identify which defects are most detrimental to coating performance, and which aspects of coating production are responsible for them, a set of samples with 4 different surface finishes were chosen: ground to 1-2 Ra, ground to 1200 grit, electropolished and microblasted.

In addition to the different surface finishes on the substrates, the effect of details of the deposition conditions was investigated. Coatings were deposited on the 1200 grit substrates under 4 different conditions: standard clean conditions, clean room conditions (including a thorough clean of the chamber prior to deposition). The effect of intermediate etching is also investigated.

9:40am **B1-3-6 Effect of Cathode Composition on Cathodic Arc Synthesis of Multi-element Material from Compound Cathodes**, ***I. Zhirkov*** *(igozh@ifm.liu.se), J. Rosen*, Thin Film Physics Division, IFM, Linköping University, Sweden

Cathodic arc and compound cathodes is viewed as a convenient approach to generate plasmas with several ionic species for synthesis of multi-element films. However, there is generally a discrepancy between the cathode composition and the resulting plasma- and/or film composition. We present analysis of plasma chemistry and charge-state-resolved ion energy of dc arc plasma generated from $Ti_{1-x}Si_x$ ($0 \le x \le 0.25$) $Ti_{1-y}Al_y$ ($0 \le y \le 1$) and $Ti_{1-z}C_z$ ($0 \le z \le 0.25$) cathodes, commonly used for synthesis of, e.g., hard and wear resistant coatings. In vacuum, the metal ion energies range up to > 100 eV, though this range, as well as the average ion energy, can be tuned by choice of cathode composition. Through related thin film synthesis and cathode surface analysis, the correlation between cathode-, plasma-, and film composition has been explored. There is a loss of primarily lighter elements (C, Si) in the film as compared to cathode composition. Our analysis indicates that this is likely due to a combination of processes at the cathode surface during plasma generation, and ion-surface interaction at the film during synthesis. Furthermore, for selected Ti-Si and Ti-Al cathodes, the plasma composition showed a lower Si/Al content compared to the cathode composition, yet concurrently deposited films were in accordance with the cathode stoichiometry. Hence, a significant contribution to film growth from neutrals is inferred. The macroparticle generation is also a function of cathode composition as well as process gas and pressure. Cathode surface analysis show correlated differences in phase formation and type of arc spots, and we therefore suggest macroparticle formation to depend on surface chemistry and cohesive energy of the phases present.

10:00am **B1-3-7 Investigations on Erosion Behavior of TiAlSiN Nanocomposite Coatings Deposited by High Speed-physical Vapor Deposition**, *K. Bobzin, N. Bagcivan, T. Brögelmann,* ***B. Yildirim*** *(yildirim@iot.rwth-aachen.de)*, RWTH Aachen University, Germany

Compressor blades consisting of martensitic steel are exposed to foreign particles like sand, dust, ice particles and volcanic ash causing erosion. Depending on the angle of impact of the erosive particles the blade geometry changes due to damages at the edges. Such effects lead to the reduction of efficiency and increased fuel consumption. For protection of compressor blades, PVD coating systems are used. Nanocomposite (nc) coatings such as TiAlSiN are a promising candidate for the use as erosion resistant coating. TiAlSiN coatings consisting of hard (Ti, Al)N particles in an amorphous Si_3N_4 matrix are characterized by a high hardness up to 40 GPa or higher and plastic deformation resistance with increasing ratio of hardness H to elastic modulus E_{IT}. Typically, nc-TiAlSiN is deposited by means of different physical vapor deposition (PVD)-technologies. The low deposition rates limit the coating thickness to a few microns causing an early delamination of the coating under erosive particle bombardment. High Speed (HS)-PVD technology is a promising alternative for the deposition of nc-TiAlSiN coatings. The non line-of-sight characteristic allows the deposition of nc-TiAlSiN on compressor blades with a homogenous coating distribution. High gas flow rates ensure the deposition of coatings with a thickness up to 50 µm in less time compared to conventional PVD techniques.

In this study, TiAlSiN nc coatings were deposited by HS-PVD technology on martensitic steel X3CrNiMo13-4 (AISI F6NM) used in compressors. In this work, the investigations are focused on adhesion towards substrate and erosion resistance behavior. The morphology and the coating thickness were analyzed using scanning electron microscopy (SEM). The nc-TiAlSiN coating revealed a coating thickness of about 50 µm. Chemical composition of Ti, Al and Si was measured using X-ray spectroscopy (EDS). X-ray diffraction (XRD) measurement was used for phase analysis and proved the presence of crystalline AlN and TiN peaks. Investigations on the formation of the nanostructure were carried out by means of high resolution transmission electron microscopy (HR-TEM). The nanocrystalline (Ti,Al)N grains are embedded in an amorphous Si_3N_4 matrix. Hardness and elastic modulus were analyzed using nanoindentation method. Evaluation of the adhesion between substrate and nc-TiAlSiN coatings was made by scratchtest and impact testing. At the end nc-TiAlSiN coatings were tested regarding erosion resistance in a test rig for solid particle erosion. The angle of impact was varied between 0°-90°. The results revealed the ability of nc-TiAlSiN for an application as erosion resistant coating on compressor blades.

10:20am **B1-3-8 High-Rate Deposition of AlTiN and Related Coatings with Dense Morphology by Central Cylindrical DC Magnetron Sputtering**, ***M. Jilek*** *(jilek.jr@shm-cz.cz)*, SHM s.r.o., Czech Republic, *F. Mendez Martin*, Montanuniversität Leoben, Austria, *P.H. Mayrhofer*, Vienna University of Technology, Austria, *S. Veprek*, Technical University Munich, Germany

An industrial coating equipment, commercially used for the industrial-scale deposition of wear protection coatings on tools by means of vacuum arc evaporation with the rotating cylindrical cathodes technology, has been modified for reactive magnetron sputtering. We use a central cylindrical magnetron to achieve high-rate deposition of dense hard $Al_xTi_{1-x}N$, $Al_xCr_{1-x}N$, TiN and related coatings. With a D.C. power of 25 kWatt and one-fold rotation of the substrate tools, the resulting deposition rate is 10 µm/hr over a total area of 0.3 m^2. Thus the resultant high throwing power amounts to 3 $\mu m \cdot m^2$/hr. Scanning electron microscopy studies were not able to resolve any columnar structure, they actually suggest a featureless, somewhat fibrous morphology of the coatings. Investigations with transmission electron microscopy at higher resolution revealed a fine columnar (diameter of about 25 nm) and extremely dense microstructure, with columns oriented in the direction of the film growth. Atom probe tomography studies perpendicular to the growth direction of the coatings proofed this extremely dense microstructure by exhibiting no change in chemical composition across the column boundaries over an investigated length of about 200 nm. The load-invariant hardness of the $Al_{0.57}Ti_{0.43}N$ coatings reached a value of 33.4 ± 1.5 GPa and the elastic modulus amounted to 466 ± 15 GPa. Along with a high deposition rate, significantly higher than that achieved by vacuum arc and by conventional DC as well as by high power pulsed magnetron sputtering, the surface of the deposited coatings is very smooth with average roughness R_a= 0.06 µm and maximum roughness R_z= 0.72 µm. We present the design of the system and the method of the control of the operation of the magnetron in the transition regime between metallic- and partially- poisoned target mode that assures high deposition rates of stoichiometric nitrides. Several examples of cutting tests of different operations (milling, drilling) will be presented to show the excellent cutting performance of tools coated with this techniques as compared with

conventional one. This technique is available in the commercial industrial coating unit π 411 of the company Platit.

10:40am **B1-3-9 Oxidation Resistance and their Applications of Multicomponent TiAlSiN and CrAlSiN Hard Coatings Synthesized by Cathodic Arc Evaporation**, ***Y. Chang*** *(yinyu@mail2000.com.tw)*, National Formosa University, Taiwan **INVITED**

Surface engineering, in particular, the design of multicomponent and multifunctional nanostructured coatings with crystallite size less than 100 nm, is an important and developing trend in the field of nanomaterials and nanotechnology. In this study, the deposition approach, mechanical property, high temperature oxidation behavior and cutting performance of multicomponent TiAlSiN and CrAlSiN coatings were studied. These high performance coatings can be deposited by using cathodic-arc deposition with arc cathodes or unbalanced magnetron sputtering. Various cathode targets, such as titanium, chromium, TiAl, TiAlSi, CrAlSi, and AlSi, are used for the deposition of TiAlSiN and CrAlSiN coatings. The nanohardness, which measured by nanoindentation, of these coatings possessed hardness higher than 40 GPa, depending on the gradient and multilayer coating structures. In this study, the microstructure of the as-deposited and high temperature annealed coatings was characterized by field emission scanning electron microscope (FESEM), high resolution transmission electron microscope (HRTEM) and X-ray diffraction (XRD) using Bragg-Brentano and glancing angle parallel beam geometries. The mechanical properties including hardness and elastic modulus of the deposited TiAlSiN and CrAlSiN coatings were analyzed by a nanoindenter with Berkovich indenter tip.

The high temperature oxidation test showed the oxidation rate during annealing depends on film composition and microstructure. The oxide layer formed on the TiAlSiN coatings consists of large TiO_2 and TiAlSiN grains at the oxide-coating interface, followed by a layer of protective Al_2O_3 in the near-surface region. Interestingly, the oxidation rate of the CrAlSiN coated sample was much lower than that of the TiAlSiN. The dense Al_2O_3 near the surface without large grains at the oxide-coating interface retarded the diffusion of oxygen into the CrAlSiN. The gradient, multilayered, and nanocomposite TiAlSiN and CrAlSiN show significantly improvement of the lifespan of cutting tools and mechanical parts. In addition, the wettability of the the CrAlSiN, TiAlSiN and AlTiN coated tungsten carbides by molten glass at temperatures between 300°C and 700°C in controlled air under 1.6 Pa was measured by using an improved sessile drop method. The CrAlSiN had a lower oxidation rate and a higher contact angle than the TiAlSiN and AlTiN coatings. Therefore, the kinetic oxidation behavior and wettability varied with the alloy content and phase segregation via high temperature oxidation.

11:20am **B1-3-11 Oriented Cubic Al-Ti-N Films with Large Compressive Stress Deposited by Dual Source Type Reactive Plasma Deposition System**, ***K. Tanaka*** *(tanak@mmc.co.jp)*, *M. Takahashi*, Mitsubishi Materials Corporation, Japan

Reactive Plasma Deposition (RPD) is a new method which enables to deposit various kinds of thin films without metal particles. Furthermore, RPD system, compared to conventional sputtering or cathodic arc ion plating (CAIP) technique, is expected to achieve highly ionized plasma. With the highly ionized plasma, the mechanical properties and wear resistance of the films deposited by RPD method are expected to be different from other processes, but few researches related to deposition of quasi-binary nitride films by RPD method are carried out.

In this paper, in order to investigate mechanical properties of cubic Al-Ti-N films deposited by RPD method, Al-Ti-N films were deposited onto cemented carbide substrates by using a dual source type RPD coating system. Ti and Al were evaporated respectively by plasma irradiation from pressure gradient plasma guns in nitrogen atmosphere. Deposition temperature was 420^{o}C and negative bias voltage of 100V was applied to the substrates. Evaporation rate from each source was measured by quartz crystal microbalance sensor and fixed to certain value by adjusting the gun power. By changing these rates, atomic ratio of Al / (Al+Ti), x, in the films was changed from 0.38 to 0.88. The films were characterized by X-ray diffraction (XRD), electron probe microanalyzer (EPMA), transmittance electron microscopy (TEM) and nano-indentation. The degree of ionization of the metal plasma was estimated by quartz crystal microbalance and biased grid mesh.

The film with x = 0.66 showed dual phase, mixture of NaCl type (B1) and Wurtzite (B4) structures, while the film with x = 0.44 and x = 0.88 showed B1 and B4 single phase. The films with x = 0.44 exhibited cubic phase and as high hardness as CAIP. The compressive stress of the B1 film was greater than 9 Gpa while the films by CAIP showed 5 Gpa. The films were oriented to (2 0 0) or (2 2 0) for B1 and (1 1 -2 0) for B4.

The relationship between compressive stress in the film and energetic factors of plasma, e.g. the degree of ionization of depositing atomic flux, is explained by C. A. Davis [1]. The model states that magnitude of the maximum stress of the films is dominated especially by the degree of ionization of atomic flux onto the substrate. The degrees of ionization γ in RPD were estimated to be approximately 0.7, and compressive stress of 9 Gpa obtained by RPD method presented good agreement to a calculated value from Davis's equation with this γ. The Al-Ti-N film with high compressive stress presented longer tool life and better wear resistances than conventional Al-Ti-N films by CAIP in the continuous turning of alloy steel.

[1] C. A. Davis, This Solid Films, 226 (1993), 30-34

11:40am **B1-3-12 Oxidation Resistance and Mechanical Properties of CrTaSiN Coatings Prepared using Co-sputter Deposition**, *Y.I. Chen (yichen@mail.ntou.edu.tw)*, ***H.H. Wang***, National Taiwan Ocean University, Taiwan

CrTaSiN coatings were prepared using reactive magnetron co-sputtering on silicon wafers and cobalt-cemented tungsten carbide substrates to evaluate its feasibility for protective purpose on glass molding dies. A $Ta_{22}Si_{19}N_{59}$ coating process was used as the basis to evaluate the effects of Cr addition in oxidation resistance and mechanical properties. The nitrogen flow ratio (N_2/(N_2+Ar)) was set at 0.4 to fabricate the CrTaSiN coatings with an over-stoichiometric ratio, N/(Cr+Ta+Si)>1, for a rock salt structure. The CrTaSiN coatings, with a Cr content of 1–11 at.%, exhibited a nanocrystalline or near amorphous phase, a nanohardness of 14.6–16.0 GPa, and a surface roughness of 0.4–1.0 nm. Annealing treatments were conducted in a 1%O_2–99%Ar atmosphere at 600 ° C for 500 min, an oxidation-accelerating condition, or a thermal cycling annealing at 270 and 600 °C under an atmosphere of 15 ppm O_2–N_2, a realistic glass molding atmosphere in mass production. The outward diffusion of Si resulted into the formation of an amorphous oxide scale, which maintained a surface roughness of 1 nm. The Cr-addition maintained the nanohardness at 19 GPa after 1500 cycles thermal annealing.

Hard Coatings and Vapor Deposition Technology
Room: Sunset - Session B5-3

Hard and Multifunctional Nano-Structured Coatings
Moderator: J. Paulitsch, Vienna University of Technology, Austria, J. Houska, University of West Bohemia

8:00am **B5-3-1 Struture of CrN/NbN Nano-scale Multilayer Coating Deposited by Cathodic Arc Technique**, *J. Araujo*, *R. Souza*, University of São Paulo, Brazil, *N. Lima*, Energetic and Nuclear Research Institute, Brazil, ***A.P. Tschiptschin*** *(antschip@usp.br)*, University of São Paulo, Brazil

Nano-scaled multilayer CrN/NbN coatings were produced in an industrial-size cathodic arc physical vapor deposition (PVD) chamber, with an alternate three cathodes (Cr/Nb/Cr) configuration. Microstructural and compositional characterization of the CrN and NbN nanolayers was obtained. Sharp interfaces between the nanolayers were obtained. Four multilayer NbN/CrN coatings were produced with different periodicities (20 nm, 10 nm, 7.5 nm and 5 nm) with total thickness of 30µm in all cases. The coatings were characterized by X-Ray diffraction (XRD) and Transmission Electron Microscopy (TEM), which provided the lattice parameter in each of the constituent layers and structural description of the multilayers, respectively. Coatings were also analyzed in terms of hardness, using an instrumented micro-hardness tester. The multilayer coating system was composed of CrN and NbN with similar structures, but with a lattice mismatch, which varies the fraction of the region with lattice strain depending on periodicity. For the thicker individual layers, the adjustment of lattice parameter at the interfaces does not represent a predominant fraction of the entire structure, i.e. the separate peaks of NbN and CrN can be distinguished in the XRD analysis. In the presence of low periodicity (lower than 10nm), the lattice of each constituent may be coherently strained to each other and just one intermediate lattice (d-spacing) is detected for NbN/CrN multilayer. TEM observations showed that the interfaces were sharp with no apparent interdiffusion. The formation of columnar polycrystalline grain structure in the multilayers of several micrometers in size appear, indicating that despite of stratified structure, grain growth is not always interrupted by the different interfaces. From high to low periodicity, the multilayer NbN/CrN coatings show promising enhancements on hardness. Hence, the interfacial effects can dominate multilayer structure and properties, leading to unusually large strain and a trend for stabilization of metastable structure.

8:20am **B5-3-2 The Role of a Superelastic Interlayer on the Tribological Behaviour of Hard Coatings**, ***M. Callisti*** *(mc3a09@soton.ac.uk)*, National Centre for Advanced Tribology Southampton, UK, *B. Mellor*, *T. Polcar*, University of Southampton, UK

Hard protective coatings have been undergoing development for decades and further improvement to their mechanical and tribological properties is more and more challenging. Nowadays most research is aimed at improving the tribological behaviour of hard and functional coatings through the optimisation of their microstructure. The combination of different layers is another possible way of improving the tribological behaviour of protective coatings. The use of bonding layers mitigates the differences in mechanical and thermal properties between coating and substrate. As a consequence, the nature of this bonding interlayer plays an important role on the response of the coatings to the complex stress conditions occurring in a tribological scenario.

Among the possible interlayer candidates a layer with the capability of accommodating large deformation, thus protecting the substrate from plastic deformation as well as improving the adhesion of the top layer to substrate, was chosen. One of the potential classes of materials satisfying the above mentioned requirements is the Ni-Ti-based alloys which are known to exhibit superelastic properties also when sputter deposited.

In this study two different superelastic layers were fabricated by magnetron sputtering, namely a Ni-rich Ni-Ti and a (Ni, Cu)-rich Ni-Ti-Cu film, 2 µm thick, were deposited on steel substrates. In order to obtain superelastic properties, the films [#] were isothermally annealed for 1 hour at 500°C in a high vacuum environment. Subsequently the superelastic layers as well as bare steel substrates were coated with a 2 µm thick protective layer (hard and self-lubricant coatings) by magnetron sputtering.

The chemical composition of every single layer was measured by Energy-dispersive X-ray spectroscopy (EDS), while the structure was evaluated by grazing-incidence X-ray diffraction (GIXRD) and transmission electron microscopy (TEM). The mechanical properties of the single layers as well as those of the bilayers were measured by nanoindentation. Finally, the tribological behaviour of the bilayers and of the single layers were characterised by pin-on-disc testing.

The microstructural and mechanical properties of the different designs were correlated and discussed in relation to the measured tribological properties. A first comparison was performed in order to evaluate whether the use of a superelastic interlayer was beneficial to the tribological behaviour of a functional top layer. In addition the use of different superelastic interlayers, i.e. Ni-Ti and Ni-Ti-Cu, in the bilayers was investigated, the Ni-Ti-Cu being characterised by a different microstructure compared to the Ni-Ti composition.

8:40am **B5-3-3 Contemporary Thin Film Ceramics Behaviour in the Extreme Environments**, ***V. Vishnyakov*** *(v.vishnyakov@mmu.ac.uk)*, Manchester Metropolitan University, UK **INVITED**

All manmade relies on materials. New technologies require temperatures and working environments well beyond ability of traditional alloys and thin films. Thin films provide economy of scale, deliver exclusive properties to the point of exploitation and in many cases exist in the state which is impossible to achieve in the bulk form. The choice of thin film for the application needs to rely on understanding of the application condition and film/substrate behaviour in the application environment. The hardness and good oxidation resistance are not enough to satisfy diversity of application and environments. Slowly the pattern of thin film properties satisfying particular extreme environments is developing and this will help to predict film behaviour at the punishing conditions of multiple damage events, critical loads and high temperatures.

New ternary and quaternary ceramic films such as naturally nano-laminated MAX phases and amorphous carbonitrides have excellent potential and are the candidate materials to be used in most demanding applications. Understanding the deposition conditions and further material characterisation are vital for the insight of the link between chemistry, atomic structure, bonding and engineering properties of such films. The paper will review our contemporary understanding of the chain from basic principles to the applications.

9:20am **B5-3-5 The Microstructure and Mechanical Properties Evaluation of Cr-Si-B-N/Ti-Si-B-N Multilayered Thin Films**, ***L.C. Hsu***, *J.W. Lee (jefflee@mail.mcut.edu.tw)*, Ming Chi University of Technology, Taiwan

Recently, the boron contained transition metal nitride thin films have been studied extensively due to their excellent mechanical and thermal properties. The addition of Si element into such nitride coating also provided amorphous phase to strengthen the coating effectively by the formation of a nanocomposite microstructure. In this study, the Cr-Si-B-N/Ti-Si-B-N multilayered thin films with different Si contents were deposited by a reactive pulsed DC magnetron sputtering system using CrB2, TiB2 and Si targets. The phase structure of coatings was studied by means of the X-ray diffractometer (XRD). The microstructures of thin films were examined by the field-emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM). The nanoindentation, scratch tests, Daimler-Benz Rockwell-C (HRC-DB) adhesion tests, pin-on-disk wear tests were used to evaluate the hardness, adhesion, and tribological properties of thin films, respectively. It was observed that the nanocomposite microstructure of Cr-Si-B-N/Ti-Si-B-N multilayered thin films was obtained when the proper silicon content was controlled. Effects of silicon contents on the microstructure, hardness and tribological properties of coatings were discussed in this work.

Keywords: Cr-Si-B-N/Ti-Si-B-N multilayered thin film, nanocomposite, nanoindenter, scratch test, Daimler-Benz Rockwell-C adhesion test

9:40am **B5-3-6 Study of Sensing Properties of Zinc Oxide and Cu-doped Zinc Oxide Nanowires**, ***Y.W. Yeh***, *C.P. Liu*, National Cheng Kung University, Taiwan, *R.C. Wang*, National Kaohsiung University, Taiwan, *J.L. Huang (jlh888@mail.ncku.edu.tw)*, National Cheng Kung University, Taiwan

In this study, a single ZnO nanowire detector is described. ZnO and Copper doped ZnO nanowires have been prepared by low-temperature chemical vapor deposition method at 575°C. The morphology and microstructure of the nanowires were characterized by field emission scanning electron microscopy (FE-SEM) and high resolution transmission electron microscopy (HR-TEM), respectively. Low temperature photoluminescence spectroscopy is employed to analyze optical emissions of nanowires. With X-ray diffraction (XRD), we can investigate that Cu-doped ZnO nanowires are hexagonal phase with c-axis orientation. The X-ray photoelectron spectroscopy (XPS) data indicated that doping concentration of copper was high to 3.0 at%. The sensor device was fabricated by the e-beam lithography technology.

Keywords: ZnO nanowires, Cu-doping, chemical vapor deposition, gas sensor

10:00am **B5-3-7 Fabrication of n-type ZnO and p-type Cu_2O Nanostructures and its Photoelectrochemical Properties**, ***Y.H. Chen***, *Y.M. Shen*, National Cheng Kung University, Taiwan, *S.C. Wang*, Southern Taiwan University, Taiwan, *J.L. Huang (jlh888@mail.ncku.edu.tw)*, National Cheng Kung University, Taiwan

In this work, n-type ZnO and p-type Cu_2O nanostructures e lectrodeposited via high aspect ratio anodic alumina oxide (AAO) template assistance, using $ZnSO_4$ and $CuSO_4$ electrolyte, respectively. The ZnO and Cu_2O nanostructures of morphology and crystallinity were characterized by using X-ray diffraction (XRD), field emission scanning microscopy (FE-SEM), transmission electron microscopy (TEM), and energy-dispersive X-ray spectroscopy (EDS). The thickness and channel diameter of AAO template were about 150 µm and 110~160 nm, respectively. ZnO nanostructures fabricated under various electrolyte concentrations of 0.1M and 0.5M $ZnSO_4$ were nanotubes and nanowires, respectively. The Cu_2O contained in Cu/Cu_2O complex nanowires will increase with decreasing deposition current density. Both ZnO and Cu/Cu_2O nanostructure were uniformly corresponded to AAO's pore size, the diameter was about 140 nm. The carrier concentrations of the films were calculated by Mott–Schottky equation from Electrochemical Impedance Spectroscopy (EIS). The films were examined by one-step and two-step systems for hydrogen evolution from water splitting under visible light illumination, hydrogen generation efficiency were calculate by photocurrent from photoelectrochemical analysis (PEC) in Na_2SO_4 solution.

10:20am **B5-3-8 Fabrication and Characterization of Tungsten-Yttrium Coatings for Nuclear Reactor Applications**, ***G. Martinez***, University of Texas at El Paso, US, *C. Ramana (rvchintalapalle@utep.edu)*, University of Texas at El Paso

The challenging problem currently facing the scientific community in this 21st century is design, fabrication and engineering of novel structural materials, which will have a technological impact on the development of next-generation nuclear reactors to secure current, emerging and future energy needs of the society. Specifically, the choice of structural materials and options for nuclear reactors is very challenging for the reason that these materials experience: (a) extreme conditions of temperature and pressure, (b) high levels of nuclear irradiation, and (c) high mechanical and thermo-mechanical stresses. Tungsten-based materials have been considered for nuclear reactor applications for many years. While pure W exhibits compatible properties, it has low fracture toughness at all temperatures [#] . In addition, it exhibits a high ductile to brittle transition, which depends on the chemical and microstructure. Therefore, alloying W with other metals has been considered to further improving the physical properties and mechanical properties. In this work, alloying W with yttium (Y) has been

considered to develop the structural materials for nuclear applications. W-Y (Y<10 wt.%) coatings were deposited by RF sputtering. Characterization of these coatings is performed to derive an understanding of the micro-structure, thickness evolution, specific phase formation and/or transformation, and texturing with respect to deposition conditions. Coatings deposited at $3.4x10^{-2}$ mbar exhibit better structural order with a completely dominant β-phase when compared to the samples deposited at sputtering pressure of $1.4x10^{-2}$ mbar. The deposition rate (Γ) also decreases from 21 to 10 nm with increasing argon pressure from P_{Ar}=1.9E-2 mbar to 3.4E-2 mbar. Rutherford backscattering (RBS) spectroscopy of W-Y films demonstrated Y inclusion in the lattice [#] in the range of 1-5 wt%. The average grain size decreases with increasing pressure. Calculations were made using the Stopping and Range of ions in Matter (SRIM 2013) simulation package to understand the ion-irradiation damage as a function of time. The results will be presented and discussed.

Coatings for Biomedical and Healthcare Applications
Room: Sunrise - Session D2-1

Coatings for Bio-corrosion, Tribo-corrosion and Bio-tribology

Moderator: J. Geringer, Ecole Nationale Supérieure des Mines de Saint Etienne, T. Shokuhfar, Michigan Technological University

8:20am **D2-1-2 Properties of Waterborne Polyurethane/Graphene Coatings**, ***M. Rahman*** *(mohammadmizanur@gmail.com), Q. Habib*, King Fahd University of Petroleum and Minerals, Saudi Arabia

Recently graphene appears to be an inexpensive material available in large quantities with a well-known potential effectiveness for improving mechanical, electrical, thermal and other properties; which make it promising in many applications such as solar cells, hydrogen storage, sensors, batteries, super-capacitors and nanocomposites. Graphene is well dispersed in polymer matrix by solution mixing, melt mixing, and in situ polymerization methods. The ability of graphene to form chemical bonds in polyurethane (PU) chains, it can be effective nanofiller for the PU matrix. Moreover, due to the disk-like shape of the graphene, it is believed that graphene can be choice for improving the gas-barrier property of the nanocomposite protective coating. Waterborne polyurethane (WBPU) consists of mainly urethane and urea groups. Water is the main solvent during synthesis of WBPU. Only water evolved from WBPU at drying stage of coatings. Thus this process is environmentally friendly and free from pollution. In this report we synthesized environmentally friendly WBPU/graphene dispersions through a pre-polymer process using different graphene content (up to 3 wt%). The synthesized dispersions were used as a coating material on mild steel and evaluate the corrosion efficiency of WBPU/graphene coatings.

8:40am **D2-1-3 Corrosion and Tribological Film of CoCrMo Metal-on-Metal Hip Replacement**, ***Y. Liao*** *(yifeng.liao@gmail.com), P. Panigraphi*, Northwestern University, US, *M. Mathew, R. Pourzal, A. Fischer, M. Wimmer*, Rush University Medical Center, US, *L. Marks*, Northwestern University, US **INVITED**

Metal-on-metal hip replacements have experienced a sharp decline in the last two years due to biocompatibility issues related to wear and corrosion products. Despite some excellent clinical results, the release of wear and corrosion debris and the adverse response of local tissues have been of great concern. There are many unknowns regarding how CoCrMo metal bearings interact with the human body. In this study we investigated the corrosion of CoCrMo alloys with different heat treatments. Solution annealing the wrought alloys resulted in significant grain growth. After annealing at 1230 ^{o}C, the second phase, i.e. chromium carbide, was partially dissolved into the matrix. The corrosion current density (i_{corr}) dropped from ~1400 nA/cm^2 for the original wrought alloy to ~300 nA/cm^2 for solution annealed specimens, indicating that grain coarsening improves corrosion resistance. Pitting corrosion preferentially attacked high-angle grain boundaries with higher energy. All low-angle boundaries were immune to corrosion in the tests. We also evaluated metal-on-metal hip replacement retrieved at revision surgery using electron microscopy and Raman spectroscopy. Thin layers of films are frequently generated in-vivo on CoCrMo MoM surfaces, which are known as tribological films or tribofilms. The EELS results show that tribofilm consist of over 82% sp^2-bonded carbon while no discernible nitrogen was found, suggesting that the tribofilm is primarily graphitic carbon. High-resolution TEM micrographs showed short-range ordered fringes in the tribofilm. The results were further confirmed by the Raman spectrum. The tribofilm may be protective against the degradative processes taking place in-vivo in the host body. The composition and ultrastructure is unique and can provide insights into the basic mechanisms of tribocorrosion in metal on metal bearings.

9:20am **D2-1-5 Electrochemical and Tribocorrosion Aspects of Mixed Metal Contacts in Hip Prostheses**, *D. Royhman (droyhman@gmail.com), M. Runa, M. Wimmer, J. Jacobs, N. Hallab,* ***M. Mathew***, Rush University Medical Center, US

Modern hip prostheses feature a modular implant design with a tapered junction between the femoral neck and head, which gives the surgeon flexibility in implant assembly and reduces inventory. Despite their apparent benefits, modular junctions also introduce complications in the hip implant system by introducing additional interfaces. The implant is subjected to various loads and body movements, which may produce micromotion movement at the interface. This can lead to mechanically assisted corrosion (Fretting-Corrosion) and increased release of wear debris and metal ions. This study has two objectives. (1) To study the electrochemical behaviour of commonly used metal alloys (Ti6Al4V and CoCrMo) in a simulated joint fluid evironment with two different pHs (7.6 and pH 3.0), and (2) to implement a new fretting-corrosion apparatus in order to study the fretting-corrosion behavior of Ti-CoCrMo couple in a proteinous solution (BCS) and a saline solution (0.9% NaCl).

For corrosion tests, six Ti6Al4V discs (Mac-Master Carr, Elmhurst, IL) and six wrought high-carbon CoCrMo discs (ATI Allvac, Pittsburgh, PA) were milled from rods. The samples were divided into 4 groups (n=3) as a function of disc type (Ti6Al4V or CoCrMo) and pH level (3.0 and 7.6). For tribocorrosion tests, Ti6Al4V alloy rods (exposed surfaces: 11mm by 11mm) and 2 CoCrMo pins (exposed Surfaces: 12mm diameter x 7 mm thickness) were used. A sinusoidal fretting motion (amplitude of +150 um) was applied to the Ti alloy rod, which was generated through an Instron 8800 load frame (Canton, MA). A load of 200N was applied axially from both sides and the tangential load was monitored. The evolution of potential was monitored during test.

Significant differences were noted within both metals for Ecorr and Icorr ($p<0.05$; ANOVA). Ti6Al4V exhibited significantly lower Icorr values than CoCrMo in all pHs ($p<0.0001$; t-test). The Ecorr value for Ti6Al4V was significantly higher than CoCrMo at pH 3.0 ($p=0.004$; t-test). During the fretting motion, the potential suddenly decreased (0.15V BCS and 0.2V-NaCl) and then slowly recovered during the final stabilization period. Fluctuations of the potentials were evident in both solutions. Further studies will be done by simulating other conditions at the modular junction (pH decrease, varying protein concentrations) to understand the mechanisms driven by the synergistic interaction of wear and corrosion at the modular junction.

9:40am **D2-1-6 Hydrothermal Deposition of Bio-resorbable Calcium-Phosphate Coating on AZ31 Magnesium for Implant Application**, ***S. Kaabi Falahieh Asl*** *(sara002@e.ntu.edu.sg)*, Nanyang Technological University, School of Mechanical & Aerospace Engineering, Singapore Institute of ManufacturingTechnology, Singapore, *N. Sandor*, Singapore Institute of Manufacturing Technology, Singapore, *M.J. Tan*, Nanyang Technological University , School of Mechanical & Aerospace Engineering,, Singapore

Interest in biodegradable magnesium (Mg) implants has increased dramatically in the last decade due to their desirable mechanical properties that are close to the human bone, thus avoiding stress shielding effect. In addition, Mg is resorbed in the body and surgery to remove the implant after healing is not needed. However, the high corrosion rate of magnesium and its alloys severely limit their practical applications as implants. To control the corrosion rate of magnesium, biocompatible and bio-resorbable calcium-phosphate (Ca-P) coatings were deposited in this study using AZ31 magnesium substrate and hydrothermal deposition process. Coatings obtained at various temperatures were found to mainly consist of a mixture of monetite [$CaHPO_4$] and tricalcium phosphate [$Ca_{2.86}$ $Mg_{0.14}$ $(PO_4)_2$] with partially magnesium substituted in tricalcium phosphate structure as determined by X-ray diffraction (XRD) and Fourier transform infrared (FTIR) spectroscopy methods. Coating morphology was examined with scanning electron microscopy (SEM) and the results showed that coatings became denser with increasing temperature. Coating adhesion was examined by pull-out adhesion test indicating only coating cohesive failure at 5.2-5.8 Mpa. It was clearly observed that significant portion of the coating still remained on the substrate after adhesion test. Potentiodynamic polarization conducted in simulated body fluid (SBF) solution confirmed that coating significantly enhanced the corrosion performance of Mg substrate. The corrosion current density of Mg substrate decreased approximately 10,000-fold in the presence of coating. The mass loss for the coated samples was only around 1/3 of that observed for bare substrate, and the amount of Mg ions released from the coated samples was significantly lower than in case of bare substrate after immersion in SBF solution. The described hydrothermal method provided crystalline and compact coatings

with excellent adhesion strength and significantly improved corrosion resistance with good prospects for biomedical application.

Keywords: Magnesium, Calcium-Phosphate coating, Corrosion resistance

10:00am **D2-1-7 Layers of Nanocrystallines and Tribofilm on Artificial Hip Implants Surfaces Induced by Bio-tribo-corrosion Processes**, ***Y. Yan*** *(yanyu@ustb.edu.cn)*, Key Laboratory for Environmental Fracture (MOE), University of Science and Technology Beijing, China **INVITED**

Performance and longevity of artificial joints are highly correlated with the surface properties of the prosthesis materials. In view of the importance of this research area, this article consolidates the research work with some fundamental aspects to build up a comprehensive picture of the current state of knowledge. Tribofilm containing organometallic compounds can form on the surface of artificial joints through bio-tribocorrosion processes. Tribofilm can act as a barrier to prevent further ions release and can also act as a solid lubricant. Some test methods are presented, being applied both and . A review of recent work in this area is provided, focusing on the constitution and microstructure of the artificial joints surface.

10:40am **D2-1-9 Fretting Corrosion of Co-Cr-Mo Alloy with Ti: Specific Tribocorrosive Behavior and Benefits in Comparison with Usual Metallic Alloys Dedicated to Orthopedic Implants**, ***S. Nakahara***, Department of Material Processing, Japan, *A. Towarek*, Warsaw University of Technology, Poland, *K. Ueda*, Department of Material Processing, Japan, *T. Narushima*, Tohoku University, Japan, *J. Geringer (geringer@emse.fr)*, Ecole Nationale Supérieure des Mines de Saint Etienne, France

After the famous recall of the MoM (Metal on Metal) ASR hip implant from Depuy company, on December 2011, a lot of investigations have been carried out on the lifetime of metallic implants. It is worth noting that younger patients are implanted. Thus increasing the lifespan of hip implants is a 'hotspot' research field. This work is dedicated on comparing the fretting-corrosion (metallic sample against PMMA, ±40 µm during 4 hours), see [1,2] behaviors of 316LN stainless steel and Co-Cr-Mo alloys (with or without Ti content, max 1% wt). First of all the effect of proteins in liquid medium is a key-factor on wear. Thus the proteins content is varying from 0-10-20-30 g.L-1. With increasing the proteins content, the wear volume is equal to 20.10^4 μm^3). the lowest wear volume has been highlighted for Co-Cr-Mo alloy with 1% of Ti. On the contrary increasing the concentration of proteins is not beneficial concerning the polymeric material. It is worth noting that the polymeric material has been chosen because the mechanical properties are very close to the ones of bone. Indeed the wear volume of PMMA at 30 $g.L^{-1}$ of albumin is twice higher than the one measured without any protein. Concerning the number of wear particles this fact does not involve promising outlooks about fretting corrosion degradations. However the softer material is bone in the actual case and the remodeling of the bone always is in progress in human body. Finally, thanks to SEM images, a particular mechanism of lubrication is expected during fretting corrosion degradations. The Ti particles, i.e. particles as TiC, are not degraded during the fretting corrosion process. Thus particular pathways are highlighting after fretting corrosion experiments on the metallic surface. These patterns could be a benefit because promoting the liquid layer and the bearing effect.

11:00am **D2-1-10 Studies of Unbleached Cotton Fabric Treated with TiO_2 Anchored by Diamond-like Carbon Film: Microbiological Inhibition Growth Rate With and Without UV Exposition**, ***E.D. Santos*** *(evtdiniz@hotmail.com)*, *D.F. Furtado*, *F.S. Miranda*, *F.L.C. Lucas*, *R.S. Pessoa*, *H.S. Maciel*, Universidade do Vale do Paraíba, Brazil, *E. Esposito*, Universidade Federal de São Paulo, Brazil, *L.V. Santos*, Universidade do Vale do Paraíba, Brazil

Patients and staff transit in hospitals allows contact with clothes, enabling different micro-organisms transport , which may contribute to the cross-infection emergence . According to Church BD and Loosli CG (1953), dirty hospital clothes have average of 200 bacterium/cm^2. The main objective to be achieved after processing dirty clothes in hospital laundry, is the reduction of microbial contamination to acceptable levels. Due to it we developed a nanofilm of titanium dioxide (TiO_2) coated and anchored by a film of amorphous diamond-like carbon (DLC).These films were deposited on 4 samples of unbleached cotton fabric, following different protocols, in order to determine the best parameters and output results. For the TiO_2 deposition was used the technique of TiO_2 dilution in water and it was nebulized onto the substrate. The nebulized sample was placed into plasma reactor enhanced chemical vapor deposition (PECVD). We used different times, voltage, power, and flow rate of CH_4 for the treatment of each substrate. Thereafter, the fabric was submitted to a test of microbicide capacity using the techniques of Standard Plate Count (Pour Plate) and Membrane Filtration. We used the most present microorganisms in hospital laundry: *Tinea pedis*, *Bacillus sp*, *Escherichia coli* and other gram-negative bacteria. We determined the death rate of the microorganisms as a function of time/intensity of UV light incidence in dark room with the semiconductor laser therapy. The laser was activated by phosphate indium-gallium-aluminum (InGaAIP) and operated in continuous wave to simulate the effects of solar UV on the clothes drying on the natural environment. We notice that the 4 samples of experimental groups showed a smaller grip / number of microorganisms / cm^2 of fabric when compared to the control, which received without treatment. The results showed that this fabric is suitable to make prophylaxis of cross infections in a hospital environment caused by clothes.

Tribology & Mechanical Behavior of Coatings and Engineered Surfaces
Room: California - Session E2-2

Mechanical Properties and Adhesion

Moderator: J. Michler, EMPA (Swiss Federal Laboratories for Materials Science and Technology), R. Chromik, McGill University, D.F. Bahr, Purdue University

8:00am **E2-2-1 Tensile Deformation Behavior in Highly Nanotwinned Cu and CuAl Alloys**, ***A. Hodge*** *(ahodge@usc.edu)*, University of Southern California, US **INVITED**

Metals containing nanoscale growth twins have shown remarkable mechanical performance compared to their nanocrystalline counterparts. In particular, nt-Cu has shown concurrent increases in strength and ductility with decreasing twin spacing, in addition to enhanced mechanical and thermal stability. In order to accurately generalize the performance of nanotwinned metals, it is necessary to synthesize and test other metals containing growth twins. In this study, ultra-fine grained CuAl foils with varying amounts of growth twins were tested in tension and compression, and their mechanical properties and deformation are compared to nt-Cu. Extensive characterization of the twins and their stability under different deformation modes will also be presented.

8:40am **E2-2-3 Electromechanical and Chemomechanical Performance of Laser Oxide Coatings on Metallic Substrates**, ***S.K. Lawrence*** *(lawren13@purdue.edu)*, Purdue University, US, *D. Adams*, Sandia National Laboratories, US, *D.F. Bahr*, Purdue University, US, *N.R. Moody*, Sandia National Laboratories, US

Concentrated, nanosecond-pulsed laser exposure of oxidizing metals in ambient atmosphere produces highly colored, well-adhered oxide coatings, which are particularly interesting for use as unique authenticity identifiers on welded or sealed components. The combined properties of the oxide-substrate system control the coupled electromechanical behavior and environmental stability of the oxide. Laser-processing parameters dictate oxide thickness, which in turn defines color, residual film stress, and fracture behavior. Oxides grown on stainless steel 304L and CP grade II titanium are residually stressed in tension leading to through-thickness cracking at film thicknesses greater than ~100 nm. Hardness, fracture behavior, and residual stress are highly dependent upon thickness suggesting that internal defects influence mechanical behavior. Conducting nanoindentation reveals an increase in conductance with decreasing oxide thickness, further suggesting the dependence of mechanical behavior on fluctuations in oxide defect density. Additionally, post mortem energy dispersive spectroscopy of oxides on SS 304L exposed to an aggressive environment manifests a Cr-denuded zone in the substrate immediately beneath the oxide, ultimately creating a microstructure that is susceptible to corrosive attack. Furthermore, the fracture behavior and environmental resistance analyses can be combined, by performing high-load, conical indentation in a fluid cell containing various inert and corrosive solutions, to evaluate the coupling of mechanical stresses and environmental effects. The integration of multiple characterization techniques provides a unique approach for defining electro- and chemo-mechanical performance of the oxides in harsh operating environments. This work was partially supported by DTRA Basic Research Award # IACRO 12-2026I and by Sandia National Laboratories, a Lockheed Martin Company for the USDOE NNSA under contract DE-AC04-94AL85000.

9:00am **E2-2-4 Room Temperature Nanoindentation Creep of Nanograined NiTiW Shape Memory Thin Films**, ***N. Kaur***, *D. Kaur (dkaurfph@iitr.ernet.in)*, Indian Institute of Technology Roorkee, India

In this paper, the creep behaviours of NiTiW thin films at various W contents (2.6-33.6%) were investigated using nanoindentation creep testing method. With W content ranging from 2.6 at.% to 4.5 at.%, the films are strengthened and exhibit much reduced strain rate 6.76×10^{-4} s^{-1} indicating highest creep resistance. With further increase in W content beyond 4.5

at.% strain rate increases and therefore creep resistance of films decrease gradually. The stress exponents were calculated from the loading curves. The results shows that stress exponent for NiTi was 8.2 and increased to 20.5 for NiTiW (2.6) and 22.9 for NiTiW (4.5) and decreased rapidly to 9.5 increasing the W concentration from 9.1 to 33.6 at %. The mechanism for the room temperature creep is discussed in framework of dislocation dynamics. Grain boundaries play an important role in creep behaviour. Studying the deformation behavious of NiTiW thin films has technological importance because of their various applications in micro and nano-electro-mechanical systems.

Keywords: Thin films, nanoindentation creep, grain boundaries

9:20am **E2-2-5 Deformation and Fracture of Metal Films on Polymer Substrates**, ***M.J. Cordill*** *(megan.cordill@oeaw.ac.at), V. Maier,* Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Austria, *J. Berger, O. Glushko*, Erich Schmid Institue of Materials Science, Austrian Academy of Sciences, Austria, *J. Paulitsch*, Vienna University of Technology, Austria **INVITED**

Electro-mechanical properties of metal thin films on polymer substrates are important to understand in order to design reliable flexible electronic devices. It has long been know that deposition parameters have an effect on the microstructure of the thin films which in turn affects the electrical and mechanical behavior. Both the film microstructure and electro-mechanical behavior of metal-polymer system can be examined using in-situ SEM tensile straining and in-situ 4-point-probe resistance measurements. Both techniques can be used to measure the fracture and delamination stresses, and also allow for the strain dependent electrical properties of ductile films to be examined. In this study, Cu films deposited using e-beam evaporation and sputter deposited Cr films on polyimide are studied with regards to the resulting microstructures and electro-mechanical behavior during cyclic and static straining. From the investigation, the ideal deposition techniques and microstructures which produces electro-mechanical film properties of high fracture and delamination stresses will be determined for improved device reliability.

10:00am **E2-2-7 Numerical Evaluation of Cohesive and Adhesive Failure Modes During the Indentation of Coated System with Compliant Substrate**, ***N. Fukumasu*** *(newton.fukumasu@gmail.com), R. Souza*, University of São Paulo, Brazil

The indentation test of coated systems allows the analysis of mechanical properties of singular constituents, or of the entire system, including material constitutive behavior and failure properties. Due to the progressive loading and unloading of the indentation, both cohesive and adhesive failures can occur in the coating and at the coating/substrate interface, respectively. In this work, the Finite Element Method (FEM) was applied to develop a numerical model based on a spherical rigid indenter in contact with a coated compliant substrate. The coating behavior was defined based on the properties of a brittle pure elastic material, while the substrate was assumed as a ductile elastic-perfectly plastic material. Both cohesive and adhesive failure models were included in the analyses, allowing the evaluation of failure modes in the coating and/or at the coating/substrate interface. The eXtended Finite Element Method (XFEM) was applied to reproduce the cohesive cracks through the coating thickness, while the Cohesive Zone Model (CZM) was used to evaluate the coating/substrate interfacial crack. The failure modes were analyzed for a range of coating material properties (Young's modulus, fracture toughness and cohesive crack propagation energy) and coating/substrate interface properties (interface toughness and adhesive crack propagation energy). Results allowed identifying not only different modes of cohesive and adhesive failures, but also the main mode as a function of the constituent properties. Also, the derivatives of the forces acting upon the indenter allowed the characterization of the failure modes, indicating that both cohesive and adhesive failures may generate individual signatures on the load-displacement (P-h) indentation curves.

New Horizons in Coatings and Thin Films
Room: Royal Palm 4-6 - Session F2-1

High Power Impulse Magnetron Sputtering (HIPIMS)
Moderator: D. Lundin, Université Paris-Sud 11, France, S. Konstantinidis, University of Mons

8:00am **F2-1-1 Imaging Of Self-Organized Plasma Structures In DC Magnetron Sputtering And HiPIMS Discharges**, ***M. Panjan*** *(matjaz.panjan@ijs.si), S. Loquai, J.E. Klemberg-Sapieha, L. Martinu*, École Polytechnique de Montréal, Canada

It was recently discovered that HiPIMS plasma close to the magnetron surface is not uniformly distributed; instead it forms azimuthally organized structures that rotate in the direction of E×B electron drift [1-3]. These structures were named ionization zones or spokes and play an important role in the ionization process and transport of charged particles, as demonstrated by recent measurements [4,5].

In the present work, we show existence of organized plasma structures also in the DC magnetron sputtering discharge at current densities several magnitudes lower than in the HiPIMS regime. A high speed camera was used to study morphology and evolution of plasma structures from the top and side views. A more or less periodic plasma structures containing one or two ionization zones were observed at extremely low discharge currents (i.e. 50 mA for 4 inch magnetron). Structures were stable and reproducible for the same discharge conditions. The periodicity and morphology of patterns was found to depend on the discharge current and the working gas pressure. Using a copper spacer between the magnetron and the niobium target we also show that the intensity and morphology of light patterns is more pronounced at higher magnetic fields indicating that self-organized plasma structures are related to the E×B electron drift.

[1] A. Kozyrev, N. Sochugov, K. Oskomov, A. Zakharov, A. Odivanova, Plasma Physics Reports, 37 (2011) 621-627.

[2] A. Anders, P. Ni, A. Rauch, Journal of Applied Physics, 111 (2012) 053304-053313.

[3] A.P. Ehiasarian, A. Hecimovic, T.d.l. Arcos, R. New, V.S.-v. der Gathen, M. Boke, J. Winter, Applied Physics Letters, 100 (2012) 114101-114104.

[4] A. Anders, M. Panjan, R. Franz, J. Andersson, P. Ni, accapted for publication in Applied Physics Letters

[5] M. Panjan, R. Franz, A. Anders, in preparation for Plasma Sources Science & Technology

8:20am **F2-1-2 Ionized Sputtering with a Pulsed Hollow Cathode Magnetron**, ***F. Fietzke*** *(fred.fietzke@fep.fraunhofer.de), B.-G. Krätzschmar*, Fraunhofer Institute for Electron Beam and Plasma Technology FEP, Germany

High Power Impulse Magnetron Sputtering (HiPIMS) during the last decade has developed from an exotic idea towards a technology well understood and controlled to a large extent in laboratory scale, and now being on the cusp of industrial application. The high degree of ionization of the plasma species allows for efficient pre-cleaning processes and the deposition of layers with outstanding properties. However, at levels of 2-3 A/cm^2 and primarily caused by effects like gas rarefaction and electron losses across the magnetic field lines, a limit in peak current density becomes apparent that cannot be exceeded for the majority of target materials.

To overcome this limit, the hollow cathode magnetron might represent a promising alternative to the commonly used planar magnetron design. It combines the cup-shaped target and the annular plasma zone along the inner cylinder wall of an inverted magnetron with a special design of the magnetic field to control the fluxes of charged particles.

In the work to be presented, a hollow cathode magnetron has been operated with a HiPIMS power supply at duty cycles around 1 %, and the non-reactive sputtering of several target materials like copper, aluminum and carbon has been investigated. Systematically varying pulse length, frequency, discharge voltage, pressure and geometry of the magnetic field, waveforms of discharge voltage and current have been recorded and the state of the plasma has been characterized by different methods. Beyond a material-dependent voltage level the pulse current always shows a runaway behavior stopped only at current densities between 10 and 20 A/cm^2 due to the limits of the power supply.

Optical emission spectroscopy in time-averaged as well as in time-resolved mode has been utilized and showed the contribution of self-sputtering and the portion of metal ions rising with elapsing time during the pulse. Due to the special geometry of the sputtering cathode gas rarefaction seems to play only a minor role.

Measurement of ion currents and energy distribution functions of different species have been carried out which allow to draw conclusions on the elementary processes in the plasma zone.

8:40am **F2-1-3 High-rate Reactive High-power Impulse Magnetron Sputtering of Densified Zirconium Dioxide Films**, ***J. Vlcek*** *(vlcek@kfy.zcu.cz), J. Rezek*, University of West Bohemia, Czech Republic

In spite of several successful applications of the high-power impulse magnetron sputtering (HiPIMS) systems to reactive sputter depositions of dielectric films, there are still substantial problems with arcing on target surfaces during the reactive deposition processes at high target power densities, particularly for voltage pulses longer than 40 µs, and with low deposition rates achieved.

To avoid these problems, we have proposed a pulsed reactive gas flow control (RGFC) of the reactive HiPIMS processes. Using this process control, we are able to maintain sputter deposition of the dielectric stoichiometric films in the region between a more and less metallic mode, and to utilize exclusive benefits of the HiPIMS discharges, such as intense sputtering of atoms from the target, very high degrees of dissociation of RG molecules in the flux onto the substrate, strong "sputtering wind" of the sputtered atoms, highly ionized fluxes of particles to substrate and enhanced energies of the ions bombarding the growing films, in preparation of the films.

In the presentation, we report on details of deposition processes, including an energy-resolved mass spectrometry at the substrate position (energy distribution functions of positive and negative ions, and compositions of the integral fluxes of positive ions), and on film structure and properties.

HiPIMS with the pulsed RGFC was used for high-rate reactive deposition of densified, optically transparent zirconium dioxide films. The depositions were performed using a strongly unbalanced magnetron with a planar zirconium target of 100 mm diameter in argon-oxygen gas mixtures at the argon pressure of 2 Pa. The repetition frequency of a pulsed dc power supply was 500 Hz at the average target power density from 5 Wcm^{-2} to 50 Wcm^{-2} during a deposition with duty cycles from 2.5% to 10%. Typical substrate temperatures were less than 130°C during the depositions of films on a floating substrate at the distance of 100 mm from the target. Usual deposition rates, being around 10 nm/min, were achieved for the target power density of 5 Wcm^{-2}. An optimized location of the oxygen gas inlets above the target and their orientation to the substrate surface made it possible to improve quality of the films due to minimized arcing at the sputtered target and to enhance their deposition rates up to 120 nm/min for the target power density of 50 Wcm^{-2} at the duty cycle of 10%. The zirconium dioxide films were crystalline with a predominant monoclinic structure. They exhibited a hardness of 16 GPa, refractive index of 2.19 and extinction coefficient of 0.002 (both at the wavelength of 550 nm).

9:00am **F2-1-4 $CuInSe_2$ Thin Film Photovoltaic Absorber Layers by HIPIMS at Low Temperature**, ***A.P. Ehiasarian*** *(a.ehiasarian@shu.ac.uk), D. Loch*, Sheffield Hallam University, UK, *V. Sittinger*, Fraunhofer IST, Germany

$CuInSe_2$-based thin film photovoltaics are gaining popularity in industry due to high conversion efficiency, high productivity of the deposition process and competitive pricing against Si-based processes.

In this work CuInSe deposition experiments were carried out in a UHV system enabled with HIPIMS technology.

Energy-resolved mass spectroscopy measurements showed that the deposition plasma contained significant quantities of Cu^{1+} and In^{1+} ions which were on par with those of Ar^{1+}, whereas the Se ion flux constituted 1% of the total. The temperature of Ar^{1+} ions was 7 eV in the pulse on-time and 2 eV in the pulse off-time with maximum energy of 20 eV.

CuInSe films were deposited by HIPIMS with different composition. Films with high Cu content $Cu_2In_{0.6}Se$, had faceted columnar tops and low intensity broad $CuInSe_2$ (112) peak. A secondary phase was detected by Raman spectroscopy.

Films with near-stoichiometric composition had smooth column tops. $CuInSe_2$ phase was confirmed at 350°C by Raman spectroscopy and XRD and a high ratio of (112):(220) diffraction peaks was measured. No Cu_2Se was found by Raman with excitation wavelength of 532 nm. Regardless of Cu content, columns were well defined, ranging in size from 200 to 700 nm at film thickness of 1.5 µm.

9:20am **F2-1-5 Plasma Spokes and Particle Transport in HiPIMS Discharges**, ***A. Hecimovic*** *(ante.hecimovic@rub.de), T. de los Arcos, V. Schulz-von der Gathen, J. Winter*, Institut for Experimental Physics II, Ruhr-Universität Bochum, Germany **INVITED**

A time resolved analysis of the emission of HiPIMS plasmas reveals inhomogenities in the form of rotating spokes. The frequency spectrum analysis showed transition of the spokes from stochastic to periodic behaviour within each HiPIMS pulse. The shape of these spokes is very characteristic depending on the target material. The localised enhanced light emission has been correlated with the ion production. Optical emission spectroscopy using the bandpass interference filters isolating the emission of a single species showing enhanced ionisation within the spoke and depletion of the neutral species. Additionally, using the double flat probe, the transport of the ions and electrons outward from the closed magnetic field region has been correlated with the ionisation zone of the spoke. Based on these data, the peculiar shape of the emission profiles can be explained by the localised generation of secondary electrons (SE), resulting in an energetic electron pressure exceeding the magnetic pressure. This general picture is able to explain the observed emission profile for different target materials including gas rarefaction and second ionization potential of the sputtered elements.

This work is funded by the DFG within the framework of the SFB-TR 87.

10:00am **F2-1-7 Effects of Cr and Ta Interlayers on the Adhesion and Mechanical Properties of CN_x Thin Films Deposited by HiPIMS on Steel Substrates**, ***K.D. Bakoglidis*** *(konba@ifm.liu.se), S. Schmidt, G. Greczynski, J. Lu, E. Broitman, L. Hultman*, Linköping University, IFM, Thin Film Physics Division, Sweden

CN_x thin films were deposited on grade AISI52100 steel substrates by high power impulse magnetron sputtering (HiPIMS) in an industrial vacuum chamber. Mixed metal ion/neutral fluxes from elemental Cr and Ta targets operated in HiPIMS mode in an Ar-based plasma were used for substrate etching, metal implantation, and/or interlayer deposition in order to improve the film adhesion. The metal ion-to-neutral ratio in the material flux to the substrate was controlled by varying the pulse energy (5 J, 10 J, and 15 J). Additionally, the effects of pretreatment at different negative bias voltages ranging between 300 V and 900 V were investigated. Other process settings, including the pulse width of 200 µs and the frequency of 100 Hz as well as the deposition pressure of 200 mPa and substrate temperature of 150 °C were kept constant during interlayer formation. CN_x films with a thickness of ~1000 nm were subsequently deposited by reactive HiPIMS from a pure graphite target at an Ar/N_2 flow ratio of 0.16. Corresponding deposition processes were carried out at a pressure of 400 mPa, a pulse energy of 4.5 J and a pulsed negative bias voltage of 150 V. Transmission electron microscopy in combination with energy dispersive X-ray spectroscopy and selective area electron diffraction provided insights to which extent interlayer and substrate intermixing occurred as well as into the structural evolution of the interlayers and CN_x films. The chemical bonding structure at the interface between Cr or Ta interlayer and CN_x film was investigated by X-ray photoelectron spectroscopy. Increasing the pulse energy and the negative bias voltage during interlayer growth resulted in an effective cleaning of substrate surface oxides, pronounced interlayer-substrate intermixing, and metal carbide as well as metal nitride formation. Rockwell C tests revealed an improved adhesion (HF = 1 to 2) of CN_x films on steel with a Cr interlayer. The resultant mechanical properties of the film were assessed by nanoindentation, revealing a moderate hardness and a considerable resiliency.

10:20am **F2-1-8 Comparison of CrN/AlN Multilayer Coatings Deposited via Middle Frequency Pulsed and High Power Pulsed Magnetron Sputtering**, *N. Bagcivan, K. Bobzin,* ***R.H. Brugnara*** *(brugnara@iot.rwth-aachen.de)*, Surface Engineering Institute - RWTH Aachen University, Germany

Multilayer coatings based on transition metal nitrides such as CrN, AlN and TiN deposited via physical vapor deposition (PVD) have shown great advantage as protective coatings on tools and components subject to high loads in tribological applications. By varying the individual layer material and their thicknesses it is possible to optimize the coating properties, e.g. hardness, Young's modulus and thermal stability. Other alternative for further improvement of the coating properties is the use of different PVD technology. High power pulse magnetron sputtering (HPPMS) is an advancement of pulsed magnetron sputtering (MS). The use of HPPMS allows a better control of the energetic bombardment of the substrate. It offers the possibility to influence chemical and mechanical properties by variation of the process parameters. The present work deals with the development of CrN/AlN multilayer coatings in an industrial scale unit by using two different PVD technologies. In this work middle frequency pulsed (MF) MS and high power pulse magnetron sputtering (HPPMS) technology were used. The bilayer period Λ, thickness of a CrN/AlN, was varied between 37 and 6 nm by varying the rotational speed of the substrate holders. In a second step one rotational speed was chosen and further HPPMS CrN/AlN coatings were deposited applying different HPPMS pulse lengths (200, 80 and 40 µs) at the same cathode power and frequency. The chemical composition of the coatings was determined using Glow Discharge Optical Emission Spectroscopy (GDOES). Morphology, roughness and phase composition were analyzed by means of Scanning

Electron Microscopy (SEM), confocal laser microscopy, and X-ray Diffraction (XRD), respectively. Detailed characterization of the multilayers was conducted by Transmission Electron Microscopy (TEM). Hardness and Young's modulus were analyzed by nanoindentation measurements. The results of the phase analysis show the formation of h-Cr_2N and c-AlN for the MF CrN/AlN coatings while in the HPPMS coatings only cubic phases (c-CrN, c-AlN) were detected. A high hardness of 31 GPa was measured for the HPPMS with a bilayer period of 6 nm. Decreasing of HPPMS pulse length at constant mean power leads to a considerable increase of cathode current. It could be observed that the deposition rate of the CrN and AlN reduces with decreasing pulse length, so that a CrN/AlN coating with a bilayer period of 3 nm and a high hardness of 40 GPa was achieved using a short pulse length of 40 µs.

10:40am **F2-1-9 Microstructure and Electrical Transport Properties of HIPIMS-Deposited ZnO Thin Films**, ***A.N. Reed*** *(amber.reed.5@us.af.mil), P.J. Shamberger,* Air Force Research Laboratories, Wright-Patterson AFB, *C. Muratore,* University of Dayton, US, *J.E. Bultman,* University of Dayton Research Institute, *A.A. Voevodin,* Air Force Research Laboratory, Materials and Manufacturing Directorate

High power impulse magnetron sputtering (HiPIMS) is a promising technique for the large scale deposition of nanocrystalline ZnO thin films on temperature sensitive substrates. The most common techniques for depositing semiconducting ZnO films currently include DC and pulse DC magnetron sputtering, rf sputtering, MBE and PLD. The highest reported mobilities (110 $cm^2V^{-1}s^{-1}$) and on-of ratios (up to 10^{12})[1] are for nanocrystalline ZnO films deposited with PLD. However, these techniques are limited in that they either require high deposition temperature and epitaxy (MBE), produce films with lower electron mobilities (DC and pulsed DC sputtering) or are difficult to adapt for large-scale depositions (rf sputtering and PLD).

In this study, we investigate the interrelationship between HiPIMS plasma characteristics and resulting film microstructures for nanocrystalline ZnO films grown from ceramic ZnO and metallic Zn targets onto amorphous SiO_2. For depositions from both the ZnO and Zn targets, XRD and SEM measurements indicate highly crystalline, (002) oriented films with a layer at the SiO_2 interface where different ZnO orientations are in competition. Alignment of the (002) orientation in the films improves with decreased growth pressure until 5 mTorr. Films grown below 5 mTorr had a bimodal microstructure with larger (~25 nm) grains among the small crystals. The effect of plasma conditions on the competitive growth layer and (002) alignment was investigated by correlating time-resolved current measurements of the target and ion energy distributions to film microstructure. The results were used to optimize HiPIMS growth conditions of ZnO channels for back-gated thin film transistors. XRD, SEM and AFM studies of ZnO films deposited at optimized growth conditions show microstructures comparable to those deposited with PLD. The I-V characteristics of the produced devices are measured to determine the electrical transport properties of the ZnO films.

[1] B.Bayraktaroglu, K. Leedy, R. Neidhard. Microwave ZnO Thin Film Transistors. IEEE Electronic Device Letters V 29 Iss. 9 2008

11:00am **F2-1-10 A Comparative Study of Nanocomposite TiBCN Coatings Deposited by DC Magnetron Sputtering, Pulse DC Magnetron Sputtering and Deep Oscillation Magnetron Sputtering**, ***B. Wang****, M. Kaufman (mkaufman@mines.edu), G. Bourne, W. Sproul, J. Lin*, Colorado School of Mines, US

Nanocomposite Ti-B-C-N coatings were deposited on Si wafers and stainless steel (SS304L) substrates by sputtering a composite (80%)TiB_2-(20%)TiC target in an Ar+N_2 mixture by DC magnetron sputtering (DCMS), pulse DC magnetron sputtering (PDCMS) and deep oscillation magnetron sputtering (DOMS) at different nitrogen percentages. Deep oscillation magnetron sputtering (DOMS) is a brand new high power pulsed magnetron sputtering technique which can achieve virtually arc-free depositions of insulating films. In this research, the waveforms for target voltage and current have been compared among the three different magnetron sputtering techniques for the first time. The structural, mechanical, tribological and adhesion properties of the TiBCN coatings deposited by these three techniques will be described and compared.

Topical Symposia
Room: Tiki - Session TS1

Mechanical Properties Challenges for Greener Energy Applications and Emissions Reduction

Moderator: N.M. Jennett, National Physical Laboratory, UK, G. Dadheech, General Motors Research and Development Center

8:00am **TS1-1 Surface Engineering for Improving the Performance and Durability of Lithium Ion Batteries**, ***Y.T. Cheng*** *(yang.t.cheng@uky.edu),* University of Kentucky, US **INVITED**

Most lithium ion battery electrodes experience large volume changes caused by concentration changes within the host particles during charging and discharging. Electrode failure, in the form of fracture or decrepitation, can occur as a result of repeated volume changes. In this presentation, we will discuss our recent work on understanding the evolution of concentration, stress, and strain energy in electrodes under various charging-discharging conditions. We show that a dimensionless parameter, the electrochemical Biot number, may be used to characterize stress and strain energy evolution in an electrode. In particular, the electrochemical Biot number determines the maximum stress and strain energy. Based on analytic solutions, we propose tensile stress and strain energy based criteria for the initiation and propagation of cracks in electrodes. We will also discuss the effects of the solid-electrolyte interphase (SEI) that form naturally, as well as "artificial SEIs" by design, on the coupled chemical-mechanical degradation of electrodes. These studies may help understand the degradation mechanisms of electrodes and provide guidelines for developing lithium ion batteries with enhanced durability and performance.

8:40am **TS1-3 How Residual Stresses Affect the Elastic Properties of Ni**, *P. Gadaud,* ***X. Milhet*** *(xavier.milhet@ensma.fr),* Pprime Institute - UPR CNRS 3346 - Université de Poitiers - ENSMA - France, *O. Hubert,* ENS Cachan, France, *P.O. Renault, C. Coupeau*, Pprime Institute - UPR CNRS 3346 - Université de Poitiers - ENSMA - France

Thin films and coating are mainly used to functionalize the surface of underlying substrates. Generally, the films are not considered as load bearing since the film to substrate thickness ratio is close to zero. However, for some particular applications such as high pressure turbine blades for instance, it is necessary to relieve weight from the mechanical parts in order to limit the deformation by creep. The walls of the load bearing parts are therefore thinned and the coating to substrate thickness ratio increases as a result.

In this context, the influence of an oxide layer on the stiffening of pure nickel has been studied experimentally from 20°C to 600°C, using a resonant method. It is now known that the temperature dependence of Young modulus is not linear in nickel, resulting from magneto-elastic effects. In this study, it is shown that the stiffening of the nickel substrate can be finely tuned by the deposition conditions, up to its Curie temperature found at 370°C. A model using a magneto-mechanical coupling is proposed and discussed in this context. It supports the idea that the internal stresses of the coating play a key role in the observed behavior, even for very low levels of only few MPa.

9:00am **TS1-4 Strength and Fatigue Lifetime of Silicon in Hydrogen Atmosphere**, ***U. Arasu*** *(udhai21@gmail.com), S. Kamiya, H. Izumi*, Nagoya Institute of Technology, Japan

For the realization of green energy society with hydrogen fuel cycles, microelectronic devices especially such as physical and chemical sensors will have to go into hydrogen environment. There, many kinds of small scale structures with and without deposited thin films are expected to play also mechanically important roles. Since hydrogen is already known for its impact on metallic materials to significantly degrade the strength and fatigue lifetime, it is of urgent importance to acquire fundamental knowledge on possible effects of hydrogen also for the mechanical reliability of those microsystems [1].

When the sensors made with micro electro-mechanical systems (MEMS) technology are concerned, silicon is the most common material to compose fundamental mechanical members. From this point of view, strength and fatigue lifetime of single crystal silicon were examined in this study by applying cyclic stress to the surface while exposing to hydrogen gas atmosphere at room temperature and compared to the case in lab-air. The number of loading cycles to failure was already known to be enormously larger in less humid atmosphere, for example by a factor of 10^3 in air with 5% relative humidity (RH) than in lab-air with 40% RH [2]. However, it was newly found to be just slightly larger in hydrogen by a factor of only 10

with less than 5 % RH. In addition, static strength under monotonically increasing stress was also found to be reduced by 10% in hydrogen.

The mechanism for fatigue failure of silicon is not yet clear enough. Because of the effect of humidity mentioned above, it was once believed to be due to the surface oxide layer growing with cyclic stress even though the physical reason for intensive oxidation at room temperature is not explained [3]. Instead, hydrogen could be supplied also from surface water. The effect of hydrogen newly found suggests that fatigue degradation could possibly be caused by accumulation of internal defects such as point defects [4] or dislocations [5] whose activation energy would be reduced with hydrogen similar to the case of metallic materials. More details of fatigue and fracture behavior will be discussed in the presentation to further understand the mechanical reliability of silicon microstructures in hydrogen environment.

[1] Hirakata, H. et al., *Engineering fracture mechanics*, 77 (2010) 803-818.

[2] Tanemura, T. et al., *Journal of micromechanics and microengineering*, 23 (2013) 035032.

[3] Muhlstein, C.L. et al., *Acta materialia*, 50 (2002) 3579-3595.

[4] Kamiya, S. et al., *Proc.Transducers* (2013), 784-787.

[5] Namazu, T. et al., *Journal of microelectromechanical systems*, 11 (2002) 125-135.

Topical Symposia
Room: Tiki - Session TS4

Graphene and 2D Nanostructures
Moderator: C. Teichert, Montanuniversität Leoben, Austria, M. Chhowalla, Rutgers University, J. Huang, Northwestern University

9:20am **TS4-5 Synthesis, Properties, and Application of Two-dimensional Nano-Yttrium Oxide**, ***X. He***, *H. Liang (hliang@tamu.edu)*, Texas A&M University, US

Two-dimensional (2D) nanomaterials have attractive great attention due to their unique chemical, electrical, mechanical, and physical properties. In this research, 2D yttrium oxide (Y_2O_3) nanosheets (NS) was synthesized and characterized. Through in situ doping of copper, an interesting phase transformation from multiphase Y_2O_3 NS to single-phase cubic Y_2O_3 NS was observed. The multiphase Y_2O_3 NS-based metal-semiconductor (M-S) junction was found to be a Schottky barrier-based diode. The single-phase cubic Y_2O_3 NS was found to have negative resistance as an M-S junction. This was due to localized redox reaction/junction electronics. A case study was conducted to use the 2D Y_2O_3 NS as additives into a polishing slurry. Results showed that the global planarization was improved by 30%. This presentation discusses the structure-property of the new 2D Y_2O_3 NS and their potential applications for surface modification.

9:40am **TS4-6 Toward Growth of Few Layer Hexagonal Boron Nitride via Pulsed Laser Deposition**, ***N. Glavin*** *(Nicholas.Glavin.1@us.af.mil)*, Air Force Research Laboratory and Birck Nanotechnology Center, Purdue University, US, *M. Check*, *M. Jespersen*, University of Dayton Research Institute, US, *J. Gengler*, Spectral Energies, LLC, US, *T. Fisher*, School of Mechanical Engineering and Birck Nanotechnology Center, Purdue University, US, *A.A. Voevodin*, Materials and Manufacturing Directorate, Air Force Research Laboratory, US

Two dimensional (2D) hexagonal boron nitride (h-BN) is a unique dielectric material that can be utilized in configurations with other two-dimensional materials for next generation electronic systems. 2D boron nitride possesses key advantages over other dielectric materials in graphene-based devices by providing an atomically smooth surface free of dangling bonds and minimal sites for absorbed surface impurities. Testing of h-BN in graphene devices has been limited to exfoliation techniques and the search for synthetic synthesis of 2D h-BN is continuing with CVD technologies being recently reported, where ammonia borane decompositions at 1000°C was used [1]. Alternatively, pulsed laser deposition (PLD) techniques have a potential to create few layer h-BN at lower temperatures than CVD methods by utilizing a high energy of the plasma plumes. In this work a pulsed laser deposition from BN targets in Ar/N_2 background gas was used to explore possibilities for the h-BN growth at 700°C substrate temperatures. Substrates of Si (111), Al_2O_3 (0001) and basal planes of pyrolitic graphite were used to impose a hexagonal template for h-BN film growth. Laser power, repetition rate, background pressure, and sample-target geometry arrangements were varied to optimize film stoichiometry and structure. X-ray photoelectron spectroscopy analysis had shown BN formation but also indicated nitrogen deficiency and oxygen presence in the films. This could be corrected by Ar/N_2 mixture adjustments and inducing higher plasma ionization at the substrate with biasing. Raman spectroscopy indicated a formation of h-BN. The study had pointed one major challenge in the 2D h-BN growth by PLD, where energetic laser plasma plumes create a competition between high adatom surface mobility needed for crystalline film growth and collision induced displacements and disordering of the grown films. Possible approaches to overcome this challenge are discussed.

[1] L. Song et al., Nano Letters 10 (2010) 3209

10:00am **TS4-7 Reduction and Healing of Graphene Oxyde in Carbon Monoxide Atmosphere**, ***C. Ciobanu*** *(cciobanu@mines.edu)*, Colorado School of Mines **INVITED**

Graphene oxide holds promise as a carbon-based nanomaterial that can be produced inexpensively in large quantities. However, its structural and electrical properties remain far from those of the graphene sheets obtained by mechanical exfoliation or by chemical vapor deposition—unless efficient reduction methods that preserve the integrity of the parent carbon-network structure are found. Here, the authors use molecular dynamics and density functional theory calculations to show that the oxygen from the main functional groups present on graphene oxide sheets is removed by the reducing action of carbon monoxide; the energy barriers for reduction by CO are very small and easily overcome at low temperatures. Infrared and Raman spectroscopy experiments confirm the reduction in CO atmosphere and also reveal a strong tendency for CO to heal vacancies in the carbon network. Our results show that reduced graphene oxide with superior properties can be obtained through reduction in CO atmosphere.

10:40am **TS4-9 Mobility and Preferential Edge-Site Binding of Metal Adatoms on Graphene**, ***T. Hardcastle*** *(pmth@leeds.ac.uk)*, *C. Seabourne*, University of Leeds, UK, *R. Zan*, Manchester, UK, *R. Brydson*, University of Leeds, UK, *U. Bangert*, Manchester, UK, *Q. Ramasse*, SuperSTEM Laboratory, Daresbury, UK, *K. Novoselov*, Manchester, UK, *A. Scott*, University of Leeds, UK

Recent scanning transmission electron microscopy (STEM) observations [1 - 4] of metal-doped graphene have shown that the metal atoms bind exclusively to edge sites and contaminated regions, but not to the pristine regions of graphene. It was hypothesised from this that metal adatoms are very mobile on graphene at room temperature and therefore quickly migrate randomly across the lattice until they bind to more energetically-favourable edge sites by the time the samples reach the microscope. To test this hypothesis, we used density functional theory to optimise the structures of Al, Au and Cr atoms on the adsorption and edge sites of monolayer, bilayer and trilayer graphene and compared their energies and bonding characters. Then we calculated the migration energy barriers between the adsorption sites. It was found that Al, Au and Cr atoms form very weak bonds at the adsorption sites but form strong chemical bonds at the edge sites, and the migration activation barriers were all found to be very small: within an order of magnitude of kT at T = 300 K. These theoretical predictions are in striking agreement with the STEM observations. The implications of this are very broad. Much of nanotechnology relies on the passive manipulation physical matter on the microscopic level by means of harnessing naturally occurring processes under controlled conditions. Preferential edge-site binding is one such process which could be exploited in contexts such as patterned nanoscale devices, systematic edge-decoration of 2D nanoribbons and other nanoscale constructions where site-dependent bonding tendencies are an important ingredient in the fabrication process.

[1] R. Zan, Q. M. Ramasse, U. Bangert, K. S. Novoselov Nano Letters **12**, 3936 (2012)

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11:00am **TS4-10 High Energy Density Asymmetric Supercapacitor Based on Nitrogen Doped Graphene**, ***F.N. Sari***, *J.-M. Ting (jting@mail.ncku.edu.tw)*, National Cheng Kung University, Taiwan

Asymmetric supercapacitor has attracted a lot of attention due to its high specific energy density and power density. Carbon nanomaterials such as activated carbon, carbon nanotubes, and graphene have been demonstrated high performance of supercapacitor. However, there is still a need to improve the energy density of the supercapacitor. Transition metal oxide is one of the way to get high energy density by wide potential windows and high specific capacitance. This study demonstrates an asymmetric supercapacitors using nitrogen-doped graphene (NDG) as negative electrode and SnO_2-rGO nanocomposite as positive electrode. In this experiment, we used facile and effective method to synthesize NDG and SnO_2-rGO nanocomposite, i.e. microwave-assisted hydrothermal, to obtain

NDG with ethylene glycol as the reducing agent and ammonia as nitrogen source and to synthesize SnO_2-rGO nanocomposite. X-ray diffraction was used to investigate the crystal structure, X-ray photoelectron spectroscopy was used to observe the content of N-atom. Morphology and structural information were obtained by using scanning electron microscope and transmission electron microscopy analysis. Electrochemical measurement, such as cyclic voltammograms and galvanostatic were used to know performance of supercapacitor.

11:20am **TS4-11 Graphene-based Supercapacitors**, ***R.B. Kaner*** *(kaner@chem.ucla.edu), L. Wang, J. Hwang, S. Dubin, M. Li, H. Wang,* University of California, Los Angeles, US, *M. El-Kady,* Cairo University, Egypt, *M. Mousavi,* Tarbiat Modares University, Iran **INVITED**

Graphene is the ultimate two-dimensional material consisting of a single layer of sp^2 hybridized carbon. Chemical synthetic methods are needed in order to scale its synthesis for applications. Here we explore converting graphite into graphene oxide sheets, which readily disperse in water.[1] Using a 780 nm laser in an inexpensive LightScribe dvd drive, we can convert graphene oxide into a form of graphene with both high surface area and high conductivity.[2] This laser-scribed graphene can be patterned and used to make electronic devices such as sensors. When an electrolyte is combined with two pieces of laser-scribed graphene, a high performance supercapacitor is formed. These supercapacitors exhibit high power, good energy density and long cycle life.[3] They can be combined in series to increase voltage or in parallel to increase capacitance. By patterning the graphite oxide deposited on a plastic substrate, flexible microsupercapacitors can be made. These microsupercapacitors exhibit very high power along with enhanced energy density.[4]

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12:00pm **TS4-13 Characterization of 2D Nanomaterials with Spectroscopic Imaging Ellipsometry**, *P. Thiesen (pt@accurion.com),* Accurion GmbH, Germany, ***G. Hearn***, Accurion Inc., US, *U. Wurstbauer, A. Holleitner, B. Miller, E. Parzinger,* Technische Universität München, Germany, *U. Wurstbauer,* Columbia University, US, *C. Roling,* Technische Universität München, Germany

In the initial period of graphene research, the issue was to identify and characterize crystallites of microscopic scale. High spatial resolution imaging ellipsometry is a nondestructive optical method in thin film metrology with a lateral resolution as small as 1 µm. In a number of papers, Imaging ellipsometry has been applied to characterize graphene flakes with a size of a few micrometers. Ellipsometric contrast micrographs, delta and Psi maps as well as wavelength spectra [1],[2] and single layer steps in multilayer graphene/graphite stacks [3] have been reported.

Molybdenum disulfide is a layered transition metal dichalcogenide. From the point of current research, 2D nanomaterials based on MoS_2 are very promising because of the special semiconducting properties. The bulk material has an indirect 1.2 eV electronic bandgap, but single layer MoS_2 has a direct 1.8 eV bandgap. The monolayer can be used in prospective electronic devices like transistors (MOSFETs) or photo detectors. Delta and Psi Spectra of MoS_2 monolayers as well as maps of the ellipsometric angles will be presented. The practical aspect of single layer identification will be addressed and the capability of ellipsometric contrast micrographs as a fast tool for single layer identification will be demonstrated.

An additional focus will be on the modeling of the optical properties of 2D nanomaterials.

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12:20pm **TS4-14 Effect of Laser Irradiation on Structural and Electrical Properties of CVD Grown Graphene**, ***K. Ghosh*** *(KartikGhosh@missouristate.edu), M. Langhoff, A. Bhaumik,* Missouri State University, US, *W. Mitchel,* Air Force Research Laboratory, AFRL/RXA, WPAFB, US, *G.S. Tompa, N. Sbrockey, E. Gallo, T. Salagaj,* Structured Materials Industries Inc., US

There is a robust research effect on graphene due to its unique properties. For example, graphene exhibits remarkable electrical properties including its ability to travel ballistically over submicron distances. This motivates the scientific community to incorporate graphene into electronic devices. However, this absence of a bandgap diminishes graphene's utility in many devices. Theoretically, graphene's charge carriers can be tuned continuously to values as high as 10^{13} cm^{-2} and its mobility can be as high as on the order of 120,000 $cm^2/(V.s)$. While this entices researchers, there are difficulties due to graphene's linear *IV* curve and the lack of control over its doping levels. This research seeks to use laser irradiation to modify CVD grown graphene's properties. In the first instance, laser irradiation can be used to remove excess residue, thereby allowing graphene to better achieve its mobility potential. Nonetheless, one must remain cognizant that this process may cause differences in graphene's structural properties that may alter its electrical characteristics. Using field effect transistor measurements and Hall Effect measurements, this research addresses these alterations. It was found that laser irradiation in vacuum causes increased carrier concentration and decreased mobility. Alternatively, annealing the sample in forming gas causes decreased carrier concentration and increased mobility. Hence, it is seen that the doping level of the graphene can be modified using laser irradiation and annealing in different environments.

Exhibition
Room: California - Session Ex

Exhibition Keynote Lecture

11:00am **Ex1 Driving Commercial Applications and Exploring Scientific Questions with Reactive Multilayer Foils**, ***T. Weihs*** *(weihs@jhu.edu)*, Johns Hopkins University **INVITED**

Reactive multilayer foils are sputter deposited to contain thousands of nanoscale layers that can mix and produce bursts of heat upon ignition, through a self-propagating, exothermic formation reaction. The laminate foils are sold as a local heat source called NanoFoil® and can replace furnaces and hotplates in conventional soldering operations. The very localized heating provided by the foils enables bonding of materials with large mismatches in contraction on cooling (metals and ceramics), as well as temperature-sensitive electronic components. Other applications include sealing packages, igniting reactions, and providing controlled time delays. Multiple applications will be described in this presentation. In addition, novel in situ experiments and modeling will be described that explore the rapid formation reactions within the reactive multilayer structures. The experiments utilize nanocalorimetry, dynamic transmission electron microscopy and synchrotron X-ray diffraction to identify changes in the sequence of phase transformations that appear during the rapid reactions, as a function of heating rate, chemistry, and concentration gradients. To help understand these transitions we draw on molecular dynamic simulations and analytical models.

Hard Coatings and Vapor Deposition Technology
Room: Royal Palm 1-3 - Session B1-4

PVD Coatings and Technologies
Moderator: A.N. Ranade, The Boeing Company, S. Weißmantel, University of Applied Sciences Mittweida, J.W. Lee, Ming Chi University of Technology, Taiwan

2:10pm **B1-4-3 Structural, Mechanical and Tribological Properties of VN Thin Films Fabricated by PVD**, *H. Ahmad Aghdam (huseyin.aghdam@yahoo.com)*, Ataturk University, Turkey, ***I. Efeoglu***, *K.V. Ezirmik, H. Cicek, M. Tahmasebian Myandoab*, Atatürk University, Turkey, *Ö. Baran*, Erzincan University, Turkey

Self-lubricant coatings are getting more importance and application area. VN thin films forms vanadium oxide layer on the surface easily and can be used as a self-lubricant. Vanadium nitride thin films deposited on high speed steel substrates via closed filed unbalanced magnetron sputtering systems from high purity vanadium target and Ar/N_2 gas atmosphere at different bias frequency. In this work, we investigated microstructural, mechanical and tribological properties of VN thin films comparatively. X-ray diffraction, scanning electron microscopy and energy-dispersive X-ray spectroscopy were used to analyze the microstructure and elemental composition of the films. Pin-on-disc test system was used for analysis tribological properties.

2:30pm **B1-4-4 Compressive Intrinsic Stresses in Thin Films are Caused by Atom Insertion into Grain Boundaries**, ***D. Magnfält*** *(danma@ifm.liu.se)*, IFM Linköping University, Sweden, *A. Fillon*, Groupe de Physique des Matériaux, University of Rouen, France, *R. Boyd, U. Helmersson, K. Sarakinos*, IFM Linköping University, Sweden, *G. Abadias*, Pprime Institute - UPR CNRS 3346 - Université de Poitiers - ENSMA - France

Intrinsic stresses in thin films of refractory metals or other high melting temperature materials have previously been considered to originate from two additive mechanisms; compressive stress generated by ion bombardment induced point defects and tensile stress generated from attraction over grain boundaries [1]. The situation is remarkably different in low melting temperature materials where a compressive-tensile-compressive stress evolution with stress relaxation upon deposition interruptions is observed [2]. The latter parts of the stress evolution has been suggested to be the result of adatom diffusion into (and out from) grain boundaries [3]. We have previously shown that dense Mo thin films deposited at low temperature using energetic (<120 eV) vapor fluxes exhibit large, and film density dependent, compressive stresses (up to -3 GPa) with a stress free lattice parameter only slight larger than the bulk stress free lattice parameter. This implies that the film stress is not generated by defect creation in the grain bulk but by grain boundary densification [4]. In this work we demonstrate that this indeed is the case by showing that the compressive stress magnitude is linear function of the inverse grain radius (proportional to the grain boundary length) by depositing dense Mo films using energetic vapor fluxes onto seed layers with different grain sizes under otherwise identical deposition conditions. It is thus possible to conclude that compressive intrinsic film stresses are caused by atom insertion into grain boundaries and that this mechanism can be activated in both low and high melting temperature materials.

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2:50pm **B1-4-5 Model for Growth Stress in Polycrystalline Films: Comparison with Growth on Lithographically-patterned and Randomly-nucleated Films**, ***E. Chason*** *(eric_chason@brown.edu), C.-H. Chen, A. Engwal*, Brown University, US, *J.-W. Shin*, LAM Reserearch, US, *S.J. Hearne*, Sandia National Laboratories, US, *L.B. Freund*, University of Illinois at Urbana-Champaign, US

The residual stress in polycrystalline thin films can be large and depend strongly on the growth conditions. For instance, stress in electrodeposited Ni films can be 500 MPa (tensile) if the film is grown rapidly and -500 MPa (compressive) if the film is grown slowly. Furthermore, the stress progresses through different stages (tensile and compressive) as the film thickens and the microstructure changes. We have developed a model for residual stress that focuses on the stress that develops at the point where two adjacent grains meet as they are growing (i.e., the triple junction where the surface intersects the top of the developing grain boundary). The model predicts that the stress depends on the rate at which the grain boundary height increases, scaled by the parameter D/RL where D is the effective diffusivity, R is the growth rate and L is the grain size. Predictions of the model are compared with real-time measurements of stress evolution obtained using wafer curvature. In addition to randomly-nucleated films, we present results on lithographically patterned films in which the island spacing and grain boundary kinetics are controlled by the geometry

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3:10pm **B1-4-6 Influence of Tantalum on Structure, Electrical Resistivity and Corrosion Behavior of Sputtered Molybdenum Films**, ***A. Hofer*** *(anna.hofer@unileoben.ac.at)*, Montanuniversität Leoben, Austria, *N. Reinfried*, PLANSEE SE, Business Unit Coating, Austria, *G. Mori, C. Mitterer*, Montanuniversität Leoben, Austria

Molybdenum films are used as back-contact layers in solar cells and thin film transistor-liquid crystal displays. Corrosion has a major influence on the performance of these layers; however, it is challenging to select suitable alloying elements to enhance the corrosion behavior without deteriorating their electrical properties.

Within this work, Mo films with Ta contents ranging from 0 to 100 at.% have been deposited in a laboratory-scale unbalanced d.c. magnetron sputter system on glass substrates. All Mo-Ta films investigated show a body-centered cubic solid solution, without significantly effecting the electrical resistivity. To determine the electrochemical and the oxidation behavior, current density vs. potential measurements and climatic chamber exposure tests were done. Current density vs. potential measurements in a ventilated 0.9 % NaCl solution at room temperature show that the corrosion current decreases by a factor of 10 from 0.2 $\mu A/cm^2$ for pure Mo to 0.02 $\mu A/cm^2$ for about 20 at.% Ta. X-ray photoelectron spectroscopy of films exposed to a relative humidity of 85% at 85°C for 168 h indicates formation of a few nanometer thin and dense Ta_2O_5-rich layers providing an efficient barrier for further oxidation.

3:30pm **B1-4-7 The Fabrication and Property Evaluation of Zr-Ti-B-Si Thin Film Metallic Glass Materials**, ***Y.L. Deng***, *J.W. Lee (jefflee@mail.mcut.edu.tw)*, Ming Chi University of Technology, Taiwan

Recently, the thin film metallic glass (TFMG) materials have attracted lots of attentions due to their amorphous structure and unique properties. In this work, four Zr-Ti-B-Si TFMGs were fabricated on Si wafer and AISI 420 stainless steel disk substrates using four pure targets by a co-sputtering system. The target power of Ti target was adjusted to achieve TFMGs with different Ti contents. The amorphous phase of TFMG was determined by the X-ray diffractometer (XRD). The microstructures of thin films were examined by the field-emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM). A nanoindenter and scratch tester were used to evaluate the hardness and adhesion properties of TFMGs, respectively. The anti-corrosion properties of thin films were evaluated by the potentiodynamic polarization tests in 5.0 wt.% NaCl aqueous solution. Effects of Ti content on the microstructure, mechanical property and corrosion resistance of Zr-Ti-B-Si TFMGs were discussed in this work.

Keywords: Zr-Ti-B-Si, thin film metal glass, nanoindenter, scratch test, potentiodynamic polarization test

3:50pm **B1-4-8 The Effect of Pulse and Bias DC Voltage on Crystallization of TiNi Shape Memory Thin Films Deposited by Unbalanced Magnetron Sputtering**, ***H. Cicek*** *(h.cicek@atauni.edu.tr), I. Efeoglu*, Atatürk University, Turkey, *Ö. Baran*, Erzincan University, Turkey, *Y. Totik*, Atatürk University, Turkey

TiNi films were synthesized by unbalanced magnetron sputtering using a Ti51Ni49 target under four different deposition parameters to obtain crystalline structure. Silicon and thin copper plates were used as substrates. Structural, mechanical and transformation temperatures of TiNi films were investigated. To examine the structural properties of the fabricated films, XRD, SEM and EDS were used. Austenitic and martensitic transformation temperatures and hysteresis were observed via DSC (differential scanning calorimeter). We were obtained B2 (110) peaks from deposited films

without heat treatment. The lowest surface roughness value (Ra) obtained from R4 deposition condition (pulse dc power) as 0,012 µm.

4:10pm **B1-4-9 Influences of TMS Flow Rates on the Structure and Mechanical Properties of Cr-Si-C-N Thin Films Deposited by Pulsed DC Reactive Magnetron Sputtering**, ***D.H. Kao***, National Taiwan University of Science and Technology, Taiwan, *J.W. Lee (jefflee@mail.mcut.edu.tw)*, Ming Chi University of Technology, Taiwan, *C.J. Wang*, National Taiwan University of Science and Technology (NTUST), Taiwan

A series of Cr-Si-C-N thin films have been deposited by a pulsed DC reactive magnetron sputtering system with tetramethylsilane (TMS) gas addition as the Si and C source. The contents of Si and C in the thin film were increased by the TMS flow rate varied from 3 to 30 sccm. The hardness, adhesion and tribological properties were investigated by nanoindenter, scratch and wear test, respectively. The chemical composition and microstructure of Cr-Si-C-N thin films were determined by an Electron Probe Microanalyzer (EPMA), X-ray diffractometer (XRD), field-emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM), respectively. It was found that the nanocomposite microstructure was produced when the TMS flow rate increased to higher level. The hardness of thin film was strongly influenced by the TMS flow rate. Effects of Si and C contents on the microstructure and mechanical properties of Cr-Si-C-N thin films were further discussed in this work.

Keywords: Cr-Si-C-N thin film, tetramethylsilane (TMS), nanocomposite, nanoindenter, scratch tester

4:30pm **B1-4-10 Growth of Silicon Germanium Nanowires by Physical Vapor Deposition**, *K. Mahmood (khalid_mahmood856@yahoo.com)*, ***M. Asghar***, The Islamia University of Bahawalpur, Pakistan, *A. Ali*, GC University Faisalabad, Pakistan

In this study we report an economical way to grow silicon germanium ($Si_{1-x}Ge_x$) alloy of varying composition that has a number of potential applications in high speed electronic and optoelectronic devices. $Si_{1-x}Ge_x$ alloy was formed by physical vapor deposition (PVD) technique, where a silicon wafer of 300 μm was cleaned and placed in the PVD chamber. At a chamber pressure of 5×10^{-6} torr, the current of the molybdenum boat containing germanium metal was slowly increased till 150 A in 90 minutes. The as grown film was annealed at 800 ^{o}C for 50 minutes in a conventional furnace where temperature was increased/decreased in steps. X ray diffraction measurements reveal the presence of pure germanium, silicon germanium and silicon peaks at 2θ = 27.4, 28 and 28.45, respectively. Scanning electron microscopy (SEM) shows the presence of nanowires protruding out from the surface of the annealed film, whereas no such nanowires were found on the surface of as deposited samples in the SEM measurements. EDS and Raman measurements were found to be in consistent with the XRD and SEM results.

Advanced Materials for Modern Device Applications
Room: Sunset - Session C4-1

Thin Films for Energy Related Applications
Moderator: K. Yu, Lawrence Berkeley National Laboratory, US, J. Partridge, RMIT University

1:30pm **C4-1-1 Intermediate Band Materials for High Efficiency Solar Cells**, ***Y. Okada*** *(okada@mbe.rcast.u-tokyo.ac.jp)*, The University of Tokyo **INVITED**

For an ideal case where all the nonradiative recombination processes within solar cell were removed, the maximum conversion efficiency to thermodynamic upper limit becomes ~85% for a fully concentrated solar radiation. The maximum efficiency of a single-junction solar cell, however, is given by the Shockley-Queisser limit of ~31% for AM1.5 spectrum. The main physical processes that limit the efficiency of solar cell are the losses by thermal dissipation or thermalization, and non-absorption of low-energy below-bandgap photons. Thus improving the efficiency means developing methods to reduce these losses. One of the concepts well established today is to split the solar spectrum among multiple bandgap absorbers or sub-cells, e.g. tandem or multijunction cells. The other approaches employ advanced techniques such as hot carrier effects, multi-exciton generation (MEG), and intermediate-band (IB) [1]absorption in highly-mismatched semiconductor alloys and low-dimensional nanostructures such as quantum dots. Among various approaches studied, this presentation is devoted to reviewing the basic principle and development of the state-of-the-art technologies for quantum dot-based IB solar cells.

Quantum dot (QD) superlattice incorporated in the active region of a p-i-n single-junction solar cell can be used as a potential means of utilizing sub-bandgap infra-red photons to generate additional photocurrent, through absorption via superlattice miniband states, beyond that corresponding to the valence-to-conduction (VB-CB) band transitions.

Proposed implementation of QD-IB solar cell must be accompanied by two-step carrier generation via IB states, but it has been difficult to clearly demonstrate this concept at *room temperature* [2,3]. The demonstration of QD-IB solar cell is presently undergoing two research stages. The first is to develop technologies to fabricate high-density QDs array or superlattice with low interface defect densities at the heterointerfaces. The fabrication of QDs array is most commonly achieved by taking advantage of spontaneous self-assembly of coherent 3-dimensional islands in lattice-mismatched epitaxy, long known as Stranski-Krastanov (S-K) growth. The second stage is to realize partially or half-filled IB states in order to ensure an efficient pumping of electrons by providing both the empty states to receive electrons being photo-excited from VB, and filled states to promote electrons to CB via absorption of second sub-bandgap photons.

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2:10pm **C4-1-3 Growth of Cu_2ZnSnS_4 by Reactive Magnetron Co-sputtering**, ***P-A. Cormier*** *(pierre-antoine.cormier@umons.ac.be)*, University of Mons, Belgium, *G. Guisbiers*, Materia Nova Research Center, Belgium, *O. Lozano-Garcia*, *S. Lucas*, University of Namur, Belgium, *R. Snyders*, University of Mons, Belgium

The quaternary semiconductor Cu2ZnSnS4 (CZTS) is a promising material as absorber for thin film solar cells. Compared with conventionally polycrystalline cadmium telluride (CdTe), copper indium diselenide (CIS) and copper indium gallium diselenide (CIGS), CZTS is composed on earth abundant and non-toxic elements. Moreover, CZTS has an optimal band gap of 1.5 eV and a high absorption coefficient of 104 cm-1 [1].

The synthesis of CZTS thin films conventionally consists in a “two-step” process: metallic precursors are deposited by pulsed laser deposition, RF sputtering, electro-deposition or sol gel methods, and then thin films are annealed in presence of sulfur gas [2]. For large scale applications, it is necessary to develop a “one-step” process. Reactive magnetron sputtering, which is widely used in the coating industry, allows a good control of the plasma parameters, thin film growth conditions and thus film characteristics. Keeping in mind that the efficiency of the final solar cell strongly depends on the cristallinity of the CZTS absorber layer, reactive magnetron sputtering is a relevant technique for the growth of solar cell absorbers.

In this work CZTS films were synthesized by reactive magnetron co-sputtering and a particular attention was given to the influence of the experimental parameters (powers, pressure, gas mixture) on the thin film properties (micro-structure and composition).

CZTS thin films were deposited on Mo-coated soda lime glass substrates. H2S was used as reactive gas. Two metallic targets, zinc and copper-tin alloy were sputtered simultaneously in DC and pulsed DC mode, respectively. Experimental parameters such as the powers applied to the metallic targets, the total pressure, the H2S/Ar flow ratio were varied. The crystalline constitution, the chemistry as well as the microstructure of the deposited layers are evaluated by XRD, XPS and SEM, respectively.

A pure phase of kesterite CZTS was obtain at 5 mtorr, 10 sccm of each gas and a ratio of powers (CuSn/Zn) equal to 0.4. The increase of both the pressure and the gas flow rate was found to promote the synthesis of films composed on wurtzite and stannite CZTS phases with the presence of impurity phases such as Cu2SnS3, Cu2-xS, SnS and ZnS.

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2:30pm **C4-1-4 Preparation of Cu_2ZnSnS_4 Thin Films Using Pulsed Electrodeposition and Sulfurization**, ***L.J. Wang***, *J.-M. Ting (jting@mail.ncku.edu.tw)*, National Cheng Kung University, Taiwan

Cu_2ZnSnS_4 (CZTS) thin film solar cell is a low cost, environmental harmless solar cell. CZTS is a I_2–II–IV–VI_4 quarternary compound semiconductor. All the elements in CZTS compound are abundant on earth and non-toxic.

Up to now, several techniques have been used to fabricate CZTS thin films, including vacuum and non-vacuum methods. Vacuum methods include thermal co-evaporation, sputter deposition, pulsed laser deposition, and etc. Non-vacuum methods include electrodeposition and solution processes. Among the various methods, the electrodeposition followed by sulfurization

method has been found to be a low-cost and simple way to fabricate CZTS thin films.

In this research, various precursor films containing Cu, Zn, Sn, and S were first obtained by the electrodeposition of Cu , Sn, Zn, and ZnS in sequence on Mo coated glass substrates. The Sn and the ZnS layers were deposited under pulsed powers. For depositing the Sn layer, the current was pulsed while the voltage was pulsed for depositing the ZnS layer. The pulse frequency was varied when depositing ZnS. The deposition of ZnS was aimed to enhance the film quality, anticipating to receive the same advantage, i.e., improved conversion efficiency, as the precursor films obtained using sputter deposition. Before, CZTS precursor films were made by sputtering Cu, Sn, and ZnS (instead of Cu, Sn, and Zn). In doing so, the conversion efficiency of the CZTS films increased. If using Zn/Sn/Cu/Mo stacking sequence as the precursor layer ,the volume will become three times large after sulfurization, which may lead to defect in the CZTS film. Then, the quality of the CZTS film is reduced and the conversion efficiency is low compared to the ZnS/Zn/Sn/Cu/Mo sequence. So it is considered that using electrodepositing ZnS on Zn/Sn/Cu/Mo can also lead to the same advantage and reduce the cost of production. The obtained electrodeposited samples were then subjected to sulfurization in H_2S at 500℃ to 550℃ for 60 to 120 minutes. The as-deposited samples and the sulfurized samples were characterized using scanning electron microscope, X-ray diffraction, atomic force microscopy, Raman spectroscopy, ultraviolet-visible spectroscopy and Hall measurement .

2:50pm **C4-1-5 Solid-State Solar Cell-Based on $CH_3NH_3PbI_3$ Perovskite Sensitizer and Mesoporous Anatase TiO_2 Beads**, ***F. Firdausi***, *J.-M. Ting (jting@mail.ncku.edu.tw)*, National Cheng Kung University, Taiwan

Mesoporous metal oxide films have been usually adopted for solid-state dye sensitized solar cells (DSSC); however, difficulty in pore filling has been an issue in such nanoparticulate films. Beads structure were reported have higher surface area and to be better in electron transport than commercial nanoparticles P25. These characteristics makes anatase TiO_2 beads are capable to enhance the dye loading, leading to light absorbance and overall cell efficiency. Mesoporous anatase TiO_2 beads were prepared over two steps, including sol-gel and hydrothermal processes. In other hand, the $CH_3NH_3PbI_3$ perovskite material shows a direct bandgap and wide range of light absorption covering the visible to near-IR spectrum as well as high extinction coefficient, that would be very advantageous as a sensitizer. Here, anatase TiO_2 beads were used for the fabrication of solid-state perovskite sensitized solar cell, which can acts as an electron transporting layer. The perovskite sensitizer then were deposited onto the electron transporting layer. The crystal structure and the morphology of the resulting beads powders were examined using x-ray diffraction and scanning electron microscope, respectively. The surface area of final beads product were measured using BET analysis. And the cell performance were evaluated using a solar simulator.

3:10pm **C4-1-6 Preparation of Inkjet-printed Titanium Monoxide as p-Type Absorber Layer for Photovoltaic Purpose**, ***T.T.N. Nguyen*** *(thuysnga@gmail.com), Y.H. Chen, J.L. He*, Feng Chia University, Taiwan

Photovoltaic (PV) energy, concerned as the most abundant, clean and sustainable of all the renewable energy resources, is one of the most promising alternative solutions for the escalating demand of energy until date. It has reached a turning point for further penetrating the usage of various photovoltaic devices due mainly to the material and production costs. All photovoltaic devices practically combine a p-n junction, where one side as the absorber material ejects e-hole pairs, namely, electricity. The absorber layer can be organic material, inorganic material and/or the combination, while the approaches for manufacturing the absorber layer either in thin-film form or in bulk material have been paid much attention these days, all aiming to reduce material cost and production cost.

The intrinsic p-type cubic structure titanium monoxide (TiO) with suitable band gap energy, reasonable raw material cost and particularly simple stoichiometry has been chosen as a potential candidate in microelectronic applications and may have the opportunity to use as a p-type absorber layer for photovoltaic purpose. Among various printing technologies recently explored to fabricate solar cell layers, inkjet printing technology is really promising by virtue of the compatibility with distinct substrates and the non-contact ability with the substrate surface, leading to precisely patterned areas when using drop on demand (DOD) technology. Therefore, this work aims to fabricate TiO film by using inkjet printing technique.

Importantly, utmost efforts were made to adjust parameters when preparing TiO ink for optimal printability. After finishing ink-jet printing work, post-annealing treatment was carried out for obtaining final dense layer. Microstructure, optical and electrical properties of the printed TiO layer were revealed so as to evaluate the feasibility of using ink-jet printed TiO layer for photovoltaic system application.

3:30pm **C4-1-7 Magnetron Sputtering Deposition of Pd-Ag Thin Film Membranes onto Tubular Ceramic Supports for Hydrogen Separation**, *A.I. Pereira*, University of Minho, Campus Azurém, Portugal, *P. Perez, A. Mendes, L.M. Madeira*, University of Porto, Portugal, ***C.J. Tavares*** *(ctavares@fisica.uminho.pt)*, University of Minho, Campus Azurém, Portugal

Pd-Ag thin films were deposited by magnetron sputtering onto tubular alumina supports for hydrogen selective separation and purification purposes. The thin film columnar microstructure dictates the permeation fluxes through the membrane. From scanning electron microscopy analysis it was observed that different sputtering deposition pressures can lead to distinct columnar structure growth. X-ray diffraction patterns provided evidence of a Pd-Ag solid solution whose crystalline texture can be altered by the deposition pressure. The gas-permeation results, involving both nitrogen and hydrogen, have shown that the Pd-Ag membrane supported on porous Al_2O_3 is selective towards H_2, which demonstrates that the membrane has a reasonable capacity to hinder the permeation of this gas, providing only catalytic diffusion of atomic hydrogen. The selectivity factor α (H_2/N_2) obtained for the optimized membranes was studied as a function of temperature.

3:50pm **C4-1-8 Structural Evolution of Bias Sputtered $LiNi_{0.5}Mn_{1.5}O_4$ Thin Film Cathodes for Lithium Ion Batteries**, ***S.-H. Su*** *(minimono42@gmail.com), K.-F. Chiu, H.-J. Leu*, Feng Chia University, Taiwan

$LiNi_{0.5}Mn_{1.5}O_4$ (LNMO) thin films on stainless steel sheets have been synthesized using radio frequency magnetron sputter deposition followed by thermal anneal in atmosphere. Various negative biases were applied on the substrate during deposition. The structural evolution of LNMO thin films under different negative biases have been characterized by Raman spectroscopy and X-ray diffraction. The films under various biases exhibit crystalline spinel structure with ordered and disordered phases. The results indicate that the content of disordered phase LNMO increases with increasing negative bias. The electrochemical properties of LNMO thin films as cathode materials for lithium ion batteries were investigated. Two distinctive regions around 4.7 V and 4 V can be found in the discharge curves, corresponding to the reactions of ordered phase and disordered phase, respectively. The capacity of LNMO thin film electrodes under suitable negative bias can be optimized.

4:10pm **C4-1-9 CdSe Quantum Dots Decorated Doped and Pure α-Fe_2O_3 Thin Films for Hydrogen Production**, ***A. Ikram***, *S. Sahai, S. Rai, S. Dass, R. Shrivastav, V. Satsangi (vibhasatsangi@gmail.com)*, Dayalbagh Educational Institute, India

CdSe quantum dots decorated hematite (α- Fe_2O_3) thin film has been first time explored for its use in Photoelectrochemical water splitting for Hydrogen generation. Although hematite is a promising candidate for PEC system due to its optimum band gap (~2.1eV), chemical stability and low cost, but experimentally it does not met with the expected theoretical limit of efficiency for H_2 production. To improve its performance, various strategies viz bilayering, doping, swift heavy ion irradiation, quantum dots & dye sensitization etc have been adopted and reported in literature. This investigation point outs the simultaneous effect of quantum dots sensitization, doping and nanostructuring of hematite on the PEC response of hematite thin films. Quantum dot modified hematite film has secured the additional benefit of band edge alignment, high absorbance intensity despite of possessing its own nature. However poor conductivity still creates the hindrance to achieve the high efficiency which has been cast away by doping.

Thin films of pure and Zr doped α- Fe_2O_3 was prepared by sol-gel spin coating method. For the preparation of α- Fe2O3 thin film, precursor solution was made with 0. 3M $Fe(NO_3)_3.9H_2O$ in 2-Methoxyethanol and calculated amount of zirconyl chloride was added for 3 at% doping of Zr. These doped and undoped α- Fe_2O_3 films were then subjected to sensitization for 42hours in pre-prepared solution of CdSe quantum dots (purchased from Sigma-Aldrich). These films were implemented as photoanode in photoelectrochemical (PEC) cell for photoresponse measurements. XRD, SEM, Mott-Schottky and UV-visible spectroscopy techniques were used to characterize these thin films for deeper analysis. UV-Vis spectra reveals that CdSe sensitized hematite films showed higher absorbance in both doped and undoped form, but the effect of sensitization is more dominant with the doped sample of hematite thin films. Highest photocurrent density of 1.9 mA/cm^2 at 0.5 V/SCE was observed for doped 42H CdSe decorated α- Fe_2O_3 film. This remarkable enhancement in photoreponse is attributed to higher absorbance of CdSe sensitized doped α-Fe_2O_3 film.

Coatings for Biomedical and Healthcare Applications
Room: Sunrise - Session D2-2

Coatings for Bio-corrosion, Tribo-corrosion, and Bio-tribology

Moderator: J. Geringer, Ecole Nationale Supérieure des Mines de Saint Etienne, T. Shokuhfar, Michigan Technological University

2:10pm **D2-2-3 Discovering Nanotechnology and Picotechnology for Medical Applications**, ***T. Webster*** *(th.webster@neu.edu)*, Northeastern University, US **INVITED**

Inspired from biological systems, nanotechnology (and more recently, picotechnology) is beginning to revolutionize medicine including improving the prevention, diagnosis, and treatment of numerous diseases. This talk will summarize efforts over the past decade that have synthesized novel nanoparticles, nanotubes, and other nanomaterials to improve medicine. Efforts focused on the use of nanomaterials to minimize immune cell interactions, inhibit infection, and increase tissue growth will be especially emphasized. Tissue systems covered will include the nervous system, orthopedics, bladder, cardiovascular, vascular, and the bladder. Materials to be covered will include ceramics, metals, polymers, and composites thereof. Self-assembled nano-chemistries will also be emphasized.

Thus, this talk will:

· Summarize recent advances in novel coatings for medical devices

· Emphasize novel properties of nano and pico-technology derived materials, and

· Identify how such materials can be used to decrease inflammation, infection and improve tissue growth.

2:50pm **D2-2-5 Improved Corrosion Resistance of Mg-Y-RE Alloy Coated with Niobium Nitride**, ***W.H. Jin***, *G.S. Wu, P.H. Li, P.K. Chu (paul.chu@cityu.edu.hk)*, City University of Hong Kong, Hong Kong Special Administrative Region of China

Magnesium-based materials have attracted much attention in recent years due to their potential applications on cardiovascular stents and bone implants. However, their inadequate corrosion resistance in a physiological environment is the major obstacle limiting wider applications. In this work, a niobium nitride (NbN) film is deposited on Mg-Y-RE alloy (WE43) by reactive magnetron sputtering to improve the corrosion resistance. The structure of the nitride film is determined by X-ray photoelectron spectroscopy. The corrosion behavior of the untreated and NbN-coated WE43 is evaluated in simulated body fluids by electrochemical impedance spectroscopy, polarization tests, and immersion tests. The surface morphology of the samples before and after the immersion tests was examined by scanning electron microscopy to assess the extent of corrosion. Our results indicate that the corrosion resistance of the WE43 substrate is enhanced due to the formation of an anticorrosion nitride film and the NbN-coated WE43 may be promising in biomedical applications.

3:10pm **D2-2-6 Achieving Controlled Degradation and Better Biocompatibility of Magnesium by a Combination of Microarc Oxidation and Highly Textural Lamellar Mesostructured $Mg(OH)_2$ Coatings**, ***S. Nellaiappan***, *I.S. Park, M.H. Lee (mhl@jbnu.ac.kr)*, Chonbuk National University, Jeonju, Republic of Korea

The development of magnesium based biodegradable implants is indeed a fascinating area of research. The rapid corrosion rate, generation of a large volume of hydrogen gas, accumulation of the hydrogen bubbles in gas pockets adjacent to the implant, increase in local pH of body fluid, are the most critical limitations in using Mg and its alloys as implant materials. Surface modification is a viable approach to overcome these limitations and among them microarc oxidation (MAO) has received considerable attention. The architecture of MAO coatings on Mg and its alloys has a three-layered structure; a porous outer layer with several large-sized, deep pores/cavities, a middle layer with less porosity and a thin barrier layer. The presence of pores and cracks in the MAO coatings on Mg and its alloys has both beneficial and detrimental effects. The micropores and cracks generated during the microarc discharges helps to release residual stress of the coating. The presence of a porous outer layer would significantly improve the mechanical interlocking effect, the bonding area and stress distribution across the adhesive-substrate interface of the joints, resulting in higher bond strength. However, the presence of a higher pore density on the surface of the MAO coatings increases the effective surface area and thus the tendency of the corrosive medium to adsorb and concentrate into these pores. This would facilitate quicker infiltration of the corrosive medium into the inner regions of the coating and subsequently down to the substrate, thus deteriorating the corrosion resistance of the coating by changing its local pH. The porous nature of MAO coating deposited on Mg and its alloys promotes inhomogeneous degradation due to severe localized corrosion attack and an ever-increasing surface area to volume ratio. The pores could be sealed using sol-gel and polymer coatings. However, this could impair the bioactive property of the coating, limiting the growth of calcium phosphates. The approach made in the present study aims to improve the corrosion resistance and biocompatibility of Mg by a duplex treatment - microarc oxidation (MAO) as the first stage treatment followed by deposition of a highly textural lamellar mesostructured Mg(OH)2 coating by a chemical treatment. The MAO coating deposited on Mg offers an improvement in corrosion resistance. The lamellar mesostructured Mg(OH)2 coating deposited on MAO coated Mg provides a unique morphological features and a higher surface area to promote deposition of calcium phosphate. The beneficial role of this duplex treatment in achieving a controlled degradation and better biocompatibility of Mg is addressed in this paper. (This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MEST) (2011-0028709 & 2013R1A1A2012322)).

3:30pm **D2-2-7 Improvement of Titanium Wear and Corrosion Resistance by Plasma Electrolytic Oxidation: Effects of Applied Voltage and Annealing Treatment**, ***C. Laurindo*** *(carlos.laurindo@pucpr.br)*, *R.D. Torres, P. Soares*, Pontificia Universidade Católica do Paraná, Brazil, *J. Gilbert, S. Mali*, Syracuse University, NY, US

Despite the excellent properties of titanium such as, low density, corrosion resistance and biocompatibility, it usually presents poor tribological behavior. The Plasma Electrolytic Oxidation (PEO) promotes the transformation of the titanium substrate into a high hardness ceramic layer by the interaction of anodic oxide growth and plasma channel shock caused by the dielectric break down at high voltages, taking place in an aqueous electrolyte. The characteristics of the oxide layer, as well as its crystallinity can be tailored by changing the applied voltage during the PEO process or by a posterior annealing treatment at 600 – 800 ^{o}C. The aim of this work was to evaluate the influence of the PEO voltage and annealing treatment on the surface, wear and corrosion properties. Samples of cp-titanium were submitted to potentiostatic PEO treatment at 250 – 400V for 60 s in an electrolyte containing Ca and P. The surface morphology, cristallinity and roughness were evaluated by X-ray diffraction (XRD), scanning electron microscopy (SEM) and profilometer. The corrosion properties were evaluated by open circuit potential, electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization. The wear resistance was evaluated using a reciprocating linear ball on flat test machine. The results show that the annealing treatment increases the amount of rutile phase in the samples anodized with 250 and 300 V, but do not affect the crystallinity of the 350 and 400 V samples. The annealing also originated several cracks on the oxide layer for all annealed samples. There is an increase of wear resistance for the 250 and 300 V anodized samples after the annealing treatment. Rutile phase originated by annealing treatment or higher applied voltage is responsible for the wear resistance enhancement. However, the corrosion resistance is compromised due to the appearance of cracks on the oxide layer.

3:50pm **D2-2-8 Microstructure And Physical Properties Of Thermal Spraying AZO Coatings**, ***M.S. Leu*** *(menson@itri.org.tw)*, Material and Chemical Research Laboratories, Industrial Technology Research Institute, Taiwan

Zinc-oxide (ZnO) is a good photocatalyst in environmental purification owing to its simplicity, mild reaction conditions, and low cost. The novel Al-doped ZnO (AZO) powders with 3wt.% Al_2O_3 have been prepared as a photocatalytic coating ($>$ 1 0 μ m) by using the air plasma spraying system. During thermal spray process, the AZO photocatalysts could be made as nano-particles composite coating structures. In this study, t he obtained AZO coatings were characterized by an optical microscop (OM), X-ray diffraction (XRD), scanning electron microscop (SEM) combined with EDX and UV-vis spectroscopy . According to the experimental results, the XRD patterns of both AZO powders and coatings were assigned to wurtzite structure of ZnO. The photocatalytic activities of the specimens were evaluated by phoyocatalytic degradation of methyl blue under UV-light, and sunlight irradiation. There are three different microstructures observed in the coating by using OM and SEM examination, including nano-particles, slate layers and holes. The high proportion of the nanoparticles ($>$ 20%) and porosities ($>$ 15%) distributed in the coating are helpful to improve the photocatalytic effect and its life time. The adhesion between the AZO coating and stainless substrate can be attended to about 52 MPa. By compare with TiO_2 potocatalyst, it has 20% increasing on the phoyocatalytic degradation for this AZO coating.

4:10pm **D2-2-9 Significance of Corrosion and Tribocorrosion in Dentistry**, ***V. Barão*** *(ricardo.barao@hotmail.com)*, University of Campinas (UNICAMP), Piracicaba Dental School, Brazil, *M. Mathew*, Rush University Medical Center, US, *L. Faverani*, *W. Assunção*, Sao Paulo State University (UNESP), Brazil, *J. Yuan*, University of Illinois at Chicago, US, *M.F. Mesquita*, University of Campinas (UNICAMP), Piracicaba Dental School, Brazil, *C. Sukotjo*, University of Illinois at Chicago, US **INVITED**

The use of dental implant for tooth rehabilitation has increased significantly in the past several years.In oral cavity, dental implant is exposed to many challenging environment such as saliva, different pHs, food, mouthwashes, infection and mastication load.Titanium and its alloy have been used for dental implant due to their good strength, corrosion resistance, and biocompatibility. However, titanium reacts chemically in electrolytic solution, and degrades mechanically during mastication. This corrosion/wear process causes the release of metal ions and wear particles into the surrounding tissue. Titanium ions and particles induce cytotoxicity and inflammation at the implant-bone interface and surrounding soft tissue, contributing to bone loss, and possibly implant failure. Other factors such as smoking and diabetes have long been indicated as risk factors for dental implants survival. In this presentation, we will discuss the basic corrosion kinetics and tribocorrosion behavior of titanium into simulated oral environment (saliva pH, temperature, mastication load). The roles of infection (simulated by the presence of lipopolysaccharide), smoking products (e.g. nicotine and cotinine), caffeine and mouthwashes (e.g. chlorhexidine gluconate, cetylpyridinium chloride and hydrogen peroxide) on the electrochemical activity of titanium will be presented. The influence of hyperglycemic condition observed in patients with diabetes will also be discussed. The possible implications of corrosion on the lipopolysaccharide affinity and periodontopathogenic bacteria attachment will be assessed.

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Tribology & Mechanical Behavior of Coatings and Engineered Surfaces
Room: California - Session E1-2

Friction, Wear, and Lubrication: Effects and Modeling

Moderator: M. Chandross, Sandia National Laboratories, O.L. Eryilmaz, Argonne National Laboratory, K. Polychronopoulou, Khalifa University of Science, Technology & Research

2:10pm **E1-2-3 On the Effect of Substrate Structure on the Tribological Behavior of Coatings: an Orthogonal Design Study**, ***V. Fridrici*** *(vincent.fridrici@ec-lyon.fr)*, *J. Yang*, *P. Kapsa*, LTDS - Ecole Centrale de Lyon, France

Fretting wear is a complex phenomenon related to interactions between two sliding bodies under a low displacement amplitude. It can often occur in joints, oscillating splines, coupling, bearings… At the contact areas, liquid lubrication can be easily squeezed out, resulting in metal-to-metal contact and consequently an important local wear. To prevent from wear damage, therefore, many efforts have been done. Solid lubrication has been proven as an effective way to protect the surface of materials and to prolong the service lifetime of elements. Previous studies focused on the tribological behavior of various solid lubricants on the same substrate and then the best functional solid lubricant can be selected. In this study, in contrast, the research is performed on the effect of different substrates on the tribological behavior of a solid lubricant, with consideration of contact pressure, displacement amplitude, contact configuration, coating position (coating on flat substrate, coating on ball or cylinder substrate or coating on both substrates), and thickness of coating. The purpose of this study is to investigate the effect of different substrate structures on the lifetime and friction coefficient of a coating and to assess its importance when compared with the importance of other test conditions, with the use of statistical methods.

An aerosol sprayed MoS_2-based varnish was deposited on a cleaned and polished 304 stainless steel or AISI M2 flat surface and AISI52100 ball or cylinder surface at room temperature. The thickness of the coating was about 10 µm or 20 µm. The normal force was varied from 100 N to 700 N and the displacement amplitude was from ± 10 µm to ± 40 µm.

Some results could be drawn from this study. Firstly, the structure of the substrate does not affect the friction coefficient of the coating but it could change the coating lifetime greatly. The porosity in the substrate can greatly increase the lifetime of the coating by about a factor three. This is because the porosity in the substrate can increase the adhesion force between the coating and the substrate. The effect of structure of substrate on coating lifetime can be ranked in the first place, followed by the effect of contact configuration and displacement amplitude. Secondly, the friction coefficient is mainly dependent on the contact pressure which is mainly determined by both contact configuration and contact force. The friction coefficient is inversely proportional to the contact pressure. Thirdly, the thickness of the coating has no significant effect on the friction coefficient and lifetime of the coating.

2:30pm **E1-2-4 Investigation of Quaternary Metal Oxide Coatings for High Temperature Solid Lubrication**, ***V. Ageh***, *H. Mohseni*, *T. Scharf (scharf@unt.edu)*, University of North Texas, US

This presentation will discuss new solid lubricant coatings based on quaternary metal oxides with comparisons made to more traditional, lubricious ternary metal oxides. While much is known about ternary metal oxides in terms of their solid lubrication behavior and mechanisms from room to higher temperatures, little is known about quaternary oxides. For example, the role of the fourth element in determining the crystalline state and defect structure in relation to friction and wear properties. To this end, the system $(ZnTiZr)_xO_y$ was deposited by atomic layer deposition (ALD) and compared to our previously studied lubricious nanocrystalline ALD $ZnTiO_3$ coatings. The investigation focuses on the processing-structure-tribological property interrelationships of as-deposited and annealed (550, 700 or 850°C) coatings. ALD growth parameters, such as metal precursor pulse ratios and purge times, were varied to determine their effect on crystallinity and tribological properties. It was determined that the 550°C annealed coatings exhibited improved friction (steady-state friction coefficient of ~0.1 at higher normal loads) and wear rate ($\sim 1 \times 10^{-7}$ mm^3/Nm) compared to the as-deposited films. In contrast, degradation in tribological properties was determined for coatings annealed at 850°C due to the formation of spinel oxides. Overall, these quaternary metal oxides were determined to exhibit improved wear behavior compared to ternary metal oxides.

2:50pm **E1-2-5 Wear Characteristics of Mixed Lubricious Oxide Coatings**, ***S. Dixit*** *(sdixit@ptise.com)*, Plasma Technology Inc., US, *A. Erdemir*, *O.L. Eryilmaz*, Argonne National Lab, US, *R. Dixit*, DRS Research, US

Recently, solid lubricant materials have been developed to meet the engineering requirements. The applications of solid base lubricant materials have two prominent advantages. Firstly, the limitations of liquid base lubricant materials arising from the environmental conditions such as temperature and degree of vacuum can be effectively solved. Secondly, the dead weight of machine system can be reduced by removing the components required for feeding the lubricants. Although the most common dry-solid lubricants are graphite, MoS2, WS2, TaS2, and PTFE, they are limited in terms of their high temperature capabilities as well as their wear characteristics. Also, the lifetime is limited by the thickness of the coating overlay. There is a need for more robust coating system which is not only lubricious at room temperature and high temperature but also has inherent wear resistance.

Hence in this paper we propose novel thermal spray lubricious oxide coatings based on a crystal chemical approach as proposed by Ali Erdemir. The crystal-chemical approach can be used to predict the extent of adhesive interactions between two or more oxides at a sliding interface; hence, it can be used to predict frictional performance. Different combinations of the oxide materials are chosen based on their ionic potential differences and plasma sprayed to a thickness of 150 to 200 microns. Their composition, microstructure and room temperature and high temperature wear characteristics are reported in this paper.

3:10pm **E1-2-6 Empirical Interaction Potentials for Transition Metal Dichalcogenides from Force Matching Algorithm and Ab Initio Simulation**, ***P. Nicolini*** *(nicolpao@fel.cvut.cz)*, *T. Polcar*, Czech Technical University in Prague, Czech Republic

Among the various compounds of the transition metal dichalcogenides (TMD) family, MoS_2 is the most known member. Being used as a solid lubricant for several decades, it has been intensively studied both theoretically and experimentally. Nevertheless, there are still many unclear points regarding the lubrication mechanism.

Classical simulations have the potential of providing decisive insights into the tribological behavior of MoS_2. The key point of this kind of calculations is the particles interaction potential (also called force field, FF). In fact, the reliability of the results depends in large part on the FF ability to reproduce interactions with sufficient accuracy. This calls both for a carefully choice of the particular functional form of the FF and for an optimization of the parameters that comes into play in the FF.

The force matching (FM) approach[1] is a powerful technique to develop new FFs. Briefly, it consists of a least-squares fitting of the FF potentials to positions/forces data obtained from reference calculations at a higher level of description using sophisticated *ab initio* methods. Given these data as input, one optimizes the value of FF parameters minimizing the difference between reference and classical forces. In this way it is possible to parameterize FFs that not only allows to carry out classical molecular dynamics simulations (with reduced computational costs), but also permits to reach a high level of accuracy comparable with the one of the reference simulations.

In this contribution, we present the novel FF for MoS_2 developed using the FM approach and based on many-body interaction potentials. We then use the FF for simulating a sliding of TMD crystals, allowing us to understand the microscopic events that take place during the dynamical process. Moreover, this knowledge could lead to get insights into the tunability of factors involved in the tribological behavior.

[1] F. Ercolessi and J. B. Adams, *Europhys. Lett.*, **26**, 583 (1994).

3:30pm **E1-2-7 Local Friction of Rough Contact Interfaces with Rubbers using Contact Imaging Approaches**, ***A. Chateauminois*** *(antoine.chateauminois@espci.fr), C. Fretigny*, ESPCI / CNRS, Paris, France **INVITED**

When macroscopic bodies are pressed together, it is widely acknowledged that contact only occurs at localized spots between surface asperities. Friction thus involves the shearing of a myriad of micro-contacts which are distributed over length scales ranging from micrometers to nanometers. Although widely debated, the manner in which these micro-contacts locally dissipate energy remains obscure. In order to get more insights into this widely debated problem, spatially resolved measurements of frictional stresses are much needed. Unfortunately, most experiments only rely on measurements of friction force and of its dependence on load and velocity which are averaged quantities of local frictional properties. Then, validation of the local friction law and a fortiori of the related models remains rather indirect. In order to overcome these limitations, we have developped a method to measure local friction of rubbers by means of a contact imaging approach. Silicon rubber substrates marked on their surface are prepared in order to measure the lateral displacement field induced by the steady state friction of a glass lens. Then, deconvolution of this displacement field provides a spatially resolved measurement of the actual shear stress distribution at the contact interface. Using this technique, we will discuss how local friction of rubbers with randomly rough rigid surfaces depends on the details of surface topography. Some new developement with patterned surfaces will also be presented where crack like motions at the interface are evidenced during stick-slip motions.

4:10pm **E1-2-9 The Role of Mechanical Property Mismatch Between Film and Substrate on the Tribology Behavior of (Ti,Al,Si)N Coated Systems**, ***X. Huang***, *T.M. Shao (shaotm@tsinghua.edu.cn)*, State Key Laboratory of Tribology, Tsinghua University, China

(Ti, Al, Si)N nanocomposite coatings have been extensively studied due to their good tribological performances. The application of (Ti, Al, Si)N coatings on cutting tools has dramatically extended the tool lifetime and enables higher speed machining. However, the tribological behavior of a coating system is determined by both the coating and substrate. Generally, the superhard coatings have a high Young's modulus yielding the elastic mismatch between the coating and substrate. This elastic mismatch is possible to induce an early delamination or substrate plastic flow in the coating system and weakens the tribology behavior.

In this paper, the (Ti, Al, Si)N superhard coatings as well as traditional TiN and (Ti, Al)N coatings were deposited on high speed steel (HSS) and WC-Co by sputtering. The friction measurements were carried out to determine the failure load and stress of different coating systems. The cross-sections of the wear scars were prepared by focused ion beam (FIB) microscopy to analyze the failure modes in the friction tests. The electron back-scattering diffraction (EBSD) were used to determine the plastic flow underneath the wear scar. It was found that the failure mechanism of a superhard coating system is mainly due to the substrate yielding and interfacial shear. The large elastic mismatch between coating and substrate can weakens the tribology behavior of a coating system even though the coating is superhard.

4:30pm **E1-2-10 Stress Analysis of TiSiN Coatings Using Scratch Testing and Raman Spectroscopy**, ***J. Restrepo*** *(johansrestrepo@hotmail.com)*, Universidad Nacional Autónoma de México - Instituto de Investigaciones en Materiales, Mexico, *E. Camps*, Instituto Nacional de Investigaciones Nucleares, Mexico, *S. Muhl*, Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Mexico

The TiSiN coatings were deposited using Pulsed Laser Deposition such that the samples had a range of silicon contents. The films were characterized by SEM-EDS (chemical composition and surface morphology), X-ray diffraction (crystalline structure and grain size) and Nanoindentation (hardness and Young's modulus). Other tribological properties of the coatings were evaluated using scratch testing, this was carried out without causing severe cracking or total spallation of the coatings, using two counter materials (1/16" balls of 100CR6 and Al2O3). To study the plastic deformation caused by the application of the load during the scratch measurements we used 3d profilometry. Finally, micro-Raman spectroscopy was employed to study any deformation-induced morphology changes and the chemical reactions produced, under the different loads, by the contact with the counterpart materials. The results showed that the silicon content increased the mechanical properties of the coatings but the effect was greatest around to 8 at Si%, with this resulting in a hardness of 35Gpa. The Raman spectroscopy after the scratch test showed that the load produced a lattice deformation in the crystalline structure of the coatings and that the formation of titanium oxide was dependent on the applied load and the counterpart material.

4:50pm **E1-2-11 Tribology of Silica Nanoparticle-Reinforced Hydrophobic Sol-Gel Derived Composite Coatings**, ***D. Banerjee*** *(dbanerje@mix.wvu.edu), A. Kessman, E. Chambers, K. Sierros, D. Cairns*, West Virginia University, US

Hydrophobically functional coatings can be used to protect surfaces and therefore improve the performance and lifetime of a broad range of applications such as optoelectronics and touchscreens. Organic-inorganic hybrid materials such as silica sol-gel coatings are particularly effective and allow for advantageous low-temperature processing and substrate compatibility. However, the functional molecules in these coatings are susceptible to abrasive wear and thus lose their performance over time in the harsh environments typically encountered. Moreover, the matrix of the coating itself is inherently porous and susceptible to wear.

To combat these problems, a silica nanoparticle reinforced matrix was developed to increase hardness and wear resistance of the overall coating. This study involved the abrasive wear analysis of fluorinated composite silica particle reinforced sol-gel silica coatings dip-coated on glass substrates. Varying amounts of silica nanoparticles from 0.5 to 10 wt% of the precursor weight were added to examine the structural dependence of abrasive wear mechanisms to elucidate strengthening mechanisms that could lead to improvements of coating properties. Abrasion was conducted using an in-house built reciprocating polishing wear apparatus. Characterization of the water contact angle of the coating was conducted to determine the hydrophobic functionality after wear cycles. Atomic force microscopy, lateral force microscopy, nanoindentation, nanoscratch, contact angle goniometry, XPS, SEM, and optical microscopy were performed at intervals of abrasive wear testing to characterize these wear mechanisms and the functional degradation of the coating.

5:10pm **E1-2-12 Friction Effects During the Extrusion of Al Alloy Through Severe Plastic Deformation**, ***A. Sahai*** *(sahaiankit13@gmail.com), K. Hansraj*, Dayalbagh Educational Institute, Agra, India

Severe Plastic Deformation (SPD) is well known process for producing nano-structured material from coarse material. The Equal Channel Angular Pressing (ECAP) is the most efficient SPD solution that allows very high strains to be imposed, leading to extreme work hardening and microstructural refinement. Microstructure and mechanical properties of ECAPed specimen are governed by ECAP die geometry and process conditions. It is of interest to control the mechanical properties in order to maximize the efficiency and industrial feasibility of ECAP process. In this work the effect of friction is studied for different die geometries upto 4 passes on ECAPed specimen (Al alloy, Al6061) using Finite Element simulation technique. The microstructural analysis is performed for best die geometry in different friction conditions. Also, FEM results concluded that the value of equivalent strain obtained in the processed specimen and extrusion force required for pressing the specimen shows a close dependency on ECAP die geometry (Intersection angle), die and billet interface friction. It is also observed that via multiple passes, with each pass, corner gap in the die changes with modifications in the friction conditions. This study is beneficial in developing high quality, high strength products in manufacturing industry on account of its ability to change microstructure of materials.

New Horizons in Coatings and Thin Films
Room: Royal Palm 4-6 - Session F2-2

High Power Impulse Magnetron Sputtering (HIPIMS)
Moderator: D. Lundin, Université Paris-Sud 11, France, S. Konstantinidis, University of Mons

1:50pm **F2-2-2 HiPIMS Deposition of Titania Coatings for Photocatalytic Applications**, ***G. West*** *(g.west@mmu.ac.uk)*, Dalton Research Institute, Manchester Metropolitan University, UK, *M. Ratova*, Queen's University, UK, *P. Kelly*, Dalton Research Institute, Manchester Metropolitan University, UK

Titanium dioxide is a material that has been used in a range of thin-film applications, particularly as on optical coating, but more recently in the exploitation of its inherent photocatalytic and hydrophilic properties – self cleaning, anti-fogging, or antimicrobial surfaces, for example. In order to exhibit photocatalytic activity, it requires the necessary anatase, or mixed anatase/rutile crystalline phase to be achieved during film growth, or via post-deposition treatments. However, these growth or post-deposition treatment conditions generally require the substrate to withstand elevated temperatures (>400^{o}C), which precludes the use of thermally sensitive substrates such as polymeric web. The ability to produce crystalline photocatalytic titania onto such substrates would provide significant opportunities for commercial exploitation in a range of industries.

HiPIMS deposition has been shown previously to be able to deliver high energy to a depositing film, whilst maintaining a relatively low substrate temperature, enabling the deposition of high-quality functional films on thermally sensitive substrates such a polymeric web. This paper provides a study of the growth of as-deposited crystalline titania coatings via the HiPIMS process, the effect on photocatalytic and hydrophilic activity, and their application onto polymer substrates.

Activation of titania photocatalysts normally requires incident UV radiation, due to the high band gap of titania (~3.2 eV). In order to achieve activity at wavelengths approaching or including visible light, a variety of dopant materials can be used to modify the bandgap of the titania coating. In addition to the study of HiPIMS deposition of pure titania, an investigation of the growth and properties of coatings reactively sputtered from a tungsten-doped titanium target, also via HiPIMS, is presented.

2:10pm **F2-2-3 Reactive HiPIMS of Oxides: Discharge Current Evolution and Hysteresis Behaviour**, ***T. Kubart*** *(Tomas.Kubart@angstrom.uu.se)*, Uppsala University, Angstrom Laboratory, Sweden, *D. Lundin*, Université Paris-Sud 11, France, *U. Helmersson*, Linköping University, IFM, Plasma and Coatings Physics, Sweden **INVITED**

In High Power Impulse Magnetron Sputtering (HiPIMS), high degree of ionization of the sputtered material is achieved thanks to the high instantaneous peak powers and thus high plasma densities. HiPIMS is therefore beneficial for deposition of dense films, uniform coatings on complex-shaped surfaces as well as interface engineering for improved adhesion. In reactive HiPIMS, compound thin films are deposited from metal targets in an atmosphere of argon and a suitable reactive gas, such as oxygen. As a result of the interaction between sputtered metal and the reactive gas, the relation between the deposition rate and reactive gas flow is nonlinear and typically exhibits hysteresis behaviour.

This contribution deals with reactive HiPIMS, mainly with the effect of HiPIMS on the hysteresis. First, results from various hysteresis studies are summarized. We show that the frequency dependence indicates an influence of gas rarefaction. The optimum frequency is related with the gas refill time as demonstrated by experiments with targets of different dimensions. Formation of compound at the target surface is also accompanied by a pronounced change in the shape of discharge current waveforms. In HiPIMS, the discharge behaviour is dominated by ionized oxygen sputtered from the target. This is shown from the ion energy distribution functions of different species characterized by energy and time resolved mass spectroscopy. Finally, we simulate the target surface sputtering by TRIDYN code. The predicted time to completely remove the compound from a target is in reasonable agreement with measurements.

2:50pm **F2-2-5 Chopped-HiPIMS for the Deposition of Films of Ti, TiN and Ti-Si-N**, ***P. Barker*** *(Paul.Barker@empa.ch), J. Patscheider*, EMPA (Swiss Federal Laboratories for Materials Science and Technology), Switzerland

Chopped-HiPIMS (c-HiPIMS), a modified version of High Powered Impulse Magnetron Sputtering, HiPIMS, has been employed for depositing Ti containing thin films on various substrates. The technique consists of decomposing single HiPIMS pulses into a sequence of pulses. In this manner, the pulse is a 'chopped' variant of HiPIMS, thus termed chopped-HiPIMS. This technique has been used to deposit films of metallic titanium, titanium nitride, TiN, and titanium silicon nitride, Ti-Si-N. These coatings were characterized by XPS, XRD, SEM and nanoindentation. Higher deposition rates than under equivalent HiPIMS parameters were attained, with increases in deposition rates of up to 150 % by c-HiPIMS for Ti deposition. At the same time, stoichiometric TiN and Ti-Si-N films could be grown without the need for a substrate bias or additional heating of the substrate during deposition, as is required when using traditional direct current magnetron sputtering, DCMS. The c-HiPIMS TiN films have comparable hardnesses to DCMS films grown with heat or bias, at around 25 GPa (compared to ~ 20 GPa for HiPIMS with similar conditions).

Data from optical emission spectroscopy, OES, and atomic absorption spectroscopy, AAS, showed little differences between HiPIMS and c-HiPIMS. This suggests that the ion density and ion-to-atom ratios reaching the substrate, produced by both methods, are similar. Thus the increase of sputtered particle flux in c-HiPIMS appears not to be a result of relaxed ion retention (ion trapping) in the near-cathode region. Further, temperatures recorded at the substrate are similar for both methods, indicating similar ion energies. Thus, in c-HiPIMS the reduced gas rarefaction and increased gas refill at the substrate leads to the prevention of self-sputtering and thereby favours increased argon bombardment of the target.

3:10pm **F2-2-6 Cr and CrN Thin Films Deposited by HiPIMS-DOMS**, ***J.C. Oliveira*** *(joao.oliveira@dem.uc.pt), F. Ferreira, R. Serra, A. Cavaleiro*, SEG-CEMUC, University of Coimbra, Portugal

Magnetron sputtering technologies are widely used for the deposition of thin films in many commercial applications. In recent years, high power impulse magnetron sputtering (HiPIMS) and modulated pulse power magnetron sputtering (MPP), a variation of HIPIMS, have shown great advantages as compared to the conventional (DCMS) and pulsed dc magnetron sputtering (PMS) techniques. Unlike the simple one pulse shape in HIPMS, MPP generates a high density metal ion plasma by first producing a weakly ionized plasma followed by a transition to a strongly ionized plasma within one overall pulse. However, commercially available HiPIMS plasma generators have not been able to create stable and arc-free discharges in many reactive processes.

In this work a new method of generating an arc free discharge for reactive HiPIMS has been used. A Cyprium plasma generator from ZPulser has been used to deposit both Cr and CrN thin films on silicon and steel substrates using the new deep oscillation magnetron sputtering (DOMS) technique. The effect of the peak current and deposition pressure on the structural (X-Ray diffraction), chemical (Electron Probe Micro-Analysis) and morphological (Scanning Electron Microscopy) properties of the films was studied. All depositions were done at constant average power (1.2 KW) and a constant thickness of 1 micrometer was deposited for all the films. The peak current increases with the deposition pressure while the peak voltage behaves in a symmetrical way. Increasing the peak current at constant pressure (0.8 Pa) allows the deposition of more compact Cr films. The columnar structure similar to the one obtains by DCMS slowly transforms in a dense morphology without any porosity. The hardness of the Cr films also increases from 9 to 16 GPa. The mechanical properties of the CrN thin films (hardness and friction coefficient) were studied by nano-indentation and pin-on-disk tests on the films deposited on steel substrates. The wear rate of the films was evaluated from the inspection of the pin-on-disk tracks by white light interferometry.

3:30pm **F2-2-7 Effect of Synchronized Pulsed BIAS on the Properties of Reactive HiPIMS Sputtered Al-Cr-N Thin Films**, ***G Mark*** *(guenter.mark@melec.de), J. Loeffler, M. Mark*, MELEC GmbH, Germany

SIPP – technology (**SIPPS**uper **I**mposed **P**ulse **P**ower) offers significant advantages in HiPIMS sputtering combined with a synchronized pulsed BIAS. The synchronized pulsed BIAS is able to operate fully synchronized or phase shifted. The phase shift can be set at any time of the pulse period. Variances of the pulse duration, pulse period or phase shift settings directly result in different thin film properties like microstructure, morphology or mechanical properties especially with respect to residual stresses. Using the example of reactive sputtered Al-Cr-N thin films we demonstrate the influence of **H**ighly **C**harged **M**etal **I**ons **P**article **E**xtractions using SIPP on the texture, film morphology and stress development. The characterization of the plasma with respect to the ionization moment of the sputtered metal particles was carried out by spectrometer analysis. In order to examine and compare the metal ion density the spectrometer analysis was performed both at the target and the substrate.

3:50pm **F2-2-8 The Influence of Deposition Parameters on the Structure and Properties of Aluminum Nitride Coatings Deposited by High Power Impulse Magnetron**, ***C.T. Chang***, *Y.C. Yang*, National Taipei University of Technology, Taiwan, *J.W. Lee (jefflee@mail.mcut.edu.tw)*, Ming Chi University of Technology, Taiwan

Among the design of experiment (DOE) methods, Taguchi experimental design is becoming a popular one for industrial application due to its efficiency and convenience.

The aluminum nitride thin film is an important coating material due to its unique properties, such as wide band gap, good thermal and chemical stability and dielectric property. In this work, the aluminum nitride thin films were fabricated using the high power impulse magnetron sputtering (HIPIMS) process through the Taguchi experiments to determine the optimum deposition condition. The duty cycle, pulse frequency and substrate bias were varied to systematically study the structure and property evaluation of AlN coatings. The crystalline phase and microstructure of AlN coatings were evaluated by X-ray diffractometer (XRD) and scanning electron microscopy (SEM), respectively. The mechanical properties of AlN coatings were explored by nanoindenter, scratch tester and wear tester. Influences of duty cycle, pulse frequency and substrate bias of HIPIMS on the peak power density, microstructure and mechanical properties of coatings were discussed in this study through the Taguchi analysis.

Keywords: high power impulse magnetron sputtering, aluminum nitride thin film, duty cycle, pulse frequency, mechanical properties, Taguchi analysis

4:10pm **F2-2-9 Investigation of Negative Ions in Reactive HIPIMS Discharges Operating in Different Inert Gases**, *M. Bowes*, The University of Liverpool, UK, ***P. Kelly***, Surface Engineering Group, Manchester Metropolitan University, UK, *J. Bradley (J.W.Bradley@liverpool.ac.uk)*, University of Liverpool, UK

During reactive magnetron sputter deposition of oxides, bombardment by high-energy negative oxygen ions can have detrimental effects on the structural, optical and electrical properties of developing thin films. The amount of high-energy atomic oxygen negative ions (O^-) detected at the substrate has been found to be strongly correlated to the secondary electron emission coefficient of the target surface.

By means of energy-resolved mass spectrometry, time-averaged O^- ion energy distributions (IED) have been obtained during reactive high power impulse magnetron sputtering (HiPIMS) of titanium in the presence of oxygen and different inert gases: X/O_2 where X = Ne, Ar, Kr or Xe. The high-energy population of O^- ions was found to peak close to the value of the absolute applied target potential averaged over the pulse on-time. The high-energy O^- ion yield was estimated by integrating over the high-energy population of the IEDs and was found to decrease markedly for heavier inert gases. The decrease in negative ion emission is believed to be a consequence of lower potential secondary electron emission coefficients for heavier gases due to lower ionization potentials.

Surface analysis techniques were applied to titania samples deposited onto both glass and silicon substrates via reactive HiPIMS of titanium in Ar/O_2 and Kr/O_2 gas mixtures for a number of different discharge conditions.

Applications, Manufacturing, and Equipment
Room: Tiki - Session G1

Innovations in Surface Coatings and Treatments
Moderator: M. Arndt, OC Oerlikon Balzers AG, C. Metzner, Fraunhofer FEP, Germany

2:10pm **G1-3 Engineered Coatings for Machining High Temperature Alloys and Stainless Steel**, ***A. Inspektor*** *(aharon.inspektor@kennametal.com), C. McNerny, M. Rowe, M. Beblo, N. Waggle*, Kennametal Incorporated, US

During the cutting process the tool undergoes a number of wear processes that depend on the properties of the cutting tool, on the nature of the machined part and on the particular machining conditions. This paper will discuss the challenges in machining high temperature alloys and Stainless Steel and present recent advances in the development of new tools for these applications. The paper will discuss new PVD coating architecture for precise control of tool properties during the cut and will be illustrated by a case study in turning Stainless Steel.

2:30pm **G1-4 State-of-the-Art in Al_2O_3 Deposition by Industrial-Scale Dual Magnetron Sputtering**, ***D. Diechle*** *(dominic.diechle@walter-tools.com), V. Schier*, Walter AG, Germany

High performance metal cutting applications require wear-resistant PVD coatings. The exceptional properties of aluminum oxide predestine this material as tool coating due to high temperature stability and low thermal conductivity. The talk will give an overview on the state-of-the-art in industrial-scale production of Al_2O_3 thin films and a detailed analysis.

The first part of the talk gives an introduction in the principals and the advantages of the dual magnetron sputtering system at the example of an industrial-scale PVD coater. The Al_2O_3 deposition by dual magnetron sputtering from metallic aluminum targets at non-equilibrium conditions will be described in detail.

The second part focuses on the analysis of the aluminum oxide coatings. The metastable thin films were characterized by determining the nano hardness and reduced elastic modulus by nanoindentation, the thickness by calo test, the surface and cross-section by scanning electron microscopy and the microstructure by X'ray diffraction.

In the end an example for the industrial application of Al_2O_3 thin films in tool coatings will be presented. Furthermore a short description of future challenges in the industrial-scale production of high quality Al_2O_3-based coatings will be given.

2:50pm **G1-5 Coating Design at Work**, ***J. Rechberger*** *(johann.rechberger@fraisa.com)*, Fraisa SA, Switzerland **INVITED**

Coating design is certainly a popular key word in thin film technology. If applied to high performance cutting tools and components this expression covers a broad field of technical aspects and has many interdisciplinary facets. The coating itself may be perfectly fine but in the end it is the application that decides if the design was good or insufficient. A weak interface can be as detrimental as a rough surface structure or a highly stressed film at corners and sharp edges . Cutting tool tests have told us how sensitive tool performance can be to seemingly minor wear protection design changes. The actual coating architecture with texture and grain size control, multilayer sequence, composition gradients, etc. are certainly the basis for a good coating. But the substrate surface grinding structure, mechanical pre- and after- treatments, ion etch procedures, and modern laser surface modifications are certainly additional possibilities and necessities to achieve the best "design to work". Performance analysis of carbide endmills, and high speed steel taps will be shown. The results of these case studies explain how important the design is for the development of successful wear protection thin films.

3:30pm **G1-7 A Novel Mathematical Approach to Surface Engineering Subject to Blistering**, ***M.H. Nazir*** *(hnazir@bournemouth.ac.uk), Z. Khan, M. Hadfied*, Bournemouth University, UK

This paper presents a new conceptual and analytical model for blistering initiation and propagation especially useful in predicting the service life of coating systems. The model proposes novel equations governing blister growth combining the concepts of fracture mechanics and diffusion law.

This paper presents the case study of blistering problem as two parts namely: diffusion and fracture mechanics problems. The governing equations for both the parts have been designed separately and combined in order to form the governing law for blister propagation based on specific toughness functions.

These toughness functions introduce the concept of dual-mode propagation (mode 1 and mode 2) of the interfacial crack depending upon the two mode adjustment parameters. The two-parameters family of toughness functions are useful not only for analysing various levels in blister growth but also for analysing the toughness of crack edge interfaces which are considered to be tougher in mode 2 compared to mode 1. The developed modelling approach provides with a reliable and efficient prediction method for blister growth rate and mechanism.

The mechanistic and diffusion based approaches are combined to provide a platform for generalised solution. This model plays an important role in understanding the dislocation at the interface of thin elastic film of coat and the substrate.

Keywords

Mathematical modelling, simulation, coatings, delamination, blistering, buckling

3:50pm **G1-8 Wettability Control of Nano-columnar DLC Coating by Electron Beam Post-Treatment**, ***T. Aizawa*** *(taizawa@sic.shibaura-it.ac.jp)*, Shibaura Institute of Technology, Japan, *F. Hoe*, University Malaysia Technology, Malaysia

Amorphous carbon, either with or without hydrogen (a-C:H or a-C), or diamond-like carbon (DLC) is characterized by its disordered state of sp2

and sp3 nanostructure. This hybrid system in the amorphous film controls the functionality of final product to suit various applications, in particular, biomedical applications. Aiming at the surface energy control of DLC, the vague columnar structure of PVD-DLC (DLC via physical vapor deposition) is strictly modified to a finer and self-organized columnar structure, where a new phase of high-density, graphitic inter-columnar structure is embedded into the originally low-density columnar matrix. This self-organization process is confirmed by the structural and surface characterizations. Contact angle measurement is performed to demonstrate that the low surface energy of the as-deposited PVD-DLC is changed by post-treatment via the electron beam irradiation. That is, the original hydrophobic state is chemically modified to be hydrophilic or super-hydrophilic states by formation of network structure of high surface energy phase among low surface energy matrix. This surface modification is accompanied with nano-columnar regularization. The wettability control process of the nano-columnar DLC film is driven by the mechanism of columnar growth and interconnected network formation of columns during the post treatment.

Coatings for Use at High Temperatures
Room: Sunrise - Session A1-1

Coatings to Resist High Temperature Oxidation, Corrosion and Fouling
Moderator: M. Weaver, The University of Alabama, V. Kolarik, Fraunhofer Institute for Chemical Technology ICT, D. Litton, Pratt & Whitney

8:00am **A1-1-1 Modification of Aluminide Bond Coatings for EB-PVD TBCs with Pd and Pt Using a Novel CHC-PVD Method**, ***R. Swadzba*** *(rswadzba@gmail.com)*, Institute for Ferrous Metallurgy, Poland, *T. Jung*, Fraunhofer IST, Germany, *U. Schulz*, DLR - Deutsches Zentrum für Luft- und Raumfahrt, Germany, *L. Swadzba*, *M. Hetmanczyk*, *B. Mendala*, *B. Witala*, Silesian University of Technology, Poland

The study concerns diffusion aluminide coatings modified with Pd and Pt using a novel CHC-PVD technique as a cost-effective alternative for Pt-aluminide bond coatings conventionally used for EB-PVD Thermal Barrier Coatings.

While Pt-aluminide diffusion coatings provide excellent high temperature oxidation resistance and are commonly applied as bond coatings for EB-PVD TBCs new alternatives are being sought for due to high prices of Pt. In order to maintain high oxidation protection along with simultaneous cost reduction alternative Pd+Pt-aluminide bond coatings have been developed using a novel technique applying Physical Vapor Deposition method and high activity "out of pack" diffusion aluminizing. The obtained coatings with varying thicknesses of Pt and Pd were compared and studied using FEG-SEM and EBSD techniques as well as XRD. The microstructures of the coatings were studied after every technological step including annealing of Pd-Pt layers, diffusion aluminizing and heat treatment. Prior to YSZ deposition using EB-PVD the coatings were put under pre-oxidizing treatment in order to form a thin α-alumina TGO. The microstructure of the pre-oxidized TGO was studied in detail using high resolution S/TEM and TEM.

8:20am **A1-1-2 Modeling of the Interdiffusion Between a γ- Ni-Al Alloy and a Pt Coating for Thermal Barrier Coating System Applications**, ***P. Audigié*** *(pauline.audigie@ensiacet.fr)*, *A. Rouaix-Vande Put*, CIRIMAT, University of Toulouse, France, *A. Malié*, *S. Hamadi*, Snecma, SAFRAN Group, France, *D. Monceau*, CIRIMAT, University of Toulouse, France

In the last 10 years, the Pt-rich γ-γ' bond-coatings have been studied for their corrosion and oxidation resistance, and as a lower cost alternative to β-(Ni,Pt)Al bond-coatings in thermal barrier coating (TBC) systems. To optimize their fabrication and durability, it is essential to investigate how the interdiffusion with the Ni-base superalloy substrate takes place and what are the factors which can influence it. This study deals with the interdiffusion modeling of a γ-Ni-Al alloy with a pure Pt coating. Heat treatments at 1100°C for 15 min to 10h were performed in-situ in a high temperature X-ray diffraction apparatus under primary vacuum. The α-NiPt(Al) phase with the $L1_0$ crystal structure formed very rapidly as it was already observed after a fast heating (40°C/min) and a 100 sec dwell at 1100°C. This implies the very fast Al diffusion to the surface. This α phase vanished after 45 min – 1h at 1100°C and the γ'-$(Ni,Pt)_3Al$ phase appeared. A two-phase γ-γ' microstructure was obtained and no significant evolution was observed from 2h30 to 10h. Cross-sections of annealed samples were analyzed by SEM, EDS and EPMA. It was observed that voids formed at the interdiffusion zone / base material interface. Concentration profiles and EDS maps confirmed that voids were located at the Pt diffusion front and in the Al depletion zone. Then, a finite-difference method was used to model the fluxes and the concentration profiles in the Ni-Al-Pt system by considering the chemical potential gradients. Experimental and calculated profiles were found to be in good agreement for the γ-phase systems. The fitted interdiffusion coefficients were in the range of those found in the literature. The diffusion paths were determined and compared with the predicted results. Simulations in the γ-phase were performed to predict the possible nucleation and location of the α-phase. The diffusion of vacancies was also considered in order to test its ability to predict the occurrence of Kirkendall voids.

8:40am **A1-1-3 Role of Boron on Oxidation Behavior of NiCrAlYHfTi Alloy in H_2O and CO_2 Environments**, ***K.A. Unocic*** *(unocicka@ornl.gov)*, *B.A. Pint*, Oak Ridge National Laboratory, US

Cast NiCrAl alloys, co-doped with Y, Hf, Ti and/or B, were evaluated at 1100°C and 1150°C in dry air, wet air (10 and 50% H_2O) and CO_2-10%H_2O in order to study the effect of boron on alumina scale growth and adhesion. Ti and B additions were combined to potentially form stable TiB_2 precipitates in the alloy. Cyclic (1-h cycle time) testing at 1150°C in air with 10%H_2O clearly showed improved scale adhesion with the addition of B after 500 cycles. After only 200 cycles at 1100°C, only minor differences in mass change were observed. Microstructural characterization is in progress including quantifying the effect of boron on internal oxidation and alumina microstructure using transmission electron microscopy (TEM).

The environment effects (10%H_2O+air vs. 10%H_2O+90%CO_2) were also studied at 1100°C on the oxidation behavior of co-doped NiCrAl alloys with no significant difference being observed. Further analysis will be carried out.

Keywords: NiCrAl, water vapor, CO_2, Reactive Elements, a-Al_2O_3, Boron

9:00am **A1-1-4 Effect of Overaluminizing on Microstructure and High-temperature Degradation of a CoNiCrAlY Coating**, ***D. Naumenko*** *(d.naumenko@fz-juelich.de)*, *A. Jalowicka*, Forschungszentrum Jülich GmbH, Germany, *M. Ernsberger*, *R. Herzog*, MAN Diesel & Turbo SE, Germany, *L. Singheiser*, *W.J. Quadakkers*, Forschungszentrum Jülich GmbH, Germany

MCrAlY (M = Ni, Co) coatings are commonly used on gas-turbine and jet-engine components as oxidation resistant overlay coatings and bondcoats for thermal barrier coatings. In order to further improve the oxidation resistance and/or increase the reservoir of the scale forming element (Al) the MCrAlY coated components are often subjected to an additional treatment using e.g. CVD or slurry aluminizing. In the present work the microstructure and oxidation behavior of an overaluminized Co-rich MCrAlY-coating on a Ni-based superalloy has been investigated in the temperature range of 925 to 1075°C for exposure times up to 5000 hours. The analytical studies of the oxidized coatings by SEM were complemented with numerical thermodynamic calculations using the software package Thermocalc.

The microstructure of the studied CoNiCrAlY coating was observed to change dramatically due to the applied aluminizing treatment. As expected, the amount of the Al-rich beta NiAl phase increased considerably in the outer part of the coating. In addition, the Al-enrichment resulted in precipitation of Co and Cr rich phases and reduction in the amount of the matrix phase (gamma Ni solid solution). During high-temperature oxidation exposure, depletion of the studied overalumized coating did not result in formation of the gamma prime (Ni3Al) phase. Rather the sub-scale formation of the Co/Cr-rich phases was observed, which was found to affect the alumina scale growth. Therefore the effect of aluminizing on the microstructure of the studied CoNiCrAlY coating appeared to be different from that commonly observed with Ni-rich MCrAlY-coatings.

9:20am **A1-1-5 Comparison of the High Temperature Oxidation Behavior of the Nano and Conventional NiCrAlY Coatings Developed by LVOF Process**, ***N. Rana*** *(nidhiranathakur@gmail.com)*, *R. Jayaganthan*, *S. Prakash*, Indian Institute of Technology Roorkee, India

Development of thermally sprayed nanocoatings is attracting attention of the various researchers due to the improved performance of the nanocoatings as compared to its corresponding conventional coating. On other hand thermal spray process is best suited for the application of high temperature resistant coatings for oxidation, corrosion, erosion and wear. The present investigation deals with the high temperature oxidation performance of the thermally sprayed NiCrAlY nanocrystalline on superalloy substrate. The NiCrAlY nanocoatings deposited by LVOF technique on the superalloy substrate were oxidized cyclically at 900°C upto 100 cycles. The weight change per unit area and its square were plotted against number of cycles to monitor the kinetics of oxidation. It was compared with the similar curves obtained by oxidation of the NiCrAlY conventional coatings sprayed by similar process. The oxidized coatings were further characterised by XRD, FESEM/EDS and X-ray mapping techniques. The NiCrAlY nanocotings found to be more resistant to the oxidation as compared to the conventional NiCrAlY coatings due to the formation of more adherent, uniform and compact oxide layer.

9:40am **A1-1-6 Hot Corrosion Behavior of MCrAlY Coatings Containing Ru, Mo and Ir**, ***K. Yuan*** *(kang.yuan@liu.se)*, *R. Lin Peng*, Linköping University, Sweden, *X.H. Li*, Siemens Industrial Turbomachinery AB, Sweden, *S. Johansson*, Linköping University, Sweden, *Y.D. Wang*, University of Science and Technology, Sweden

With the increasing requirement of improved fuel efficiency and reduced CO_2 emission, the operation temperature of components, like turbine blades and vanes, is being pushed to higher and higher levels in modern gas turbines. To maintain the high performance of the components at higher

temperatures, high-temperature coatings are needed to provide the resistance against oxidation and corrosion. In a variety of coatings, such as bond-coats in thermal barrier coating system or overlays, MCrAlY coating (M usually for nickel and/or cobalt) is one such candidate, capable to be further developed by modifying its composition. For instance, alloying elements such as yttrium, silicon and tantalum, at small proportions, have been added into MCrAlY coatings to enhance their oxidation resistance and/or mechanical properties. The aim of this study is to investigate the corrosion behavior of the coatings with Ru, Mo and Ir during high temperature exposure. Coatings with and without Ru, Mo and Ir were denoted as alloyed coatings and reference coatings, respectively.

The reference and alloyed coatings were sprayed by high-velocity oxy-fuel process on a Ni-based superalloy IN792 to form overlays. The hot corrosion tests on those coatings were performed by cyclic exposures in a mixture of Na_2SO_4 and K_2SO_4 at 900°C. Thereafter, the surfaces and cross-sections of the tested samples after different cycles were investigated in scanning electron microscope (SEM) equipped with energy dispersive system (EDS) and wavelength dispersive system (WDS). The technique of X-ray diffraction (XRD) was used to distinguish the surface species formed during the corrosion process.

A variety of oxides, e.g. α-Al_2O_3 and Cr-Co rich spinels, were found on the coating surface after the hot corrosion process. The formation of the oxides was significantly affected by the coating composition. The surface of the reference Ni-based coating was mainly covered by a dense and nodule-shaped alumina. But a more complex morphology of isolated islands embedded in a plate-shaped matrix was found in the alloyed Ni-based coatings. In the Co-based coatings, alloying Ru, Mo and/or Ir promoted the formation of Cr-Co spinels even though Al_2O_3 was still the matrix oxide to cover the whole coating surface. It seems as if the addition of Ru, Mo and/or Ir in MCrAlY coatings plays a role on promoting the formation of non-α-Al_2O_3 oxides to respond to the hot corrosion attack.

10:00am **A1-1-7 Low Temperature Hot Corrosion of Disk Alloys**, ***J. Nesbitt*** *(JNesbitt@nasa.gov), S. Draper, A. Martone, R. Miller, J. Smialek*, NASA Glenn Research Center, US **INVITED**

Hot corrosion can occur in gas turbine engines in the presence of sulfur and salt in the temperature range of approximately 650°C to 900°C. At lower temperatures, the sulfates are not molten, and at higher temperatures, component temperatures are above the dew point of the sulfates and little sulfate deposition may occur. Hence, this type of attack has previously been observed in the lower temperature regions (below blade or vane platforms) of aero gas turbines as well as on blades and vane airfoils of marine gas turbines which typically operate at temperatures below those of aero gas turbines. In the lower portion of this temperature range (~650°C to ~750°C), the attack occurs by pitting and is referred to as Type II attack. Due to increasing temperatures in aero gas turbines, this type of pitting attack is now being seen in turbine disks. Previous experimental work has shown that low temperature corrosion can significantly decrease the low cycle fatigue (LCF) life of disk alloys. However, coatings used to protect blade alloys are not always suitable for disk alloys due to different mechanical properties of the different alloys and components.

The low-temperature, hot corrosion behavior of an advanced disk alloy has been examined in the temperature range of 650°C to 800°C. Tests have been performed with coupons coated with Na_2SO_4 or $60Na_2SO_4$-$40MgSO_4$ salt mixtures and exposed to low gas flows containing various O_2/SO_2 concentrations (10-1000 ppm SO_2). The extent of attack has been determined by sample weight change or pit depth. Both uniform attack and pitting has been observed with various O_2/SO_2 concentrations. For the uniform, non-pitting attack, the corrosion increased with increasing temperature and increasing SO_2 concentration in the cover gas. A summary of the work to date including pit morphology and chemistry will be presented as well as coating requirements and future coating directions.

10:40am **A1-1-9 Nano-Structured Coatings For Supercritical Steam Turbines Applications**, ***F. Perez*** *(fjperez@quim.ucm.es), M. Mato, M. Lasanta, G. Alcala, S. Castañeda*, Universidad Complutense de Madrid, Spain

In many applications at high temperature, micro-structured coatings have been applied in order to protect structural materials against a wide range of different environments: oxidation, metal dusting, sulphidation, molten salts, steam, etc… The resistance achieved by the use of different kind of coatings have been optimum, and with late design such as TBC´s and FGM´s coatings. Although, the lifetime of them are related with inter-diffusion, and different CET as main degradation mechanisms.

In the case of supercritical steam turbines, many attemps have been made in terms of micro-structural coatings design, mainly based in aluminides, and another diffusion coating systems. In order to consider another alternatives to minimize those problems, nano-structured coatings, applied by PVD and HIPIMS-PVD based in Cr, Ti and Al design, have been applied onto high temperature structural materials in order to analyze their high temperature oxidation resistance in steam environments.

The gravimetric results obtained have been analysed upto 2.000 hours, jointly with the evaporation behavior analysed by TG-Mass spectromnetry. Excellent results have been achieved for the nano-structured coatings tested. Those results are comparables with the results obtained for micro-sctructured coatings, and in some case better for nano-structured coatings.

According to the results obtained, the nano-structured coatings have a potential application as protective systems in high temperature, for some applications will be proposed.

11:00am **A1-1-10 Determination of the Sources of Intrinsic Stress-state for ß-NiAl Diffusion Coatings under Thermo-cyclic Oxidizing Conditions**, ***C. Oskay*** *(oskay@dechema.de), M. Galetz, M. Rudolphi, M. Schütze*, DECHEMA-Forschungsinstitut, Germany

The oxidation protection of Ni-based superalloys under thermo-cyclic oxidizing service conditions relies on the mechanical and chemical stability of diffusion ß-NiAl coatings, which provide the necessary Al-reservoir for the protective oxide scale formation. Outwards diffusion of Al and the interdiffusion with the substrate causes Al-depletion in the coating and therefore the coating possesses different mechanical properties depending on the present Al concentration hence on the existing phases throughout the exposure. Moreover, owing to the interdiffusion with the substrate, the Al content of the substrate is increased and thereby the alloying elements such as Ta, Mo and W precipitate within the γ/γ' matrix and build up the secondary reaction zone with altered microstructure.

Imposition of intrinsic and external mechanical stresses on the oxide scale and the coating can lead to mechanical failure, if a critical stress threshold is exceeded. Intrinsic mechanical stresses in the coating and the oxide scale determine the load bearing capability of the respective zone, since their magnitude defines the tolerable external stress. In this study, sources of intrinsic stress in the oxidation influenced zones of the composite material system have been studied.

Sources of intrinsic stress under thermo-cyclic oxidizing conditions for the coating are stresses arising from temperature changes, phase transformations and the stress relaxation due to creep deformation. In the case of oxide scale, the intrinsic stress-state depends on the stresses arising from temperature changes, oxide growth, internal oxidation and surface curvature.

11:20am **A1-1-11 Oxidation Resistance of Low Velocity Oxy Fuel Sprayed Al_2O_3-$13TiO_2$ Coating on Nickel Based Superalloys at 800°C**, *N.K. Mishra,* ***S.B. Mishra*** *(sbmishra@mnnit.ac.in), R. Kumar*, MNNIT Allahabad, India

Oxidation of metals and alloys have been identified as a serious problem for high temperature applications such as boilers, internal combustion engines, gas turbines, fluidized bed combustion, and industrial waste incinerators. Superalloys are used for high temperature applications but these alloys lack resistance to oxidation. In the present investigation, Al_2O_3-TiO_2 coating is deposited on two nickel based superalloys Superni 718 and AE 435 by Low Velocity Oxy Fuel process. The coating has been characterized for SEM, XRD and surface roughness. . Cyclic oxidation experiments with one cycle of heating at 800 °C for 60 min and cooling in air for 20 min were conducted for up to 50 cycles. The kinetics of oxidation of coated and bare superalloys is established with the help of weight change measurements. The LVOF sprayed coating has shown good adherence to the substrate. The AE 435 superalloy has shown lowest resistance to oxidation in comparison to Superni718 superalloy.

11:40am **A1-1-12 Influence of Process Parameters on the Microstructure of Aluminide Coatings Obtained by VPA on Directionally Solidified NI Superalloy**, ***B. Witala*** *(bartosz.witala@polsl.pl), L. Swadzba, M. Hetmanczyk, B. Mendala, G. Moskal,* Silesian University of Technology, Poland, *R. Swadzba,* Institute for Ferrous Metallurgy, Poland, *L. Komendera*, Subcarpathian Aviation Cluster, Poland

Ni-based superalloys are usually employed in industrial applications where good mechanical performance, corrosion and oxidation resistance at high temperatures is required. The present study describes microstructure investigation in relation to process parameters of diffusion aluminizing of directionally solidified Ni superalloy and Ni alloy with VPA method. Estimating parameters such as time, temperature, chemical composition of granules, used chlorides or fluorides activators has been related to the evolution of microstructure. Vapor phase aluminizing process has been carried out at 900 - 1100°C. Aluminide coatings formed on a nickel-base superalloy have been characterized in their as-coated condition. The studies were focused on thickness, chemical composition, mechanism of coatings formation and diffusion processes. The microstructural characterization

involved use of X-ray diffraction (XRD), electron microscopy (SEM), chemical analysis in microareas (EDS) and glow discharge optical emission spectroscopy (GDOS).

Hard Coatings and Vapor Deposition Technology
Room: Royal Palm 1-3 - Session B4-1

Properties and Characterization of Hard Coatings and Surfaces

Moderator: C. Mulligan, US Army ARDEC, Benet Laboratories, J. Lin, Southwest Research Institute, U. Beck, BAM Berlin

8:00am **B4-1-1 Development of a Systematical Methodology for Predicting Coated Milling Tools' Efficiency Including its Qualification Based on a Comparison of PVD-Coatings Deposited by the DC- and HIPIMS-Process**, *M. Busch (Marc.Busch@ipt.fraunhofer.de), F. Klocke, T. Bergs,* ***M. Ottersbach***, Fraunhofer Institute for Production Technology IPT, Germany, *K.-D. Bouzakis, E. Bouzakis,* Aristoteles University of Thessaloniki, Greece, *W. Kölker, O. Lemmer*, CemeCon AG, Germany

Eventough approximately 80% of all cutting tools applied in industrial shop floors are coated, the tools' cutting performance very often is far behind performance potentials promoted by many researchers. A reason for this is that in demanding applications (e.g. turbomachinery manufacturing) the coating properties have to be exactly customized to cope with the individual machining conditions. If this is not the case, a reliable improvement in the tool performance cannot be guaranteed. For instance, PVD coatings' performance varies depending on the temperature in the cutting zone. In turn, the temperatures generated during the machining process are mainly influenced by the applied machining conditions, in special the cutting velocity, as well as the definition of the tool and coating materials. In case of the cutting process milling the challenges even itensify owing to the repetitive and discontinuous tool engagement. Therefore, the objective must be to ensure the reliability of (newly) developed coatings in a production environment, without resorting to the extensive and expensive practical testing that is currently used for evaluating proper tool specifications and machining conditions.

Against this background, in this paper a systematical methodology based on analytical, experimental and numerical investigations for predicting coated tools' efficiency in milling is introduced. In the frame of the investigations different types of coatings are examined regarding their adherent cutting wedge thermal and mechanical loadings during the material removal process. The Ti-based PVD coatings are deposited using the standardized DC and the innovative HIPIMS process. After a metallographic analysis of the coatings, nano-indentation and impact tests at ambient and elevated temperatures are performed. On this base the strength properties as well as the brittleness and fatigue behaviour of the coatings can be modeled. Moreover, inclined impact tests for evaluating the films' adhesion are applied. These results, along with FEM-based calculations of the cutting wedge thermo-mechanical loads facilitate the prediction and explanation of the coated inserts' cutting performance at various conditions. The findings are validated by dint of endurance testing.

8:20am **B4-1-2 Origin of Compressive Stress in CVD TiB_2 Hard Coatings**, ***N. Schalk*** *(nina.schalk@unileoben.ac.at), C. Mitterer, J. Keckes,* Montanuniversität Leoben, Austria, *C. Czettl,* Ceratizit Austria GmbH, Austria, *M. Penoy, C. Michotte*, Ceratizit Luxembourg S.àr.l., Luxembourg

CVD hard coatings deposited on cemented carbide substrates typically exhibit tensile residual stresses, which are mainly due to differences in the thermal expansion coefficients of coating and substrate material. However, CVD TiB_2 coatings have been reported to show high compressive residual stresses, although their thermal expansion coefficient is larger than that of the cemented carbide substrate. Within this work, TiB_2 coatings were deposited on TiN base-layers using thermally activated CVD. The coating composition was examined using wave-length dispersive X-ray spectroscopy and electron energy-loss spectroscopy, yielding compositions close to stoichiometry. Slices of the coating were prepared and synchrotron X-ray nanodiffraction experiments were performed in transmission geometry to illuminate the origin of the compressive stresses. Thus, the gradients of stresses and texture could be determined as a function of the coating thickness with a resolution of 100 – 200 nm. Coating microstructure as well as mechanical and tribological properties were investigated by scanning and transmission electron microscopy, the $\sin^2\psi$ method, nanoindentation and ball-on-disc tests. Pole figure measurements revealed no pronounced texture for the TiN base-layer and a (111) texture for the TiB_2 top-layer, evidencing that there is no epitaxial relation between both layers. Hardness and compressive residual stresses of ~45 GPa and ~2.4 GPa, respectively, could be determined for the morphologically almost featureless TiB_2 coatings. The combination of high hardness and compressive residual stresses results in excellent wear properties.

8:40am **B4-1-3 Effect of Zr on Thermal Stability and Oxidation Resistance of Cr-Al-N**, ***L. Chen*** *(chenli_927@126.com),* Central South University, China

Multinary Cr-Al-N coatings are excellent candidates for advanced machining processes due to their excellent mechanical and oxidation resistance. However, the transformation of Cr-Al-N into stable structure w-AlN above 1000 ^oC results in a rapid decline of the mechanical properties, which limits their applications with work temperature exceeding 1000 ^oC. Here, we study the effect of Zr on thermal stability and oxidation resistance of Cr-Al-N with cubic structure. Alloying with Zr into Cr-Al-N results in a hardness increase from ~25.7 GPa for $Cr_{0.49}Al_{0.51}N$ to ~32.4GPa for $Cr_{0.45}Al_{0.49}Zr_{0.06}N$. An early formation of w-AlN (~1000 ^oC) followed by the transformation to Cr_2N and finally Cr via N-loss during annealing of Cr-Al-N occurs. Zr is very effective in promotion of the thermal stability of Cr-Al-N, where the formation of w-AlN, Cr_2N and Cr at ~1300 ^oC during annealing of Cr-Al-Zr-N follows the first precipitation of c-ZrN at ~1200 ^oC. However, Zr addition leads to a decrease in oxidation resistance of Cr-Al-N coatings. After 10h exposure in air at 950 ^oC, Cr-Al-N and Cr-Al-Zr-N coatings exhibits oxide scales of ~0.11 and 1.86 um, respectively. Interest is that elevating oxidation temperature up to 1000 ^oC for 10h results in a decline in oxide scale to ~0.78 um for Zr-containing coating, whereas Cr-Al-N coating shows an oxide scale of ~0.17 um.

Keywords: CrAlN; CrAlZrN; thermal stability; oxidation resistance

9:00am **B4-1-4 An In-situ Study of the Fracture Toughness and Cracking Behaviour of the CrAlN/Si_3N_4 Nanocomposite Coatings**, ***S. Liu*** *(sl559@cam.ac.uk), C.E. Davis,* University of Cambridge, UK, *X. Zeng,* Singapore Institute of Manufacturing Technology, Singapore, *W. Clegg,* University of Cambridge, UK

Cr-based nanocomposite coatings are attracting increasing attention as wear protection coatings in dry machining and on aero-engine compressor blades where the components are consistently subjected to high loading, high impact or heavy erosive environments. Although generally attributed to the high coating hardness, this can also be influenced by the fracture toughness, particularly in extreme applications. In this paper, we study the fracture toughness and cracking behaviour of the CrAlN/Si_3N_4 nanocomposite coatings and demonstrate how these properties depend on the coating composition. The nanocomposite coatings were deposited with different silicon contents using a lateral rotating cathode arc technique. Their composition, microstructure, chemical bonding states and mechanical properties were characterized using EDS, XRD, XPS and nanoindentation respectively and compared with CrN and CrAlN coatings deposited under the same conditions. The fracture toughness of the coatings was characterized by an *in-situ* double cantilever beam (DCB) compression method. It is found that the CrAlN/Si_3N_4 nanocomposite coatings are significantly tougher than the CrN and CrAlN coating, and the fracture toughness values increase with the coating's Si content. The *in-situ* observations also demonstrated that the cracking of the coatings was influenced by the microstructural variability of the coatings.

9:20am **B4-1-5 Mechanical Properties and Cutting Performance of MT-TiCN Coated Carbide Tools as a Funtion of Carbon Content**, ***A. Paseuth*** *(paseuth-anongsack@gr.sei.co.jp), H. Fukui, S. Okuno, H. Kanaoka,* Sumitomo Electric Hardmetal Corp., Japan, *Y. Okada*, Motherson Techno Tools Ltd.

Moderate temperature (MT)-TiCN is one of the most important components in modern coating systems for cutting tools. Hardness, adhesion and wear resistance can be affected strongly by the controlled adjustment of structure and chemical composition. The aim of this study is to investigate the effect of MT-TiCN coated carbide tools, as a function of carbon content, on mechanical properties and cutting performance. Deposition of high carbon contented MT-TiCN was conducted by doping a hydrocarbon gas for the CVD process with varied hydrocarbon gas to CH_3CN mole fraction from 0 to 30 at 840°C and 9kPa. The carbon content x in TiC_xN_{1-x} measured from change in lattice constant, increased with hydrocarbon gas to CH_3CN mole fraction and saturated at x=0.73. Crystalline size derived from XRD showed a minimum size of 39nm when carbon content x varied from 0.66 to 0.69. Hardness and adhesion was evaluated by indentation and scratch tests. Indentation hardness increased according to the increase of carbon content and maximum hardness reached 2920mgf/μm^2 when carbon content x =0.69. The adhesion of film to carbide substrate showed a decrease of critical load when carbon fraction was increased. Furthermore, a cutting test for ductile cast iron (AISI:100-70-03) was performed with different kinds of carbon content x (x =0.55 to 0.73) in MT-TiC_xN_{1-x}(10μm)/Al_2O_3(5μm)

coated carbide tools. $TiC_{0.69}N_{0.31}/Al_2O_3$ coated carbide tools showed significant increase in tool-life by 30-50% compared to commercially available MT-$TiC_{0.55}N_{0.45}/Al_2O_3$ coated carbide tools.

9:40am **B4-1-6 Influence of Oxygen Impurities on Structural, Mechanical Properties and Age Hardening of Ti-Al-N**, ***H. Riedl*** *(helmut.riedl@tuwien.ac.at)*, Christian Doppler Laboratory for Application Oriented Coating Development at Vienna University of Technology, Austria, *A. Vlasova*, Vienna University of Technology, Austria, *R. Rachbauer*, Oerlikon Balzers Coating AG, Liechtenstein, *S. Kolozsvári*, Plansee Composite Materials GmbH, Germany, *J. Paulitsch*, *P.H. Mayrhofer*, Vienna University of Technology, Austria

Recent investigations showed that even small amounts of impurities, such as oxygen, affects the growth process, the crystal structure, and the grain size of ceramic-like hard coatings. $Ti_{1-x}Al_xN$ is due to the excellent mechanical and thermal properties a well-established hard coating system, used for various industrial applications. We have used $Ti_{1-x}Al_xN$ as a model system to study the influence of oxygen impurities on growth and film properties. By using $Ti_{0.50}Al_{0.50}$ targets with different oxygen contents (< 950, 950-2000, > 2000 ppm) and base pressures of either 10^{-5} mbar or 10^{-8} mbar, we are able to identify the major oxygen impurity source for reactively sputtered $Ti_{1-x}Al_xN$ coatings. Furthermore, the coatings were prepared at 500 and 800 °C and when using the target with the highest O-content we also varied the sputtering power for 2 selected deposition conditions. Consequently, 14 different $Ti_{1-x}Al_xN$ coatings with a similar Al content of x~0.6 have been prepared.

The crystallite sizes of the coatings, which vary between 20 and 80 nm, are strongly determined by the O content as well as deposition temperature, as proven by x-ray diffraction, transmission electron microscopy, and atom probe tomography. Coatings prepared from the highest purity target (O < 950 ppm) exhibit hardness values between 29 and 34 GPa, depending on the substrate temperature or base pressure used. A much higher variation in hardness between 18 and 35 GPa is obtained when using the target with the highest O-content of > 2000 ppm.

But not only the as-deposited structure and properties of $Ti_{1-x}Al_xN$ are strongly influenced by the oxygen impurities, also their age-hardening behaviour and hence thermal stability strongly depends on the purity of the target as well as the base pressure and deposition temperature used.

10:00am **B4-1-7 Structure, Mechanical and Adhesion Properties of CuZr Metallic Glass and CuZrN Nitride Thin Films**, *F. Challali*, *F. Tetard*, LSPM-CNRS, Université Paris 13, Sorbonne Paris-Cité, France, *G. Abadias*, Pprime Institute - UPR CNRS 3346 - Université de Poitiers - ENSMA - France, *L. Belliard*, UPMC, Paris,France, *T. Chauveau*, *O. Brinza*, ***P. Djemia*** *(djemia@univ-paris13.fr)*, LSPM-CNRS, Université Paris 13, Sorbonne Paris-Cité, France

We investigated the structure and mechanical properties of ZrCu metallic glass and ZrCuN thin films deposited by rf magnetron sputtering from a $Zr_{50}Cu_{50}$ target in Ar or $Ar+N_2$ plasma discharge, respectively. Process parameters such as rf power, Ar and N_2 flows, and time of deposition were varied and the conditions for glass forming ability identified. Their influence on the thickness, the films microstructures, the chemical composition and the mechanical properties were explored. The structural properties of the metallic glass and nitride compounds were characterized by X-ray Diffraction and X-ray reflectivity, and chemical composition by wavelength-dispersive spectroscopy. The picosecond ultrasonic, the Brillouin light scattering and the nanoindentation techniques were employed to measure their acoustic, elastic and hardness properties whereas nanoscratch tests evaluated their adhesion performance. The strength and the ductility of the films were inferred from comparative tensile tests on coated and uncoated metallurgical substrates realized inside a scanning electron microscope.

10:20am **B4-1-8 Evaluation of Fracture Toughness of ZrN Hard Coatings using Internal Energy Induced Cracking**, ***J.-H. Huang*** *(jhhuang@mx.nthu.edu.tw)*, *Y.-H. Chen*, *G.P. Yu*, National Tsing Hua University, Taiwan

The objective of this study was to evaluate the fracture toughness and to investigate the effect of texture on the fracture toughness of ZrN hard coatings. We employed a recently developed energy-based method named internal energy induced cracking (IEIC) method to evaluate the fracture toughness. ZrN film was continuously deposited until reaching the thickness at which the film was fractured due to stored energy accumulation. The residual stress before crack initiation was used to calculate the stored energy (Gs), from which fracture toughness (Gc) can be derived. The residual stress of the ZrN coating was measured by laser curvature method, the Young's modulus of ZrN coatings was determined by nanoindentation, and the film thickness was determined from SEM cross-sectional image. The results showed that for a ZrN coating with (111) texture coefficient of 0.71, the fracture toughness was estimated to be ranged from 23.9 to 42.4 J/m^2. The hardness of the ZrN coatings was not changed with increasing film thickness. Stress gradient may play an important role in the fracture mode. Fracture of the ZrN coating may be initiated at a position of local maximum stress gradient accompanying with defects. The stress gradient in the ZrN coating may be originated from the competitive stress generation mechanisms. As the film thickness was above 4.2 μm, the (200) orientation increased in the strongly (111) textured ZrN coatings, which may be related to the stress relief . When the stored energy in the ZrN coating was higher than 31.6 J/m^2, it was partly released accompanying with the stress relief. The release of stored energy was considered to be the driving force of texture inversion. The advantages of this method are without externally applying stress and special sample preparation, and the substrate effect can be avoided. However, there are some disadvantages in applying the IEIC method. To insure that the fracture process is within the film, good adhesion and high residual stress are required. In addition, this method can only applied to hard coatings due to the requirement of small plastic zone size.

10:40am **B4-1-9 Modified W-S Coatings for Reducing Friction in Rubber Seal Applications**, ***A. Manaia*** *(ana.manaia@ipn.pt)*, Instituto Pedro Nunes, Portugal, *A. Cavaleiro*, Coimbra University, Portugal, *T. Polcar*, University of Southampton, UK

Rubber seals are commonly used in lubrication systems and bearings in order to avoid contamination of the systems and leakage of lubricants. However in dynamic contact where sliding contact conditions are present, rubber seals are easily damaged due to the high friction coefficient developed between the rubber and the seal.

The surface protection of rubber seals by applying a low friction coefficient coating is being studied in the last years; however this application requires specific materials properties either in terms of thermo-mechanical or tribological behaviours that are not yet developed.

Due to their layered structure and weak inter-layer bonding, transition metal dichalcogenides (TMD) has been studied in last decades in the field of low and super low friction coatings. Alloying TMD sputtered coatings has been the most attractive solution for improving and optimizing their friction behavior in a large range of loading environments, in order to overcome the two main drawbacks which have impeded their widespread application for reducing friction: the low loading bearing capacity and the high sensibility to moisture.

The aim of this work was to develop TMD+C coatings by PVD, in order to lowering the friction in mechanical contacts and studying the thermo-mechanical and tribological behavior of the system when applied on rubbers.

For these purposes, W-S thin films were alloyed with different C contents using magnetron sputtering and deposited on nitrile butadiene rubber (NBR) substrates.

The adhesion of the W-S-C coatings was improved by playing with the functionalization of the rubber surface by plasma etching as well as using a chemical composition gradient during the film deposition. Changing the C content of the coatings allowed to achieve hardness in the range from 6 to 10 GPa and friction coefficient as low as 0.02. Induced cracking was studied as a function of the preliminary etching substrate conditions and coatings parameters.

11:00am **B4-1-10 Effect of Annealing Treatment on Sputtered Cobalt Sensing Response Toward Inorganic Phosphate Ion**, ***Z. Endut*** *(zulkarnain.endut@mimos.my)*, MIMOS Berhad, Malaysia, *M. Hamdi*, *W.J. Basirun*, University of Malaya, Malaysia, *A.Z. Abdullah*, *N.A. Rais*, MIMOS Berhad, Malaysia

Label free, reagentless and on-site analysis of phosphate ion concentration using electrochemical method has been of tremendous interest in recent years. Potentiometric based phosphate sensor by exploiting cobalt (Co) mixed potential corrosion in phosphate contained water samples has been considered as a promising solution. Mixed potential corrosion occurs when a nonequilibrium state exists at the electrode surface involving two or more electrochemical reactions. In this reaction, slow oxidation of Co and simultaneous reduction of both oxygen and Co^{2+} occur at the surface of electrode. This paper presents an investigation of annealing treatment on Co surface properties and its sensing response toward different phosphate concentration. Co thin film was prepared by radio frequency sputtering in room temperature and annealed in oxygen and hydrogen plasma at temperature range between 200 deg C to 500 deg C. Cobalt surface morphology, chemical composition and crystal structure after annealing treatment were analyzed using FESEM, EDX, XRD while its phosphate sensing response properties were investigated using cyclic voltammetry, linear polarization and electrochemical impedance spectroscopy (EIS). Based on the results, effect of annealing in oxygen and hydrogen plasma

has a significant effect in cobalt sensing response toward phosphate concentration.

11:20am **B4-1-11 Mechanical and Electrochemical Behaviour of TiN and TiCN Deposited on XC48 Steel Substrates by Magnetron Sputtering**, ***N. Saoula*** *(nsaoula@yahoo.fr)*, Division des Milieux Ionisés et Lasers, CDTA, Algeria

Transition metal carbides and nitrides attract large technological interest due to their unique properties like high hardness and young's modulus, high electric conductivity, a considerable high-temperature strength, high corrosion resistance and high melting or decomposition temperatures. They have been applied as coatings for tools because of their superior properties. The deposition of TiN and TiCN coatings by sputtering has important specific advantages such as low levels of impurities and easy control of deposition rate. This method also enables the production of thin coatings of various morphology and crystallographic structure. When a sputtering technique is used for depositing coatings, the properties are widely changed by the variation of the sputtering conditions, such as reactive gas pressure, total pressure, and substrate bias voltage. Therefore, it is interesting to study the effects of the deposition parameters on these coatings. In this work, the attention is given to the study of the effect of the bias substrate on the properties of TiN and TiCN coatings deposited by r.f. reactive magnetron sputtering (13.56 MHz) from a titanium metallic target at different reactive gases partial pressures and substrate bias voltages. The deposited coatings were characterized by X-ray diffraction (XRD) in thin film mode (offset angle = 2◦), energy dispersive spectroscopy (EDS), Raman spectrometry, and micro-indentation.

Hard Coatings and Vapor Deposition Technology
Room: Royal Palm 4-6 - Session B6

Coating Design and Architectures
Moderator: R. Daniel, Montanuniversität Leoben, S. Ulrich, Karlsruhe Institute of Technology (KIT)

8:00am **B6-1 Advances in Design and Architecture of TM-Al-N based Coatings for Severe Applications**, ***P.H. Mayrhofer*** *(paul.mayrhofer@tuwien.ac.at)*, Vienna University of Technology, Austria **INVITED**

This work summarizes recent developments on applying thin film structure and architecture concepts to hard coatings for optimized performance in various application fields. Hard coatings deposited by plasma-assisted vapour deposition are widely used to reduce friction and wear of tools and engineering components.

We will look in more detail into the correlation between growth processes, microstructure, mechanical properties and thermal stability of hard ceramic coatings. This is done for single-phase coatings and composition or phase modulated layers within the model systems Ti–Al–N, Cr–Al–N, and Zr–Al–N.

The hardness of materials rapidly decreases at elevated temperatures as generally the density of structural defects, such as point defects, dislocations, and grain boundaries, decreases. Additional strengthening can be provided by age-hardening mechanisms, which originate from decomposition-processes of supersaturated phases to form new obstacles retarding plastic deformation. Furthermore important is the resistance against oxidation. Here, we will show, that in addition of supporting the formation of a dense corundum structure on these ternary TM-Al-N coatings, it is of utmost importance to minimize or even completely suppress any phase changes taking place within the growing oxide scale.

By using *ab initio* calculations and sophisticated experimental methods we will have a detailed insight into various mechanisms responsible for excellent mechanical strength, thermal stability and oxidation resistance properties of Ti–Al–N, Cr–Al–N, and Zr–Al–N hard coatings. For these materials we will also compare the effect of various architecture and alloying concepts with e.g., Y, Zr, Hf, Nb, and Ta.

As the brittleness of such ceramic-like coatings often negatively influences their performance, especially when used in conditions with an increased need for crack resistance, we will also discuss this topic by using *in-situ* electron microscopy micro- and nano-mechanical investigations of CrN/AlN multilayers.

The various thin film structure and architecture concepts allow the utilization of multifunctional properties facilitating the development of next generation's hard coatings.

8:40am **B6-3 Nonmetal Sublattice Population Induced Defect Structure in Transition Metal Aluminum Oxynitrides**, *K.P. Shaha, H. Rueβ, S. Rotert, M. to Baben, D. Music,* ***J. Schneider*** *(schneider@mch.rwth-aachen.de)*, RWTH Aachen University, Germany

The influence of oxygen concentration on the structure and mechanical properties of $V_{0.5}Al_{0.5}O_xN_{1-x}$ thin films ($0 \leq x \leq 0.8$) was investigated. The unexpected experimental lattice parameter decrease with increasing oxygen concentration can be understood based on ab initio data: the oxygen incorporation induced formation of metal vacancies reduces the equilibrium volume and stabilizes the metastable solid solutions. Charge balancing is identified as the underlying physical mechanism by Bader decomposition analysis. Hence, property predictions for these oxynitrides are only meaningful if the defect structure is described.

9:00am **B6-4 Theoretical Investigation of Phase Stability and Electronic Structure of Ordered and Disordered $Ti_{1-x}Mg_xN_y$ Alloys**, ***B. Alling*** *(bjoal@ifm.liu.se)*, Linköping University, IFM, Thin Film Physics Division, Sweden

Multicomponent nitrides is one of the major classes of materials in use for protective and decorative coatings. In particular the Ti-Al-N system is in extensive use as wear resistant coatings on cutting tools owing to good mechanical properties, high thermal stability and good oxidation resistance. There is a huge scientific literature covering the synthesis, structure, and properties of $Ti_{1-x}Al_xN$ thin films but in contrast very few investigations have been made on the neighbouring Ti-Mg-N system [1,2]. In this work theoretical first-principles methods based on the density functional theory and alloy theory have been employed to investigate the phase stability and electronic structure of $Ti_{1-x}Mg_xN_y$ solid solutions and ordered compounds. We demonstrate that the solution of Mg into TiN forming rock salt structure $Ti_{1-x}Mg_xN$ is thermodynamically stable at least up to $x \leq 0.5$ with respect to the TiN and Mg_3N_2 parent compounds in contrast to the TiAlN coatings which tend to phase separate. The electronic structure displays a transition from metallic TiN to semiconducting at x=0.5 explaining the drastic change in colour as observed experimentally [3]. The connection between the electronic structure and the phase stability as well as the possibility to synthesise ordered $TiMgN_2$ compounds with respect to disordered solid solutions is discussed.

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[3] M. Fenker,T, M. Balzer, H. Kappl, O. Banakh, Surface & Coatings Technology **200,** 227 (2005)

9:20am **B6-5 Roads to Tougher Nanostructured Coatings for Cutting at Intermediate Temperatures**, ***M. Morstein*** *(m.morstein@platit.com), A. Lümkemann*, PLATIT AG, Switzerland, *B. Torp*, PLATIT Inc., US

This paper deals with the toughness optimization of hard, wear-resistant coatings by structural design on the nano- and microscale. The coatings were produced on the industrial π 411 platform, using lateral (LARC®) and central (CERC®) cylindrical rotating arc cathodes PVD technology. On the microscale, the new coatings were designed according to the Quad Coatings® multi-zone architecture, whereas on the nanoscale, their nanolayer- and nanocomposite structure was optimized.

Coating members from chemically different families were compared to each other with respect to their physical and structural properties both at ambient and elevated temperatures. It will be shown how processing parameters such as the choice of target arrangement and -composition can be used to alter the nanolayer structure, thereby influencing the coating properties such as toughness and cutting performance. In addition to the nanoscale design, the successful multi-zone Quad Coatings4® concept was used to optimize adhesion and fracture resistance through microscale structural design.

By performing annealing tests on a wide range of coating types and –structures, it was found that certain properties such as oxidation resistance are mainly governed by chemical effects, while under thermal load, grain growth, hardness– and stress changes can rather be controlled by applying a nanocomposite structure design.

The optimized concept coatings were applied on tools for high-performance cutting at intermediate temperatures. Interrupted cut applications such as hobbing of low-alloy steels, milling of tool steels using using indexable cutting inserts, and milling or aerospace alloys using solid carbide end mills pose different levels of challenge to the coatings' toughness and their ability to retard crack propagation, especially in wet cutting.

9:40am **B6-6 Chemical and Structural Design Concepts for Increasing the Oxidation Resistance of Ti-Al-N based Coatings**, ***R. Hollerweger*** *(robert.hollerweger@tuwien.ac.at)*, Christian Doppler Laboratory for Application Oriented Coating Development at Vienna University of Technology, Austria, *D. Holec*, Montanuniversität Leoben, Austria, *M. Arndt, R. Rachbauer*, Oerlikon Balzers Coating AG, Liechtenstein, *P. Polcik*, Plansee Composite Materials GmbH, Germany, *J. Paulitsch, P.H. Mayrhofer*, Vienna University of Technology, Austria

$Ti_{1-x}Al_xN$ is a typical protective coating to increase the lifetime of machining and forming tools especially during high temperature applications and under demanding tribological conditions. Due to thermal decomposition and severe oxidation at temperatures above ~800 °C the field of their applications is limited. To counteract these tendencies quaternary systems like $Ti_{1-x-y}Al_xTa_yN$ were developed and successfully implemented. However, especially the mechanisms for increased oxidation resistance and the necessary ideal chemical composition for an optimized behavior are still not clarified and understood.

Therefore, we have reactively deposited $Ti_{1-x-y}Al_xTa_yN$ coatings with a Ti/Al ratio of 51/49 and 35/65 and Ta contents of 0, ~8, and ~16 at%. By using isothermal Differential Scanning Calorimetry combined with Thermal Gravimetric Analysis we observe for single cubic phased $Ti_{0.32}Al_{0.60}Ta_{0.08}N$ a mass gain of only ~5% after 5h at 950 °C in synthetic air, whereas $Ti_{0.35}Al_{0.65}N$ is completely oxidized after 15 min (mass gain ~24%). Structural investigations by X-Ray Diffraction and Scanning Electron Microscopy reveal anatase-to-rutile phase transformations with increasing oxidation time and a porous scale for Ta-free $Ti_{0.35}Al_{0.65}N$. Contrary, $Ti_{0.32}Al_{0.60}Ta_{0.08}N$ exhibits a highly dense and rutile dominated and protective scale.

Density Functional Theory simulations of the phase stabilities throughout the ternary system rutile (R) and anatase (A) $(Ti,Al,Ta)O_2$, corundum (α) type $(Al,Ta,Ti)_2O_3$, and orthorhombic $(Ta,Ti,Al)_2O_5$ show that in the case of $Ti_{0.35}Al_{0.65}N$ the transformation A + α to A + R + α to R + α occurs. If Ta is alloyed a rutile phase field opens even at 0 K which allows for the direct formation of a R + α scale. This indicates that the phase transformation – which is accompanied by a volume change of 5-10% leading to the formation of pores and cracks within the scale – can be avoided for $Ti_{0.32}Al_{0.60}Ta_{0.08}N$.

Based on these results we can conclude that for increased oxidation resistance the coatings chemical composition has to be optimized to the respective oxide phase diagram to allow for alumina and a Ti-oxide-based phase without or minimal anatase to rutile phase transformation up to the application temperature of the coating.

10:00am **B6-7 Strategies for Knowledge-based Design of Thin Film Architecture at the Nanoscale**, ***K. Sarakinos*** *(kostas@ifm.liu.se)*, IFM Linköping University, Sweden **INVITED**

Thin film growth from vapour phase starts by nucleation of atomic islands on the substrate surface. Those islands grow in size, impinge on each other, coalesce into larger islands and eventually form a continuous film. These film formation stages are particularly apparent during Volmer-Weber (i.e., 3-dimensional) growth. At the same time, film growth from the vapour phase proceeds far from thermodynamics equilibrium and dynamics and characteristics of the various formation stages are mainly dictated by growth kinetics. The initial film formation stages (i.e., island nucleation, growth and coalescence) largely set the film nanoscale architecture. They are, thus, decisive for film microstructural features and evolution which, in turn, determines the film physical attributes. Fundamental understanding of how each of the initial formation stages and their complex interplay affect microstructural evolution is paramount to knowledge-based design of film architecture at the nanoscale. In this talk, well defined pulsed vapour fluxes [1] are employed to tune the kinetic conditions during growth of Ag on SiO_2 – an archetype system for the study of Volmer-Weber growth. A research strategy that entails the combined use of *in situ* growth monitoring, post-growth imaging and growth simulations is compiled to unravel to role of the initial film formation stages on the growth evolution [2]. Growth simulations are also used to obtain a universal understanding of the relationships between deposition conditions and scaling behaviour of early film growth stages [3]. The implications of the findings for surface science and surface engineering communities are discussed.

[1] D. Magnfält, K. Sarakinos *et al.*, J. Phys. D: Appl. Phys. 46 (2013) 215303.

[2] V. Elofsson, K. Sarakinos *et al.*, unpublished data.

[3] B- Lü, K. Sarakinos *et al.*, unbublished data.

10:40am **B6-9 A Study of AlCr-based Coatings Deposited by Magnetron Sputtering Using Powder Metallurgical Targets**, ***S. Kolozsvári*** *(szilard.kolozsvari@plansee.com)*, *P. Polcik*, PLANSEE Composite Materials GmbH, Germany

Recently, many different aluminium-based hard coatings deposited by physical vapour deposition (PVD) have been introduced into the market. For the deposition of wear resistant coatings for tools cathodic arc evaporation and r.f., d.c. or high power impulse magnetron sputtering or even ion and electron beam supported processes are frequently used. AlCrN-based coatings produced by cathodic arc deposition are state-of-the-art, therefore in the present work we are focussing on AlCr-based coatings deposited by magnetron sputtering in an industrial coating machine.

The influence of the composition of the AlCr powder metallurgical sputtering targets and the influence of the deposition process parameters on the coatings are investigated. The mechanical properties of the coatings - hardness, elastic modulus, adhesion, crystallographic orientation and chemical composition – have been examined. These characteristics have been examined for a range of operating parameters like bias voltage, gas ratios and different power densities.

Another goal of this work is to investigate the impact of different aluminium and chromium ratios in the target on the deposited coatings. For this reason different AlCr targets have been used for sputtering tests.

The application of powder metallurgical produced targets allows a high flexibility on the way to optimize the chemical composition of the desired coating. A benefit of the powder metallurgy is that obtaining an additional functionality of the coatings, like higher wear- or oxidation resistance, can be easily achieved by alloying of other elements into the targets like for instance B, Ta or Si.

11:00am **B6-10 Assessment of the Mechanical Performance of Oxide Coatings on Stainless Steels and Titanium Alloys in Corrosive Environments**, ***D.F. Bahr*** *(dfbahr@purdue.edu)*, Purdue University, *S.K. Lawrence*, Purdue University, US, *D. Adams, N.R. Moody*, Sandia National Laboratories, US, *M. Pang, K.R. Morasch*, Washington State University, US **INVITED**

Passive films, the primary mechanism for corrosion protection in materials such as stainless steel and titanium, form in oxidizing environments. Conventionally the films that form are a fixed chemistry, and have fixed thicknesses. While anodizing provides additional design flexibility in developing thicknesses that exceed those formed on native passive oxides, they still have limited chemistry variation. However, it is possible to grow oxides using pulsed laser oxidation, which leads to non-stochiometric oxides and/or nitrides which develop based on the underlying substrate material interacting with the surrounding environment. This presentation will focus on testing methodologies using nanomechancial probes of the surface of passivating metals to determine the toughness of the films. An approach that relies on selecting appropriate probe geometry in relationship to the film thickness and substrate properties will be described. The method and model will then be used to demonstrate the impact of environment and the exposure to corrosive environments on the resulting toughness of native passive films, anodized films, and laser-grown oxides.

11:40am **B6-12 The Enhanced Photothermal Phenomena of SiO2-Ag and TiO2-Ag Multi-layered Thin Film Structures and its use for the Annealing of TaN-(Ag,Cu) Thin Film**, *J.H. Hsieh (jhhsieh@mail.mcut.edu.tw)*, ***Y.T. Su***, Ming Chi University of Technology, Taiwan, *C. Li*, National Central University, Taiwan

Multi-layered thin films of SiO2-Ag and TiO2-Ag were prepared on glass substrates using reactive sputtering, followed by rapid thermal annealing. The mass thickness of Ag was controlled at 3~10 nm. The optical properties of these films were then studied as functions of Ag layer-thickness, annealing time, and matrix materials. These obtained results were correlated with the heat generation due to photothermal conversion under IR irradiation. It was found that the heating enhancement due to the incorporation of Ag particles is significant, especially when TiO2 was used as the matrix. Embedded Ag particles led to an increase in light absorption in the range of UV to IR region (400 nm to 4000 nm). As a result, the films' temperature can increase dramatically, caused by the irradiation of light. The largest temperature increment could reach >100 oC easily. The increments were dependent on the number of Ag layer, heat treatment conditions, light intensity, and the oxide matrix.

A theory was proposed to explain the enhanced light absorption and, therefore, the enhanced heating effect due to light irradiation. At final, an example was given to explain the possible annealing of TaN-(Ag,Cu) thin films by using the enhanced photothermal effect.

Advanced Materials for Modern Device Applications
Room: Sunset - Session C4-2

Thin Films for Energy Related Application
Moderator: K. Yu, Lawrence Berkeley National Laboratory, US, J. Partridge, RMIT University

8:00am **C4-2-1 Study of Al_xO_{1-x} /Ti Thin-film System by Complex of Methods**, *A. Nikitenkov (nik@tpu.ru), **N. Nikitenkov**, Y. Tyurin, I. Dushkin, V. Sypchenko, O. Vilhivskaya*, Tomsk Polytechnical University, Russian Federation

When studying the physical properties of thin-film structures, it is often necessary to determine both the elemental and chemical composition through out the entire thickness of the structure (depth profiles). Herein, methods of obtaining such information using secondary ion mass spectroscopy and Raman scattering spectroscopy are described. As an example, hydrogen diffusion from nanocrystalline titanium into Al_xO_{1-x} films deposited onto the flat surface of specimens by magnetron sputtering was studied.

As previously shown [1], VT-6 (Rus) titanium in the nanocrystalline (NC) state absorbs hydrogen; thus, nanocrystalline titanium may be used as a hydrogen accumulator. The development of such accumulation materials remains a significant challenge in hydrogen energetic. At high concentrations, hydrogen has a tendency to escape from the metal and disperse into the environment, which is unacceptable for efficient hydrogen storage. One way to limit the emission of hydrogen is to create a barrier on the surface of a saturated material. Thus, the aim of the present study was to investigate the penetration of hydrogen from nanocrystalline titanium through an aluminium oxide coating, which is a good barrier for hydrogen, according to previous reports [2].

In this study, thin films were produced by magnetron sputtering nanocrystalline specimens of titanium saturated in hydrogen and were evaluated by layer-by-layer secondary ion mass spectrometry (SIMS) and Raman spectroscopy. Due to magnetron sputtering, the chemical composition of the films was nonhomogeneous and was variable among layers. Moreover, in the deposition of specimens saturated with hydrogen, hydrogen diffused throughout the depth of the film; diffusion, however, was restricted to the area near the film-substrate interface, affecting less than 50% of the thickness of the film.

1. N.N. Nikitenkov, Yu.I. Tyurin, T.I. Sigfusson // Bulletin of the Russian Academy of Sciences. Physics, 2012, Vol. 76, No. 6, pp. 803–806.

2. M.P. Larin, V.V. Bystrov. Vacuum equipment and technology. 2003, 13(4). P. 221. (Rus).

8:20am **C4-2-2 Effect of Flow-channel Machining Condition on Coatings of AISI 1045 Steel Plate by Pack Chromization**, ***L.C. Tsai** (tsautu@gmail.com), C.J. Wang*, National Taiwan University of Science and Technology, Taiwan, *C.T. Yeh, M.D. Ger*, Chung Cheng Institute of Technology, National Defense University, Taiwan

The purpose of this study is to investigate the difference between coatings on AISI 1045 steel plates with machining flow-channel along with low-temperature pack chromization for preparing bipolar plates of PEM fuel cells. Within the scope of machining feed rate of 50~200 mm/min, those pack chromization specimens that flow-channel was milled at 100 mm/min are propose in this work. The results show that the specimens have a corrosion current (I_{corr}) of 6.93×10^{-7} Acm^{-2} and an interfacial contact resistance of 8.0 $m\Omega cm^2$. It is expected to be applied to manufacturing of PEM fuel cell bipolar plates.

8:40am **C4-2-3 Zinc Oxide UV Photodetectors for use in Melanoma and Vitamin D Studies**, ***MW. Allen** (martin.allen@canterbury.ac.nz)*, University of Canterbury, New Zealand **INVITED**

ZnO is a bio-compatible, earth-abundant semiconductor that has long been viewed as an attractive candidate for optoelectronic devices in the ultraviolet spectrum due to its wide direct band gap (3.35 eV at RT), large exciton binding energy (60 meV), excellent radiation hardness, and the availability of free-standing bulk single crystal substrates. ZnO is an intense UV emitter with its photoluminescence spectra containing a vast array of spectroscopic features [1]. It is also a member of a small class of metal oxide semiconductor with unusually active surfaces, characterized by persistent 2-D electron gases, that can hinder device stability while at the same time providing opportunities for the production of transparent environmental sensors [2].

We have recently developed a simple methodology for the reliable fabrication of high quality ZnO-based Schottky contacts with high rectifying barriers and ideality factors approaching the image force controlled limit [2]. This has opened the door to the low cost production of devices such as UV photodetectors and transparent metal semiconductor field effect transistors [3]. In this paper, we report on the high UV sensitivity of ZnO Schottky photodiodes and MSM photodetectors. We examine the issue of persistent photoconductivity on detector performance, explore passivation techniques to mitigate the environmental sensitivity of the ZnO surface, and provide examples of applications in public health research.

[1] Mendelsberg *et al.*, Phys. Rev. B **83**, 205202 (2011)

[2] Allen *et al.*, Phys. Rev. B **81**, 075211 (2010)

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9:20am **C4-2-5 Optimization of the Light Scattering Characteristics of Surface-textured AZO Films Prepared by Magnetron Sputtering**, *T. Minami, **T. Miyata** (tmiyata@neptune.kanazawa-it.ac.jp), T. Yamanaka*, Kanazawa Institute of Technology, Japan, *J. Nomoto*, Kochi University of Technology, Japan

For transparent electrode applications in thin-film solar cells, transparent conducting oxide (TCO) films require an optimization of surface texture to improve photovoltaic properties through induced light scattering and subsequent light trapping. The formation of a surface texture on TCO films was performed using two techniques; (1) formation by post-etchin g the deposited film and (2) formation during the crystal growth of the film deposition . In this paper, we describe the influence of post-etching on the light scattering characteristics of surface-textured Al-doped ZnO (AZO) films formed during the crystal growth of magnetron sputtering depositions. Transparent conducting AZO thin films were prepared on glass (OA-10) substrates using a dc magnetron sputtering apparatus with an oxide target. In case (1), AZO films were prepared under conventional deposition conditions such as a sputter Ar gas pressure of 0.6 Pa and a substrate temperature of 200°C. In case (2), surface-textured AZO films were prepared by varying both the sputter Ar gas pressure, 0.6-12 Pa, and the substrate temperature, 200-350°C, and post-annealing in a H_2 gas atmosphere for 30 min at the same pressure and temperature as in the film deposition[1]. The surface-textured AZO film was prepared at a pressure of 12 Pa and a temperature of 350°C without post-etching. A high haze value above 80% in the wavelength range from 400 to 800 nm was obtained in as-deposited AZO films prepared at a pressure of 12 Pa and a temperature of 350°C and post-etched AZO films prepared at a pressure of 0.6-12 Pa and a temperature of 200-350°C. However, it is known that any significant improvement of photovoltaic properties requires not only high haze values in the wavelength range most relevant for solar cells, but also large angular scattering, which is related to rougher and sharper morphologies. For the purpose of evaluating the angular scattering of AZO films, the angular resolved scattering (ARS) was measured. It was found that the light scattering at large angles could be significantly improved by post-etching the surface-textured AZO film formed by the technique used in case (2).

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9:40am **C4-2-6 Experimental and Theoretical Investigation of ScN-based Solid Solution for Thermoelectric Applications**, ***S. Kerdsongpanya** (sitke@ifm.liu.se), B. Alling, P. Eklund*, Thin Film Physics Division, IFM, Linköping University, Sweden

The development of clean and sustainable energy sources is one of the most critical objective for today's society. Thermoelectric devices have the potential to contribute to solve this problem since they can directly convert heat into electricity or vice versa. The heat source can be solar, geothermal or a waste that comes from automobiles exhaust or industrial processes. However, the conversion efficiency of thermoelectric devices of today is limited and further materials improvements are needed. The critical material-dependent parameter is the figure of merit ($ZT = S^2T/\rho\kappa$, where ρ is the electrical resistivity, S is the Seebeck coefficient and κ is the total thermal conductivity). Since, ZT value is scaled by temperature, thus good thermoelectric materials also need high thermal stability. Therefore we have chosen to study transition metal nitrides due to their high thermal stability. Here we present recent results from our experimental and theoretical investigations of the ScN thin film system. We have found that ScN thin films is a promising thermoelectric material because of its high power factor (S^2/ρ) of 2.5×10^{-3} W/mK^2 at 800 K [1]. We have suggested that this result can be explained by nitrogen vacancies generating an asymmetric sharp feature in the ScN electronic density of states which allows low electrical resistivity with retained relatively large Seebeck coefficient [2]. Unfortunately, ScN has high thermal conductivity, thus its figure of merit of is low, about 0.2 at 800 K. In order to reduce lattice thermal conductivity nanostructuring, alloying or nanoinclusion formation can be considered. To understand which alloying elements that could be of interest at elevated temperature were diffusion can be activated, we have investigated the trends

in mixing thermodynamics of ScN-based solid solutions in the cubic B1 structure by first-principle calculations. 13 different $Sc_{1-x}M_xN$ (M = Y, La, Ti, Zr, Hf, V, Nb, Ta, Gd, Lu, Al, Ga, In) and three different $ScN_{1-x}A_x$ (A = P, As, Sb) solid solutions are investigated and their trends for forming disordered or ordered solid solutions or to phase separate are revealed [3]. Moreover, experimental studies have been carried out in ScN-based solid solution thin films which were prepared by reactive magnetron sputtering. The results are used to discuss suitable candidate materials for different strategies to reduce the high thermal conductivity in ScN-based systems.

[1] Sit Kerdsongpanya *et al*. Applied Physics Letters **99**, 232113 (2011).

[2] Sit Kerdsongpanya *et al*. Physical Review B **86**, 195140 (2012).

[3] Sit Kerdsongpanya *et al*. Journal of Applied Physics **114**, 073512 (2013).

10:00am **C4-2-7 Processing and Characterization of Multilayer ZnO/Al doped ZnO Nanostrcutured Films**, *R. Jayaganthan*, IIT Roorkee, India, ***A. Rahman*** *(atikurrhmn@gmail.com)*, NIT Srinagar, india

Multilayer thin films (single layer of ZnO, ZnS and Al doped ZnO film, double layer of ZnO/Al doped ZnO film & triple layer films of ZnO/Al doped ZnO/ZnO and ZnO/Al doped ZnO/ZnS film) were deposited (at 90^{o}C, deposition time of each layer was 2 hr) on soda-lime glass substrate by electroless process. Wet deposited films were dried in air and subsequently annealed in muffle furnace in air atmosphere at 500^{o}C for 2 hr. Significant characteristics of the thin films, such as crystallinity, surface roughness, layer thickness, as well as the optical properties in a large spectral range between 300-800 nm were analyzed. Average grain size of the films was found 40-90 nm. The obtained sample of triple layer film of ZnO/Al doped ZnO/ZnS exhibits best, optimum optical characteristics i.e. intermediate range of absorbance of spectra, lowest value of photoluminescence intensity, and has minimum recombination of electron-hole pairs. Triple layer film of ZnO/Al doped ZnO/ZnS is suitable as a transparent substrate in Dye-sensitized solar cell.

Keywords: Electroless Process; Multilayer films; X-ray diffraction; FE-SEM/EDS;

Optical properties.

10:20am **C4-2-8 Combinatorial Sputtering Exploration of Zn-Sn-O (ZTO) Composition Spreads**, ***S.Y. Li***, National Cheng Kung University, Taiwan, *J.-M. Ting, K.S. Chang (kschang@mail.ncku.edu.tw)*, National Central University, Taiwan

Transparent conducting oxide (TCO) films are extensively applied as electrodes i n the fields of solar cells and displays, due to their high transparency and excellent conductivity. Multicomponent oxides such as Zn-Sn-O (ZTO) have attracted much attention resulting from no expensive elements, i.e. indium (In), involved. In addition, thermal stability and mechanical strength of ZTO could be tailored as well by varying its stoichiometry. Howev er, making different ratios of Zn/Sn compounds systematically is not trivial.

Combinatorial methodology has been proven its validity in such an application. This approach allows Zn/Sn continuously changing across the single sample area and a feasible intimate mix of Zn and Sn. Therefore, a single ZTO composition spread sample essentially includes a full spectrum of properties to be investigated.

A Zn-Sn-O (ZTO) composition spread, consisting of thickness wedges of SnO and ZnO, was prepared using a state-of-the-art combinatorial sputtering system, equipped with a moving shutter and two RF guns for the targets of Zn and Sn, respectively. The thickness gradient was determined using SEM, α-step and SIMS. It was found a smooth thickness variation across the sample area for both ZnO and SnO with the coefficient of determination (R^2) » 0.99, indicating a good control of the ZTO composition spread. Structure evolution was characterized using XRD. We found in-situ 500 °C annealing resulted in crystallization of the samples, where ZnO, Zn_2SnO_4, $ZnSnO_3$, and SnO_2 phases were observed, depending upon the ZnO/SnO ratios on the ZTO composition spread. The resistivity was characterized using a four-point probe on different substrates, which revealed lower resistivity near ZnO-rich. Morphology and optical characteristics were studied as well using AFM, SEM and UV-Vis spectrometry. A clear variation trend of both properties was observed. A systematic study of physical properties of ZTO has been successfully demonstrated.

10:40am **C4-2-9 Improved Thermal Stability of Bismuth Oxide Thin Films Presenting the Delta-cubic Phase**, *C.L. Gomez*, Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de Mexico, México, Mexico, *O. Depablos*, *P. Silva-Bermudez*, Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de Mexico, México, *S. Muhl*, Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de Mexico, Mexico, *A. Zeinert*, Laboratoire de Physique de la Matière Condensée, Université de Picardie Jules Verne, France, *E. Camps*, Instituto Nacional de Investigaciones Nucleares de Mexico, Mexico, ***S.E. Rodil*** *(ser42@iim.unam.mx)*, Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Mexico

The delta-cubic Bi_2O_3 phase posses one of the highest ionic conductivities reported, however, as bulk material it is stable in a reduced temperature range from 730 to 825 ^{o}C. On the other hand, as a thin film produced by atomic aggregation methods, the delta-phase can be produced and kept at room temperature for long periods. Nevertheless, the application of these films as electrolytes for micro-solid oxide fuel cells is limited due to the fact that the films transform into the metastable beta-phase between 250-350 ^{o}C, temperature too low for the operation of the cell. In this work, we report the stabilization of the delta-phase of Bi_2O_3 thin films from RT to about 600 ^{o}C by the addition of Tantalum (Ta) as a dopant. The films were produced by reactive magnetron sputtering and the Ta addition was achieved by attaching a pure Ta wire to the 4 inches Bi_2O_3 target. The film structure was studied by X-ray diffraction and Raman spectroscopy.

11:00am **C4-2-10 Effect of Substrate and Surfactant over the Crystallization, Growth and Luminescence of ZnO Coatings**, ***S. Brahma***, National Cheng Kung University, Taiwan, *S.A. Shivashankar*, Indian Institute of Science Bangalore, India, *J.-M. Ting (jting@mail.ncku.edu.tw)*, National Cheng Kung University, Taiwan

We report a method for producing zinc oxide coating on a desired substrate by using microwave irradiation assisted chemical synthesis. The method is illustrated by obtaining coatings of ZnO on Si(100), metal coated Si(100) and PMMA coated Si(100). A dilute solution of zinc acetylacetonate in ethanol, with a small molar proportion of a surfactant (cetyltrimethyl ammonium bromide commonly called as CTAB), is irradiated with 800 W of microwave power at 2.45 GHz for 5 min. A uniform coating of well crystallized ZnO (wűrtzite) is formed over all the substrates. Substrate surface and surfactant affect significantly over the crystallization, growth and luminescence. For example: highly oriented ZnO coating are produced over Cr/PMMA coated Si(100) followed by polycrystalline texture over Si(100). Oriented ZnO coatings show strong UV emission than visible luminescence which is more prominent for ZnO obtained on Si(100). Such ZnO coatings have been characterized in detail by X-ray and electron diffraction, and electron microscopy. The present method is scalable to larger substrates, and is promising as a low temperature technique for coating dielectric substrates, including flexible polymers.

11:20am **C4-2-11 Characteristics of Optoelectronic Properties of AZO/Au/AZO Multilayer Thin Films Prepared by RF Magnetron Sputtering and Ion Sputtering for Transparent Electrode**, ***C.H. Chu***, National Cheng Kung University, Taiwan, *H.W. Wu (qqq25q@gmail.com)*, Kun Shan University, Taiwan, *J.L. Huang*, National Cheng Kung University, Taiwan

In this study, we compared the electrical, optical and structural properties of aluminum-doped ZnO (30 nm)/Aurum (5-20 nm)/ aluminum-doped ZnO(30 nm) multilayer thin films on glass substrate deposited by RF magnetron sputtering and ion sputtering for transparent electrode. Optimization of the thin films resulted with low resistivity of 1.01×10^{-5} Ω-cm, mobility of 27.665 cm^2/V-s and carrier concentration of 4.563×10^{22} cm^{-3} were obtained at a Au layer thickness of 20 nm. Maximum transmittance of 86.18 % for wavelengths above 650 nm and Haacke figure of merit (FOM) are 9.69×10^{-3} Ω^{-1} of AZO/Au/AZO films with the Au layer thickness of 8 nm. These results indicate that AZO/Au/AZO multilayer thin films are a promising high conductivity transparent electrode scheme for solar cells and various displays applications.

Keywords: Aluminum-doped zinc oxide, AZO, multilayer, RF magnetron sputtering, AZO/Au/AZO, thin film, transparent conductive oxides.

11:40am **C4-2-12 Characterization of 1,4-Bis-(2-dimethylaminoethylamino)-9,10-anthraquinione Films Based Molecular Device by Thermal Evaporation Technique**, ***S. Bhatia*** *(sonikbhatia@gmail.com)*, Kanya Maha Vidyalaya, India, *R.K. Bedi*, Guru Nanak Dev University, India

In present work we have investigated the morphological and electrical properties of 1,4-Bis-(2-dimethylaminoethylamino)-9,10-anthraquinione using films prepared by thermal evaporation onto glass substrates maintained at different temperatures at a pressure of ~1.33×10^{-3} Pa.

FTIR spectra of 1,4-Bis-(2-dimethylaminoethylamino)-9,10-anthraquinione film which shows C=O absorption bands at 1662.52 cm^{-1}. The XRD pattern of 1,4-bis-(2-dimethylaminoethylamino)-9,10-anthraquinione films) deposited at 318 and 333K show the formation of well resolved diffraction peaks having d- values 14.14, 7.03, and 5.92 Å .SEM of 1,4-bis-(2-dimethylaminoethylamino)-9,10-anthraquinione shows crystallites as large as 0.215 μm are observed at 333K.

It has been observed that electrical resistivity decreases with an increase in temperature within the experimental range (290-380 K) investigated

The formation of nucleation centers at higher substrate temperatures results in large crystallites that ultimately decrease the barrier size. It has also been observed that the electrical resistivity of these films under investigation were found to be smaller by an order of 10^2 at higher temperatures than that of base 9,10-anthraquinone films. The activation energies obtained from the slopes of the log of resistivity vs inverse temperature plots are found to be in the range of 0.34-0.21 eV

The steady state current density – voltage (J-V) characteristics of devices based on anthraquinone layer sandwitched between Al and FTO electrodes were also studied. The forward bias direction corresponds to positive voltage on FTO electrode and their characteristics are found to be asymmetrical and non linear. Thus, FTO/ Anthraquinone /Al device clearly exhibits rectifying behavior in the dark which is very similar to that of the conventional p-n junction.. In the present case the rectifying behavior does exist in FTO/ anthraquinone /Al device thus it confirms that the anthraquinone behaves as p-type organic semiconductors. As it becomes clear from the J-V plots of forward current density Thus J-V relationship for FTO/ anthraquinones /Al devices were studied using standard equation. It has been observed that FTO/anthraquinone /Al device formed; 1,4-bis-(2-dimethylaminoethylamino)-9,10-anthraquinione device show maximum power conversion (η) of 1.03×10^{-2} and fill factor of 0.45 respectively. This indicates that photoinduced electrons and holes are effectively separated within the interface and collected by the contact electrodes.

Tribology & Mechanical Behavior of Coatings and Engineered Surfaces
Room: California - Session E1-3

Friction, Wear, and Lubrication: Effects and Modeling

Moderator: M. Chandross, Sandia National Laboratories, O.L. Eryilmaz, Argonne National Laboratory, K. Polychronopoulou, Khalifa University of Science, Technology & Research

8:00am **E1-3-1 Load Dependence of the Tribological Properties of Silver Tantalate Coatings at Elevated Temperatures**, ***S.M. Aouadi*** *(samir.aouadi@unt.edu), D. Stone, C. Paksunchai, C. Chantharangsi*, University of North Texas, US, *H. Gao*, University of California Merced, US, *T. Scharf*, University of North Texas, US, *A. Martini*, University of California Merced, US

Silver tantalate coatings were produced by reactive unbalanced magnetron sputtering from silver and tantalum sources as potential high temperature solid lubricants. The films were wear-tested at 750 °C under normal loads of 1 , 2 , 5 , and 10 N against a Si_3N_4 counterface. These sliding tests revealed that the frictionmonotonically increased as the load was increased. A systematic investigation of the surface and sub-surface region of the wear track, using techniques such as scanning Auger nanoprobe, atom probe tomography, and cross-sectional transmission electron microscopy, revealed the following trends with increasing load: (1) a decrease in the amount of Ag on the surface of the wear track; (2) a decrease in the thickness of the mechanically mixed layer that forms as a result of the reconstruction of $AgTaO_3$ to form Ta_2O_5 and Ag; and, (3) the formation of a porous structure throughout the tribofilm as a result of the segregation and migration of Ag from the original $AgTaO_3$ matrix. These results were complemented by molecular dynamics simulations, which confirmed the increase of friction with load. Further, the simulations support the hypothesis that this trend can be explained in terms of decreased presence of Ag clusters near the sliding surface and the associated decreased porosity.

8:20am **E1-3-2 Development of a New Instrument for Complex Micro-scale Abrasion Test**, ***G. Montesanti*** *(g.montesanti@stm.uniroma3.it), M. Renzelli*, University of Rome "Roma Tre", Italy, *C. Di Cesare*, Scienzia Machinale Srl, Italy, *E. Bemporad*, University of Rome "Roma Tre", Italy

The paper intends to present the development of a new tribometer (TUC), which allows producing complex mechanical stresses on samples. The literature is wide on tribological behavior of thin coatings, focusing in particular on micro-scale abrasion tests [1]. In order to characterize different stress distributions during the test, pin-on-disk test and the scratch test are also used to complement the assessment of tribological behavior. This new instrument aims to overcome the need to use three different conventional methods, providing additional features to the characterization.

The underlying idea of this tribometer is based on the cratering method [2]. The instrument is also provided with crater depth sensor and load cells, which permit to have an instantaneous measurement of the friction coefficient and the wear rate.

In order to validate the results, a broad experimental activity was carried out using both bulk and coated samples – SiC wafer and TiN coating respectively. Special care has been devoted to the calibration of the machine and the frequency content of the acquired signals. The instrument can produce both standardized micro-scale abrasion tests and tests characterized by more complex mechanical stresses. This feature allows to have more consistent results. In addition, a comparison with commercial scratch testers was performed in order to assess the response of the samples to different shear stress components.

Finally, the results of the tests are presented. In particular, the instantaneous Archard's wear coefficient is discussed, showing that useful information can be extrapolated regarding run-in and coating delamination.

[1] Rutherford, K.L., Hutchings, I.M. (1996) "A micro-abrasive wear test, with particular application to coated systems", Surface and Coatings Technology, 79 (1-3), pp. 231-239.

[2] Bemporad, E., Comis, E., Sebastiani, M., Carassiti, F., and Palumbo, B. (2009) "Complex wear measurement on thin coatings by the cratering method", Lubrication Science, 21 (7), pp. 269-288.

8:40am **E1-3-3 Surface Films at Tribo-interface in Hydrogen Gas**, ***J. Sugimura*** *(sugimura.joichi.666@m.kyushu-u.ac.jp)*, Kyushu University, Japan **INVITED**

This paper overviews the studies on surface films at tribo-interface that governs friction and wear behaviors in hydrogen gas environment. The studies include friction and wear of a range of metals, polymeric materials and coatings, and rolling contact fatigue of steels. Dry sliding of metals is governed by the formation of thin surface films, which depends on hydrogen itself but more significantly, for some important transition metals, on trace oxygen and water in hydrogen. Oxide films formed on steel surfaces show resistance against hydrogen uptake that accelerates hydrogen-assisted flaking failure under rolling-sliding contact. Tribo-chemical films at metal surfaces also affect friction and wear of polymers used in dynamic seals. These effects are enhanced in hydrogen at ultra-high pressure. Diamond like coatings are candidates for use in hydrogen applications, and some findings including delamination caused by hydrogen uptake and the effect of trace impurities on friction are shown.

9:20am **E1-3-5 Friction Behavior at the Nanoscale of Nitrided and Post-oxidized Plain Steel**, *M. Freislebem, C. Menezes, F. Costi, P. Ferreira, C. Aguzzoli, I. Baumvol*, ***C. Figueroa*** *(cafiguer@ucs.br)*, Universidade de Caxias do Sul, Brazil

The phenomenon of friction is present at every moment from to provide the braking action in vehicles up to avoid/minimize its action in mechanical devices for energy efficiency issues. Despite of the accumulated knowledge after centuries of research in such area, the phenomenon of friction is not fully understood. From a tribological point of view, the friction coefficient depends on shear strength, toughness fracture, hardness, and elastic modulus where all of them are macroscopic properties of the involved materials divided in adhesive and ploughing friction components. From a physicochemical point of view, the macroscopic properties cited before are understood in terms of attractive forces (Van der Waals and/or Casimir), strength and stiffness of chemical bonds, grain boundary interactions, and thermal conductivity involving phonons and electronic band structures. However, there is a lack of a theory that allows to connect the macroscopic behavior with nanoscopic aspects and an integrated model of friction still remains as a challenge.

The aim of this study is to investigate the friction behavior at the nanoscale of a plain steel after plasma nitriding and different processing times of plasma post-oxidation. Nanoindentation experiments under different low normal loads were performed in order to analyze the friction behavior between a conical tip (diamond) and the modified steel surface from 20 nm up to 300 nm in-depth. The chemical structure of the outermost layers was determined by GD-OES. The crystalline phases and microstructure were analyzed by GA-XRD and SEM, respectively. Moreover, hardness and elastic modulus at those depths were measured. One can see that the friction coefficient (CoF) decreases when higher oxygen content are detected on surface. However, the lower the hardness, the higher the CoF. According to recent models that correlate the friction behavior with phonons, a stiffer chemical bond must dissipate more energy increasing the CoF, which is in

opposition to our results. In our system, we propose that not only phonons contribute to thermal conductivity but also the electronic behavior is important to dissipate energy. Finally, the friction behavior will be discussed taking into account the chemical structure and physical models for thermal conductivity of materials.

9:40am **E1-3-6 Hardfacing Using Low Cost Ferro-alloy Powder Mixtures by Submerged Arc Welding**, ***R. Zahiri*** *(zahiri.ramin@gmail.com), R. Sundaramoorthy, C. Subramanian*, Black Cat Blades Ltd., Canada

Wear resistant overlays are widely used in abrasive wear applications in the mining, construction and agricultural industries. In the present study, new overlays were formed using a submerged arc welding (SAW) process using mixtures of ferro-alloy powders, cast iron chips or stainless steel shots as alloying sources on a low carbon steel substrate. These overlay coatings are essentially metal matrix composites consisting of in-situ formed $(Fe,Cr)_x(C,B)_y$ type hard phases in a metallic matrix. Microstructural analysis (optical and scanning electron microcopy) along with macro- and micro-hardness measurements were performed on the overlays to evaluate the mechanical properties of the different microstructures developed. ASTM G65 dry sand/rubber wheel abrasion testing (Procedure A) was done on samples to assess their wear resistance. Microstructural results indicate that both hypoeutectic and hypereutectic structures of Fe-Cr-C and Fe-Cr-C-B systems with and without primary hard phases could be produced using appropriate powder mixture ratios and through controlling the dilution levels. ASTM G65 test results shows that the overlays produced using lower cost materials show mass losses comparable to those produced using commercially available high alloy wires and rods.

10:00am **E1-3-7 3-D FIB Serial Sectioning to Determine Solidification and Wear Mechanisms in Laser Deposited Metal-Ceramic Coatings**, *J.E. Mogonye, H. Mohseni, R. Banerjee,* ***T. Scharf*** *(scharf@unt.edu)*, University of North Texas, US

Multifunctional, adaptive composite coatings are needed that combine the properties of solid/self-lubrication, high mechanical hardness and high fracture toughness. We have utilized a Laser Engineered Net Shaping (LENS) process to fabricate a novel Ni/TiC/graphite self-lubricating composite coating for applications that combine these three important properties: graphite phase for solid/self-lubrication and titanium carbide phase for high hardness in a relatively high fracture toughness nickel matrix. Microstructural evolution during solidification and wear were studied with 3D focused ion beam (FIB) serial sectioning in the SEM. Novel insights into surface and subsurface deformation processes and mechanisms include stress-induced phase transformation from microcrystalline graphite to amorphous carbon as well as the formation of a nanocomposite mechanically mixed layer (heavily-refined nanocrystalline Ni grains in an amorphous carbon matrix). The refined Ni grain boundaries serve as pathways for extrusion of subsurface graphite/a-C to the surface. Another insight into the self-lubricating behavior was how subsurface compressive stresses continually feed primary and eutectic graphite into the mechanically mixed layer. These processes are collectively responsible for improved properties.

10:20am **E1-3-8 Tribological Behaviour of CrN Coating in Lubricated Contact**, ***B. Podgornik*** *(bojan.podgornik@imt.si), M. Sedlaček, M. Godec*, Institute of Metals and Technology, Slovenia

By improving tribological properties, especially wear resistance of contact surfaces, hard coatings provide great opportunity for improving performance, durability and efficiency of mechanical systems, including forming tools and machine components. However, for the successful application of hard coatings, coated surfaces have to perform adequately under dry and oil-lubricated conditions, with the majority of forming tools and components still being oil-lubricated. In the case of metallic surfaces action of extreme-pressure (EP) and anti-wear (AW) additives, used to reduce friction and wear, is well understood and described in detail. However, this is not the case for coated surfaces, especially when it comes to the influence of additive type and contact conditions.

The aim of the present investigation was to determine the influence of additive type and concentration in connection to contact conditions on the tribological behaviour of boundary lubricated CrN coatings, found in many forming and machine component applications. Tests were performed under reciprocating sliding motion using ball on flat test configuration, with ball-bearing steel ball being loaded against CrN coated discs. CrN coating was tested in the contact pressure range of 1.0 to 3.0 GPa, sliding speed range of 0.01 to 0.15 m/s and oil temperature range of 20 to 200°C. Lubricants included in the investigation comprised pure PAO, and PAO mixed with commercial EP, AW and friction modifier additive.

10:40am **E1-3-9 The Effect of Adhesion-mitigating Coatings on Rolled Aluminum Surface Quality**, ***O.A. Gali*** *(gali@uwindsor.ca)*, Uniniversity of Windsor, Canada, *M. Shafiei, J.A. Hunter*, Novelis Global Research and Technology Center, US, *A.R. Riahi*, University of Windsor, Canada

The effects of work roll material on the surface quality of aluminum during hot and cold rolling has long been a subject of intense research. The roll itself is subject to wear, as well as galling or scuffing from interaction with the aluminum work piece. These defects to the roll and aluminum alloy are affected by the tribological conditions between the roll and the aluminum piece; as such lubrication and roll surface conditions are parameters of particular interest to researchers. A rolling simulator, with a roll-on-block configuration, developed at the University of Windsor has been used to study the effects of rolling conditions on the surface quality of rolled aluminum products. It simulates the tribological surface deformation experienced by the work piece during industrial rolling, allowing for the variation of rolling parameters such as roll surface conditions (e.g. surface roughness and coating), temperature, rolling load, lubrication and forward slip to examine their effects on the roll and the work piece.

In this study, the effect of roll coatings on the life time of the rolls and the rolled aluminum surface quality were of particular interest. AISI 52100 steel roll surfaces were treated with eight coatings which included non-hydrogenated DLC, chromium and six nitride based coatings; which were run against AA1100 aluminum pieces at high and low temperatures to emulate hot and cold rolling conditions. Scanning electron microscopy (SEM), focused ion beam (FIB) microscopy, and high resolution transmission electron microscopy (HR-TEM) were employed to investigate adhesion and surface conditions of the rolls and work pieces. The severity of aluminum adhesion on the rolls was found to be a function of the coating type. During dry tests aluminum adhesion was most severe on the uncoated and chromium coated rolls, with corresponding severe surface damage in the form of deep groves covering the mating aluminum pieces. Nitride coatings performed better, especially the ZrN, showing less aluminum adhesion to the roll and surface damage to the work piece. However, the non-hydrogenated DLC coatings displayed the best performance of all the coatings with no aluminum adhesion and little surface damage to the work piece surface. These observations had good correlation with the coefficient of friction plots. This research looks to evaluate adhesion-mitigating coatings for the improvement of rolled aluminum surface quality and the roll life and minimizing the use of harmful lubricants.

11:00am **E1-3-10 Ab Initio Investigation of Atomistic Mechanisms in Solid and Boundary Lubrication**, ***Righi*** *(mcrighi@unimore.it)*, CNR - Istituto Nanoscienze S3, Universita' di Modena e Reggio Emilia via Campi, Italy **INVITED**

Tribochemical reactions can highly influence the tribological properties of materials as they chemically modify the surfaces in contact with consequent modification of their adhesion, resistance to wear and friction.

One example is the environmental dependence of the tribological behavior of carbon films. We report the real-time atomistic description of the tribochemical reactions occurring at the interface between two diamond films in relative motion, by means of large scale ab initio molecular dynamics. We show that the load-induced confinement is able to catalyze diamond passivation by water dissociative adsorption. Such passivation decreases the energy of the contacting surfaces and increases their electronic repulsion. At sufficiently high coverages, the latter prevents surface sealing, thus lowering friction. Our findings elucidate effects of the nanoscale confinement on reaction kinetics and surface thermodynamics, which are important for the design of new lubricants. [1]

A second example is the functionality of chemical additives included in engine oils to reduce friction in conditions of boundary lubrication. We identified the reaction paths for phosphorus release from the dissociative adsorption of organo-phosphorous molecules and analyzed its effects in reducing the adhesion and shear strength of iron interfaces in comparison with sulfur.[2]

Lamellar materials like graphite and molybdenum disulfide are known to be good solid lubricants. In micro- and nano-scale applications, the thickness of a solid lubricant can be a very important factor. We considered few-layer films of graphene and MoS2 and studied the effects of an applied load by analyzing interlayer electronic charge displacements. [3,4]

[1] G. Zilibotti, S. Corni and M. C. Righi, Phys. Rev. Lett., in printing.

[2] M. I. De Barros-Bouchet, M. C. Righi, D. Philippon, S. Mambingo-Doumbe, T. Le Mogne, J. M. Martin, A. Bouffet, submitted.

[3] M. Reguzzoni, A. Fasolino, E. Molinari and M. C. Righi, Phys. Rev. B 86, 245434 (2012).

[4] G. Levita, A. Cavaleiro, E. Molinari, T. Polcar, and M.C. Righi, submitted.

11:40am **E1-3-12 Effect of Nitrogen Injection Surface Layer on the Tribological Performance of M50 Steel Tribo-parts**, ***B. Peng*** *(pbtaishan@163.com),* The First Research Academy of China Aerospace Science and Technology Corporation, China, *C. Zhang*, Harbin Institute of Technology, China, *L. Jia*, *L. Chi*, The First Research Academy of China Aerospace Science and Technology Corporation, China, *L. Wang*, Harbin Institute of Technology, China

In modern aircraft engines, bearings must endure heavy loads, high sliding-rolling speeds, and high temperatures while in sliding/rolling contact. Under the extreme conditions, wear and lubrication failures generally take place on the contact surfaces. M50 steel is a material used for aircraft bearings because of its excellent high temperature strength, thermal stability, and thermal fatigue resistance. Research on the surface damage of M50 tribo-parts under extreme sliding/rolling contact is essential for the development of aircraft engines.

The wear and friction behaviors of M50 steel have been widely researched. Scuffing damage is one of the catastrophic failures that happen in tribo-parts under the extreme conditions that have been studied by many researchers. However, due to different test conditions, there is no unified conclusion on which conditions initiate scuffing on the surfaces of tribo-parts. The goal of the current study is to extend our previous investigation on the tribological performance of M50 bearing steel under the extreme conditions found in aircraft engines. The effect of nitrogen injection on the tribological performance of M50 steel tribo-parts was investigated using finite element analysis as well as experimentally.

The experiments were carried out in a two-disk test rig at four slide/roll ratios with synthetic aircraft engine oil No.4050 at approximately 80 ℃ . In the two-disk test rig, one disc is a cylinder and the other one has a crowned profile in the circumferential direction. Both disks are made of M50 steel. Injection of nitogen on the surface of M50 disks was conducted. The surface failure on M50 disks was investigated. The contact surfaces and cross-sections of the worn areas were analyzed using optical microscopy and scanning electron microscopy (SEM). In addition, Vickers hardness and residual stress measurements were performed at different depths in order to analyze the tribological performance of the surfaces. The results reveal that the damage mechanisms of the slow and fast disc surface are fatigue spalling and adhesive wear, respectively. After injecting nitrogen, the surface damage on the M50 disks was greatly reduced.

The sliding/rolling contact of the tribo-parts was modeled using finite element methods in order to simulate the stress and strain fields of the two disks in the experiments. In the FE model, the nitrogen injection layer on the surface of the two disks was also modeled. The simulation results explained how the nitrogen injection layer affected the failure of the contacting M50 surfaces in the experiments.

Topical Symposia
Room: Tiki - Session TS3

Energetic Materials and Micro-structures for Nanomanufacturing

Moderator: D. Adams, Sandia National Laboratories, C. Rossi, LAAS-CNRS

8:00am **TS3-1 2-Tetrazene Derivatives as New Energetic Materials, Synthesis, Characterization and Energetic Properties**, ***C. Miró Sabaté*** *(carlos.miro-sabate@univ-lyon1.fr), H. Delalu*, Universite de Lyon, France **INVITED**

Aqueous monochloramine ($Cl–NH_2$) can be used to oxidize 1,1-dimethylhydrazine to (*E*)-1,1,4,4-tetramethyl-2-tetrazene (**1**). Compound **1** was obtained as a pale yellow liquid and has hypergolic properties. **1** can be oxidized with potassium permanganate forming formyl-substituted 2-tetrazenes, namely (*E*)-1-formyl-1,4,4-trimethyl-2-tetrazene (**2**) and (*E*)-1,4-diformyl-1,4-dimethyl-2-tetrazene (**3**). Additionally, compound **1** reacts with an ether solution of monochloramine to form a stable 2-tetrazenium cation as the chloride salt (**4**). The chloride in compound **4** was exchanged by energetic anions giving salts based on a 2-tetrazenium cation and nitrate (**5**), perchlorate (**6**), 5,5´-azobistetrazolate (**7***$6H_2O$), picrate (**8**) and azide (**9**) anions. All of the reported compounds were characterized by analytical and spectroscopic methods and, whenever possible, their solid state structure was determined using low temperature X-ray crystallography. Furthermore, we used the B3LYP method to compute the NBO charges of formyl-derivatives **2** and **3** and of the 2-tetrazenium cation. Due to the energetic nature of all materials they were submitted to standard friction and impact sensitivity tests and we used DSC analysis to assess their thermal stabilities. We also estimated the heats of formation of the energetic compounds using quantum mechanical methods (CBS-4M) and calculated their detonation parameters (pressure and velocity) and specific impulses. Lastly, the 2-tetrazene derivatives presented herein are of prospective interest as a new class of low toxicity, low sensitivity energetic materials.

8:40am **TS3-3 Detonation in Vapor-deposited Explosive Films at the Micro-scale**, ***R. Knepper*** *(rkneppe@sandia.gov), M. Marquez, A. Tappan*, Sandia National Laboratories, US

Recent advances in physical vapor deposition of explosive materials have led to films that are capable of detonating at thicknesses smaller than 100 microns. The critical thickness needed to sustain detonation can be reduced even further (down to a few tens of microns) by confining the explosive with thin layers of a dense, inert material. The ability to sustain detonation at such small length scales opens the potential for such films to be integrated into micro-scale systems using standard micro/nanofabrication methods for use in actuation, gas generation, or similar functions. In this work, we present vapor-deposited hexanitroazobenzene (HNAB) and copper films as a model system to study the effects of confinement on the detonation properties of secondary explosives. Both the HNAB and copper confinement layers are vapor-deposited to promote intimate contact between the explosive and confinement and to provide precise control over both layer thicknesses and microstructure. Confinement thickness is varied to determine the minimum necessary to behave as though the confinement was effectively infinite, and the effects on detonation properties are quantified. In addition to the practical impact of these experiments, identification of the minimum effectively infinite confinement condition can provide insight into the kinetics of the detonation reaction.

9:00am **TS3-4 Engineered Microstructures of Binary Energetic Thermites by Additive Micro-manufacturing Methods: Fabrication, Characterization and Performance**, ***K. Sullivan*** *(sullivan34@llnl.gov), C. Zhu, J. Kuntz, E. Duoss, A. Gash, C. Spadaccini*, Lawrence Livermore National Laboratory, US

Here we report the use of two additive micro-manufacturing techniques: 1) Electrophoretic deposition (EPD) and 2) Direct ink writing (DIW) as a means to prepare thin films and three-dimensional structures of well-mixed copper (II) oxide/ aluminum (CuO/Al) binary particulate composites. Films were deposited onto patterned electrodes, with very fine feature sizes, which were used for mechanistic investigations of the ignition and combustion. The EPD films were examined using electron microscopy, and their combustion characteristics were analyzed with high-speed videos. The results show that films prepared by EPD show a large enhancement in the combustion speed with total film thickness. These films are also particularly useful for developing thermites for micro-energetic applications. In further studies, the DIW method was successfully used in combination with EPD as a means to synthesize various architectures of energetic materials. Patterns of electrodes are written onto an arbitrary substrate, and EPD is then used to deposit thermite materials directly onto the patterns. This combination of techniques allows for investigations of the characteristic fuel / oxidizer ignition and reaction in engineered three-dimensional microstructures. The results thus far suggest that, in addition to good fuel/oxidizer mixing, other design criteria can be utilized to tailor the reactivity of composite thermites. This includes using large enough features to allow gas trapping and pressure unloading, and also designing microstructures which enable more directed transport of hot gases and particles in the desired propagation direction. The combination of EPD and DIW allows for the synthesis of such architectures, and this scalable capability will allow for a bottom-up development of energetic systems with micro-engineered control.

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

9:20am **TS3-5 Revealing the Reaction Dynamics and Phase Evolution in Self-propagating Reactive Nanolaminates using Movie Mode DTEM**, ***T. Lagrange*** *(lagrange2@llnl.gov)*, Lawrence Livermore National Laboratory, US, *D. Adams, R. Reeves*, Sandia National Laboratories, US, *B.W. Reed, G.H. Campbell*, Lawrence Livermore National Laboratory, US **INVITED**

Most processes in materials naturally occur in conditions far-from-equilibrium having transient states that evolve on short time scales. Due to the resolution limitations of conventional analytical techniques, we are typically confined to conduct experiments near equilibrium or observe the material post process. Though these observations have allowed useful insights about the material's behavior, attempts to understand the coupled and convoluted events in complex processes have been hampered by the difficulty of capturing the events in detail as they unfold on nanosecond and microsecond timescales, requiring a technique with improved temporal resolution. To meet this need, the dynamic transmission electron microscope (DTEM) at Lawrence Livermore National Laboratory was

developed which can capture diffraction patterns or images of a fast-evolving material process.

Prior DTEM hardware only allowed single-pump/single-probe operation, building up a process's typical time history by repeating an experiment with varying time delays at different sample locations. The Movie Mode (MM) DTEM upgrade now enables single-pump/multi-probe operation and comprises two unique technologies, a cathode laser system that allows nanosecond pulse shaping for producing electron pulse trains and a high-speed electrostatic deflector array that directs each electron pulse (image) to a separate patch on a CCD camera. At the end of the experiment, the CCD image is read-out and segmented into a time-ordered series of images, i.e., a movie.

These technical improvements allow us to track the creation, motion, and interaction of defects, phase fronts, and chemical reactions, providing invaluable information of the chemical, microstructural and atomic level features that influence the dynamics and kinetics of rapid material processes. In particular, we have used the new MM-DTEM capability to study reaction dynamics in Ti-B and Co-Al based reactive nanolaminates. By tracking the position of the reaction front with multiple image acquisition, we have precisely measured the front velocities as a function of composition, bilayer content and thickness. We have also quantified the phase evolution behind the reaction front through a MM-DTEM obtained sequence of diffraction patterns, allowing us to determine the evolution and rapid kinetics of the exothermic reactions. This presentation will discuss new insights gained about the dynamics of reactive nanolaminates using this novel MM-DTEM capability. This work was performed under the auspices of the U.S. Department of Energy, Contract No. DE-AC52-07NA27344, and supported by DOE-BES, Division of Materials Science and Engineering.

10:00am **TS3-7 Effect of Mixing Conditions on Reaction Propagation for Blade Cast Energetic Thin Films**, ***K. Meeks***, *J. Cano*, Texas Tech University, US, *M. Pantoya (michelle.pantoya@ttu.edu)*, Texas Tech University. US, *A. Apblett*, Sandia National Laboratories, US

In order to develop low cost, energetic, thin film heat sources, the mixing condition of the energetic thin film needs to be understood. In this work, magnesium and manganese oxide powders were mixed with Polyninylidene Fluoride (PVDF) with a Methyl Pyrrolidone (NMP) solvent and blade cast onto stainless steel foil and glass substrates. The rheological properties of these mixtures were investigated to quantify the mixing condition. Solids content, equivalence ratio and dry film thickness were varied and open flame propagation speed and calorific output was investigated for each mixture ratio. A 0.45 solids-liquid ratio resulted in significantly higher flame propagation rates for both open and confined configurations. Rheometry measurements and physical characterizations of the films reveal that this solids-liquid ratio produced the most homogeneous mixtures that then resulted in the highest flame speeds. On a scale beyond thin films, these results imply that for any thermite or energetic composite, changing the solids loading can affect mixing and impact the final flame speed and energy propagation mechanism. It was found that flame speed increased as a function of dry film thickness, although calorific output stayed constant. This indicates that flame speed is increased by greater available thermal energy per inch provided by a thicker film, but no additional thermal energy is available. For varying equivalence ratio, flame speeds were highest for an equivalence ratio of 1.0. Flame speed decreased for lower equivalence ratios, but would not propagate for higher equivalence ratios. Calorific output increased as equivalence ratio approached 1.0, but remained relatively constant as it increased past that, indicating that net benefit to combustion was negligible for increased equivalence ratio.

10:20am **TS3-8 Reaction Instabilities In Cobalt/Aluminum Nanolaminates Made By Sputter Deposition**, *D. Adams (dpadams@sandia.gov)*, ***R. Reeves***, Sandia National Laboratories, US

Cobalt/aluminum multilayers made by vapor deposition undergo high temperature, self-propagating formation reactions but exhibit several different reaction modes depending on multilayer design and environmental conditions. With this presentation, we describe the reaction front dynamics of Co/Al reactive nanolaminates as a function of the initial temperature of the unreacted material. Sample geometries that exhibit stable reaction fronts as well as geometries that present "spinning" reaction front instabilities were investigated at initial temperatures ranging from room temperature to 200^{o}C. It was found that reactions in samples with small reactant periodicities (<66.4 nm) were stable at all temperatures, reaction in large periodicity samples (≥ 100 nm) were unstable at all temperatures, and reactions in samples with intermediate periodicities transitioned from unstable behavior to stable behavior with increasing initial temperature. The results suggest that behaviors typical of two types of reaction kinetics are present in unstable reaction fronts: slow, diffusion-limited kinetics in the regions between reaction 'spin' bands and a faster mechanism at the leading edge of the bands.

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10:40am **TS3-9 Modelling Al-based Reactive Nanolaminates Growth: Dealing with Hyperthermal Trajectories through Combined DFT and Kinetic Monte Carlo Techniques**, ***A. Esteve*** *(aesteve@laas.fr)*, LAAS-CNRS, France

Reactive nanolaminates are characterized by a strong chemical reactivity of their interacting individual components (metal/metal or metal/ oxide alternating layers) that causes local release of large amount of chemical energy. Today, the relation between the energetic performances with their composition and micro/nanostructure is a major challenge to produce tunable and controlled material that can be integrated into MEMS chip [1] to produce local pressure, temperature or specific gas species. Along this line, the relations between detailed atomic interface arrangement and aging/initiation/self-sustained combustion remain elusive. From a modelling standpoint, Molecular Dynamics has been applied to the simulation of very early stages of energetic materials initiation on model interfaces built from crystallographic data of bulk materials. In this paper, we propose a new methodology enabling to simulate the Al-oxyde interface formation and predict its structure taking into account real experimental deposition processing conditions. To this end a multi-level approach is presented that combines DFT-based calculations (Density Functional Theory) with Kinetic Monte Carlo (KMC) techniques. In this DFT/KMC frame, we will show how to extend the kinetic-limited conventional KMC to take into account exothermic reactions and associated extra hyperthermal atomic motions beyond kinetic-based hopping from one energetical minimum to another. Presented results will include Al/oxide nanolaminates surface chemical mechanisms via DFT calculations with a specific attention on Aluminum oxidation, KMC simulations of early stages of oxide PVD deposition onto Al(111), hyperthermal surface motions of deposited oxygen atoms through a "hot atom" derived KMC.

[1] J. Micromech. Microeng. 23 (2013) 105009.

11:00am **TS3-10 Interface-layer Formation in Reactive Al-based Thin Films Studied by Spectroscopy, First Principle Calculation and Nanocalorimetry**, ***Y. Lu***, University of Texas at Dallas, US, *L. Glavier, C. Rossi (rossi@laas.fr), A. Esteve, A. Hemeryck*, LAAS-CNRS, France, *Y. Chabal*, University of Texas at Dallas, US

Interface layers in Al-based reactive thin film play a crucial role in the energetic properties and reactivity of such materials [1]. The composition and related microstructure of the interface of Al-based reactive films can greatly influence the ignition temperature, reaction kinetics and even the stability at low temperature. This works aims at developing an understanding of the interface formation processes between Al and reactive oxides and investigating its role in the reaction kinetics.

Two types of oxides (CuO and ZnO) are synthesized by Atomic Layer Deposition to obtain high-quality, thin and chemically-controlled model oxide surfaces. Al deposition is then performed by e-beam evaporation in high vacuum (10^{-9} Torr) and the Al-(Cu,Zn)-O interfaces probed as a function of deposition rate (0.5A-5A/min). Specifically, extensive characterization, combining in-situ IR, XPS and low energy ion scattering (LEIS) with ex-situ XRD and AFM are used to characterize the nature of both the thin oxide films (the crystalline ZnO, polycrystalline CuO) as well as the formation of an amorphous interfacial layer prior to pure Al deposition. The mechanism of interface formation upon Al deposition is elucidated by first principles calculations, in particular the propensity for Al atoms to penetrate into the oxide films.

Once the Al/(Cu,Zn)O nanolaminates are grown, a quantitative investigation of the interface formation and evolution at low temperature is also performed by nanocalorimetry. To that end, we use a nanocalorimeter based on a micromachined hotplate platform that has been designed, fabricated and characterized with different Al-based thin films to screen the reaction kinetics during interface formation.

[1] Appl. Mater. Interfaces 2013, 5, 605−613

11:20am **TS3-11 Spark Ignitable NiAl Ball Milled Powders and Use Thereof for Bonding Applications**, *A. Kyriakou, V. Hadjisofokleous*, University of Cyprus, Cyprus, *I.E. Gunduz*, Purdue University, US, *A. Hadjiafxenti, T. Kyratsi, C.C. Doumanidis*, ***C. Rebholz*** *(claus@ucy.ac.cy)*, University of Cyprus, Cyprus

Low-energy ball milling of aluminum and nickel particles with an overall composition corresponding to the NiAl intermetallic phase was performed up to milling durations of 13 hours. Results show that microstructural refinement with increasing milling times increases reactivity, where the intermetallic formation temperatures reduce to those of sputtered

nanostructured multilayer foils with a similar phase formation sequence during differential scanning calorimetry (DSC) analysis. Furthermore, loose NiAl particle (milled for 11-12 hours) piles, NiAl particles cold-compacted into pellets or pressed/rolled between thin metal overlayers (e.g. Al) into thin sandwich structures, and NiAl particles mixed with additional Al or coated with an Al shell, could all be ignited with a low-energy spark from a 9 V battery. Results from high-speed optical and infra-red imaging suggest that the thermal front velocities and maximum temperatures strongly depend on the produced structures/shapes. Al overlayers from the sandwich structures provide extra cooling and reduce energy density, resulting in quenching of the reactions at a sandwich thickness of 400 μm, and decreasing the maximum temperature and velocity to approximately 1300ºC and 0.16 m/s (compared to approximately 1500ºC and 0.2 m/s for 800 μm thick structures), respectively. Additional bonding experiments using the sandwiched structures as reactive inserts was successful, indicating that they can be used in a similar fashion to sputtered nanostructured foils.

11:40am **TS3-12 Reactions in Single Ball-milled Particles of Ni/Al System**, ***I.E. Gunduz*** *(igunduz@purdue.edu)*, *BA. Mason*, Purdue University, US, *LJ. Groven*, South Dakota School of Mines and Technology, US, *S. Son*, Purdue University, US

The reaction kinetics of single high-energy ball-milled Ni/Al particles were determined using high-speed optical and infrared cameras. Particles with diameters in the range 106-850 μm were (i) magnetically attached at the end of a needle and locally ignited using a spark from a thin Au wire to observe the thermal front motion, and (ii) rapidly and uniformly heated on a hot plate to record the time-temperature profiles across the particle.

The results show that thermal front velocities within an individual particle are an order of magnitude larger than their cold-pressed compacts and loose powder piles (~2 m/s vs 0.1 m/s) and closer to those observed in magnetron sputtered foils (2-13 m/s). Smaller particles react at faster front propagation rates. The rate of temperature change was similar for local and uniform heating, indicating similar reaction kinetics. The primary reason for low velocities observed in cold-compacted pellets is the thermal resistance between particles due to the formation of an oxide layer upon exposure to air.

Coatings for Use at High Temperatures
Room: Sunrise - Session A1-2

Coatings to Resist High Temperature Oxidation, Corrosion and Fouling
Moderator: M. Weaver, The University of Alabama, V. Kolarik, Fraunhofer Institute for Chemical Technology ICT, D. Litton, Pratt & Whitney

1:30pm **A1-2-1 Some Results About the Interactions Between Reactivity, Interdiffusion and Creep in Coated Thin Wall Superalloy Systems**, ***D. Monceau*** *(daniel.monceau@ensiacet.fr)*, *E. Andrieu*, CIRIMAT laboratory, University of Toulouse, France, *S. Dryepondt*, CIRIMAT laboratory, University of Toulouse, France; present address: ORNL, US, *A. Raffaitin*, CIRIMAT laboratory, University of Toulouse, France; present address: AIRBUS, France, *D. Texier*, CIRIMAT laboratory, University of Toulouse, France; present address: ENSMA, France **INVITED**

Single crystal nickel-based superalloys are used as structural materials for hot pressure blades in aeronautic gas turbines. Cooled and uncooled blades both include thin-wall sections, sometimes less than 1 mm thick. These parts are always coated with a typically 50 µm thick metallic alloy to improve their resistance to high temperature corrosion and cyclic oxidation. These architectures result in large gradients of microstructure and material properties. Moreover, these systems are subjected to thermal gradients in addition to cyclic temperature, cyclic loading and aggressive atmosphere. The thickness of the area where the substrate microstructure is affected by selective oxidation or by interdiffusion with the coating cannot be neglected anymore for thin components. Interactions among surface reactivity, interdiffusion and creep properties have hence to be considered.

In order to model the lifetime of these components, first generation Ni-based single crystal superalloys were creep tested at high temperature under controlled atmospheres. Flat thin (1mm) and ultra-thin (down to 20 µm) specimens were machined. Aged systems were also machined to extract mechanical samples from the various layers of these architectural materials. The main objective is to characterize the mechanical properties of each individual layer (coating, interdiffusion zone). This approach has been made possible by the development of new test rigs dedicated to high temperature mechanical testing of ultra-thin specimens. In addition, thicker specimens were also creep tested at constant or cyclically changing temperatures, with in some cases a switch of atmospheres during the test (high/low P_{O2}) in order to understand the nature of the coupling between the various degradation mechanisms. For example, creep tests were performed on coated and uncoated specimens in the exact same conditions to discriminate between the effects of surface reactivity and thermal cycling on creep rate. As an overall result, it was found that two kinds of interactions need to be distinguished. The first "static" interaction ,- well-known in the literature – consists of the formation of a non load-bearing section due to the irreversible evolution of the microstructure affected by oxidation and/or interdiffusion. , The building of creep database for graded materials is required to estimate the impact of the non load-bearing section. The second kind corresponds to the "dynamic" interaction between thermal cycling, "in progress" oxidation or interdiffusion, and creep. One example is the increased creep rate of a superalloy being oxidized with vacancies injection leading to a reversible vacancy super-saturation. Fundamental research is needed to better understand these dynamic coupling effects and some available examples of the research in progress will be shown .

2:10pm **A1-2-3 Characterization of the Gradient of Mechanical and Physical Properties Existing in β-NiAlPt Coated Ni-based Single Crystal Superalloy by using Ultrathin Specimens**, ***D. Texier***, *E. Andrieu*, CIRIMAT, France, *S. Selezneff*, *A. Longuet*, Snecma, SAFRAN Group, France, *D. Monceau (daniel.monceau@ensiacet.fr)*, CIRIMAT, France

In service, turbine blades are subjected to thermo-mechanical solicitation at elevated temperature and evolve in severe environmental conditions (oxidation and corrosion). Due to these harsh specifications, the use of Ni-based single-crystal superalloys overlaid with Thermal Barrier Coating (TBC) has proven to insure the integrity of this microstructure graded system for several thousands of hours of flights. NiAlPt or MCrAlY alloys generally constitute the bond coating between the superalloy and the thermally insulating zirconia. Nevertheless, microstructure and properties of the different layers constitutive of the TBC system evolve with time due to interdiffusion, oxidation and mechanical solicitations. These evolutions as rumpling/ratcheting, edge delamination, phase transformations, voids formation are deleterious for the lifetime of turbine blades. Therefore, improvements in the prediction of mechanical behavior and the lifetime of turbine blades require a data base related to the intrinsic properties of each layer at different ageing times. Such data are missing for the modeling of the overall behavior of the TBC systems.

This study deals with the local characterization of the mechanical and physical behaviors of a β-NiAlPt coated AM1 superalloy up to 1100°C. Specimens, 25 to 35 µm thick, have been machined in order to assess the mechanical behavior of the specific layers of the graded materials having experienced different creep ageing conditions. Tensile experiments have been carried out in a temperature range of 700 to 1100°C. A database on mechanical and thermal expansion properties has been set up to describe the gradient of properties existing in such a system at operating temperatures.

2:30pm **A1-2-4 The Effect of a Cr Adhesion Layer on the Protective Behavior of Al_2O_3 Coatings Against Metal Dusting**, *E. Uribe-Lam*, *O. Salas (osalas@itesm.mx)*, *D. Melo-Maximo*, ITESM-CEM, Mexico, *L. Melo-Maximo*, IPN, Mexico, *J. Oseguera*, ITESM-CEM, Mexico, ***R.D. Torres***, PUCPR, Brazil, *R. De Souza*, USP, Brazil

Metal dusting is a form of corrosion that attacks Fe, Ni, and Co alloys in environments of high carbon potential in the 400-900°C range. The application of oxide thin films on various Fe-based materials has proven to be a promising method of protection against metal dusting. In the present work, Al_2O_3 coatings were applied on 304L stainless steel substrates by reactive magnetron sputtering using an adhesion interlayer of Cr. Uncoated and coated samples were then exposed to a carburizing atmosphere via thermogravimetry (TGA) to test the protective potential of the coatings. The exposed coated substrates showed a marked decrease in weight gain respect to the uncoated sample. The structure of the uncoated and coated samples prior and after the TGA runs were investigated in detail to determine the mechanisms of protection provided by the coatings.

2:50pm **A1-2-5 The Use of Advanced Surface Analytical Techniques to Investigate Early Oxidation Stages of Aluminides**, ***P. Marcus*** *(philippe-marcus@chimie-paristech.fr)*, Chimie ParisTech (ENSCP), France **INVITED**

A detailed understanding of Al_2O_3/Ni-aluminides interfaces is a key issue for Thermal Barrier Coatings adhesion. Similarly the evolution of the oxide - intermetallic interface during the early stage of oxidation of TiAl is of primary importance in the context of increasing implementation of these alloys for high temperature applications.

The aim of this lecture is to show how advanced surface analytical techniques, Scanning Tunneling Microscopy (STM), X-Ray Photoelectron Spectroscopy (XPS), and Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) can be used to address these interfacial problems.

The selected examples will include the question of vacancies generated at the Al_2O_3/TiAl interface, studied by STM, and the Al_2O_3/NiAl interface, studied by XPS and ToF-SIMS.

The use of DFT for modeling the interface at the same scale as STM data (i. e. the atomistic scale) will also be discussed (vacancies and nanovoids).

3:30pm **A1-2-7 On the Electrochemical Features of the Intermetallics Formed During Hot Dip Aluminizing**, ***B. Lemmens*** *(babs.lemmens@ugent.be)*, Ghent University, Belgium, *B. Corlu*, *J. De Strycker*, Arcelor Mittal Global R&D Gent, Belgium, *I. De Graeve*, Vrije Universiteit Brussel, Belgium, *K. Verbeken*, Ghent University, Belgium

Zinc-based coatings effectively protect steel against corrosion but have some drawbacks related to environmental issues arising from zinc dissolution and to scarcity of zinc resources. Consequently, aluminium-based coatings gain importance both from a scientific as an industrial point of view. Despite the fact that these Al-based coatings are already being applied industrially, the electrochemical behaviour of the different intermetallic layers formed during the hot dipping process still remains under debate.

When the hot dipping process is performed in a pure Al bath, it gives rise to the formation of different intermetallic layers. The outer layer comprises nearly pure aluminium. This layer is on top of a first intermetallic layer commonly referred to as $FeAl_3$. The second intermetallic layer is a Fe_2Al_5 layer and adjacent to the steel substrate. In case Si is added to the bath, this element also affects the intermetallic layers.

In order to clarify the electrochemical nature of the different layers with respect to each other, both macroscopic and local electrochemical measurements were performed. To evaluate the performance of the different layers, craters with different depths were produced using a GDOES system, to expose the different layers to the atmosphere. Within those craters the

electrochemical behaviour of each specific layer was analysed by immersion in a chloride solution. Afterwards a characterisation of the craters was performed by material characterization techniques such as SEM-EDX and XRD.

3:50pm **A1-2-8 Effects of Ceramic Particle Size on Corrosion Behaviors of Cold Sprayed SiC_p/Al 5056 CComposited Coatings**, ***Y.Y. Wang*** *(yingying.wang@insa-lyon.fr), B. Normand, N. Mary*, Insa De Lyon, France, *H. Liao*, UTBM, France

Silicon carbide (SiC) particles reinforced Al 5056 (SiC_p/Al 5056) composite coatings were deposited by cold spray. Effects of ceramic particles on microstructure and corrosion behaviors were investigated. Microstructures were examined by optical microscopy (OM) and Field Emission Scanning Electron Microscopy (FE-SEM). Results showed that the coatings became more compact with the addition of ceramic particles. Porosity of as-sprayed composite coatings was all less than 1 % and decreased with the increase of SiC particles size. XRD patterns showed that the width of peak widened and the position shifted to higher degrees as a result of increased residual compressed stress with the increase of SiC particles size. Open circuit potential (OCP) measurements and potentiodynamic polarization scans in 0.1 M sodium sulfate (Na_2SO_4) solutions of different pH values were used to evaluate the corrosion performance. Corrosion potential and corrosion current decreased with the increase of SiC size in both solutions. Surfaces after corrosion were also checked by XRD, FE-SEM and Energy-dispersive X-ray spectroscopy (EDS). Corrosion products were AlO(OH) and Al_2O_3.

4:10pm **A1-2-9 Corrosion Resistance of Ni Coatings on Steel Deposited with Electrolytic Plasma Processing**, ***A. Smith***, *E. Meletis (meletis@uta.edu)*, University of Texas at Arlington, US

Electrolytic Plasma Processing (EPP) is a surface modification technology that can encompass surface cleaning and sequential coating. Deposition of both metallic and ceramic coatings is feasible by utilizing respectively, the cathodic or anodic version of the process. The EPP process is attracting significant interest from the engineering community due to its simplicity, economic advantages and its green character. For metallic coating deposition, the workpiece is the cathode of an electrical circuit and a conductive nozzle in close proximity is the anode. An aqueous electrolyte is then flowed through the nozzle and over the sample, closing the circuit, and a voltage is applied. The voltage, typically in the low hundreds, forms plasma on the sample surface resulting in metal deposition at a high rate. In the current study, low carbon steel was subjected to an EPP treatment with a nickel containing electrolyte in an effort to create a hard and corrosion resistant surface coating. The effect of deposition power and electrolyte concentration were examined by XRD, along with cross sectional SEM/EDS and microhardness measurements to determine their relationship to coating thickness, composition, and uniformity. The corrosion resistance was assessed by corrosion potential measurements and anodic polarization testing.

4:30pm **A1-2-10 An Investigation of Hot Dipped Zn-Mg-Al Coating with Improved Mechanical and Anticorrosion Properties**, ***C.Z. Yao*** *(cyao540@aucklanduni.ac.nz), S.L. Tay, T.P. Zhu, W. Gao*, The University of Auckland, New Zealand

Zn-Mg-Al coating was prepared by hot dipping method on carbon steel substrate. The phase structure, surface morphology, elemental composition, microhardness and corrosion property of the coatings were characterized by X-ray diffractometer (XRD), scanning electron microscopy (SEM-EDS), microhardness tester, and electrochemical workstation. Zn coating and Zn-Al coating were also prepared and tested for comparison purpose. The microhardness of Zn-Mg-Al coating is improved from 43 HV of Zn coating and 89 HV of Zn-Al coating to 178 HV. The improvement of microhardness may due to the formation of intermetallic phases. Mg addition also has the ability to decrease the crystal size of Zn, reduce the corrosion rate of Zn coating, and leading to a better anticorrosion property of Zn-Mg-Al coating.

4:50pm **A1-2-11 Influence of Ruthenium as an Alloying Element on the Corrosion Behaviour of Laser Treated AISI 316-NiTi**, ***B.A. Obadele*** *(obadele4@gmail.com), M.L. Lepule, P.A. Olubambi*, Tshwane University of Technology, South Africa

Recently, surface modification of AISI 316-NiTi with elements such as Nb, Co, Mo and ZrO_2 have been attempted. The aim of the study is to investigate the influence of ruthenium (Ru) additions and laser speed on the corrosion behaviour of AISI 316 austenitic stainless steel (ASS) reinforced with NiTi. $Ni_{54.6}Ti_{45.4}$ and $Ni_{54.60}Ti_{45.32}Ru_{0.08}$ feedstock powders blended in a Turbula mixer were laser deposited onto 316 ASS using a 4.4 kW Nd:YAG laser. Their corrosion behaviour was investigated in 0.9 % NaCl solution using potentiodynamic polarisation technique. It is well known that the corrosion performance of NiTi based alloys, especially the passivation depends on the surface conditions. Corrosion potential, E_{corr}, calculated for 316 ASSS, 316-NiTi and 316-NiTiRu were -0.38, -0.28 and -0.26 V respectively. A positive shift in E_{corr} and negative shift in I_{corr} shows a lower tendency and high resistance to corrosion for the 316-NiTiRu alloys as compared to 316 ASS. Ruthenium affects the cathodic Tafel constant (β_c) in the chloride solution, which indicates that it influences the cathodic part of the corrosion reaction. SEM micrographs revealed that the alloys were attacked by chloride ions, with different pit morphologies and depths.

5:10pm **A1-2-12 Microstructure, Mechanical and Anti-corrosion Property Evaluation of Iron-based Thin Film Metallic Glasses**, ***L.T. Chen***, *Y.C. Yang*, National Taipei University of Technology, Taiwan, *J.W. Lee* (*jefflee@mail.mcut.edu.tw)*, Ming Chi University of Technology, Taiwan

Recently thin films metallic glasses (TFMGs) represent a class of promising engineering materials for structural applications. Lots of efforts have been done on the research and development of TFMG materials. Nevertheless, the Iron-based thin film metallic glasses have rarely been investigated. In this work, the Iron-based Fe-Zr-Ti thin film metallic glasses with different Fe contents were prepared by magnetron co-sputtering system using pure Zr, Ti and Fe targets. The thermal behavior of each TFMG was determined using a differential scanning calorimeter (DSC). The crystal structure of the samples was determined by a grazing incidence X-ray diffractometer (GIXRD). Compositions of thin films were analysed by a field emission electron probe microanalyzer (FE-EPMA). Surface and cross-sectional microstructures of thin films were observed by scanning electron microscope (SEM) and transmission electron microscope (TEM), respectively. The surface roughness of thin films was explored by atomic force microscopy (AFM). A nanoindenter and scratch tester were used to evaluate the hardness and adhesion properties of TFMGs, respectively. The potentiodynamic polarization test in sodium chloride aqueous solution was conducted for each TFMG. It was discovered that the mechanical property of TFMG was enhanced as Fe content increased. The influence of Fe concentration on the amorphous state, microstructure, mechanical and anti-corrosion properties of Iron-based thin film metallic glasses was further discussed in this work.

Keywords: Iron-based, thin film metal glass, scratch tester, nanoindenter, potentiodynamic polarization test

Hard Coatings and Vapor Deposition Technology
Room: Royal Palm 1-3 - Session B4-2

Properties and Characterization of Hard Coatings and Surfaces

Moderator: C. Mulligan, US Army ARDEC, Benet Laboratories, J. Lin, Southwest Research Institute, U. Beck, BAM Berlin

2:10pm **B4-2-3 Observation of Hardness and Fracture Toughness Enhancement in Fe/VC Multilayer Films with Coherent Interfaces**, *C. Wang*, Northwestern Polytechnical University, China, *J.M. Pureza*, Universidade do Estado de Santa Catarina, Brazil, ***Y.W. Chung*** *(ywchung@northwestern.edu)*, Northwestern University, US

Under typical sputter-deposition conditions, 25-30% of the interfaces in Fe/VC multilayer films have the (100) orientation. The lattice constants of Fe and VC are such that these interfaces are coherent with a lattice mismatch of about 2.7%. It is believed that such coherent interfaces will affect the hardness and fracture toughness of these films. Fe/VC multilayer films with a fixed bilayer period (Λ = 8.8nm) and variable modulation Fe fraction (Λ_{Fe}/Λ ranging from 0.6 to 0.9) were deposited *via* dc magnetron sputtering. X-Ray diffraction and transmission electron microscopy were used to investigate the nanoscale layer structure of these films. Hardness was determined by nanoindentation and fracture toughness by microindentation techniques. Throughout the entire modulation Fe fraction investigated in this study, the hardness was enhanced over the rule-of-mixture value. Even at Fe fraction of 0.9, the hardness value was 15 GPa, enhanced by about 80% over the rule-of-mixture value of 9 GPa. If fracture toughness were to scale inversely as hardness, this film should have a fracture toughness of about 1.5 MPa-$m^{1/2}$, compared with our measured value of 3.4 MPa·$m^{1/2}$. We propose that coherent Fe/VC interfaces play an important role in the observed hardness and toughness enhancement.

Keywords: Hardness, Fracture Toughness, Multilayers, Magnetron Sputtering, Nanoindentation

2:30pm **B4-2-4 Using High Temperature Nanomechanics in Coating Design for Improved Wear Resistance in Extreme Frictional Environments**, ***B. Beake*** *(ben@micromaterials.co.uk)*, Micro Materials Ltd., UK, *G. Fox-Rabinovich*, McMaster University, Canada **INVITED**

Frictional heating results in very high operating temperatures in ultra-high speed machining. Nanoindentation tests used to evaluate the mechanical properties of novel PVD coating systems designed for extreme environments such as high speed cutting of hard-to-cut hardened steels and Ni-based aerospace alloys are invariably performed at room temperature. If nanomechanical measurements are to be used reliably in the optimisation of coatings then it is much better that the measurements are performed at the relevant temperature.

This is done using a patented method to separately actively heat and control the temperatures of indenter and sample resulting in minimal/no thermal drift during the high temperature indentation. The instrumentation allows reliable nanomechanical testing (e.g. nanoindentation, nano-scratch, micro-pillar compression, micro-cantilever bending) to 750 degrees C and above. To achieve higher temperatures without indenter or sample oxidation an ultra-low drift high temperature vacuum nanoindentation system capable of testing to 1000 degrees C has been developed.

High temperature nanoindentation data for a wide range of nitride-based hard coatings on cemented carbide have been used to develop design rules for coating optimisation for different machining applications. The coatings studied show large differences in how their hardness, modulus and H/E vary with increasing temperature. The interrelationship between the high temperature mechanical properties and the coating system's adaptive behaviour and tribo-film formation and ultimate performance is investigated. Overall, the high temperature nanoindentation data show excellent correlation to coating life under severe high speed machining applications.

3:10pm **B4-2-6 In-situ X-Ray Scattering Study of the Cubic to Hexagonal Transformation of AlN in $Ti_{1-x}Al_xN$**, ***N. Norrby*** *(nikno@ifm.liu.se)*, *L. Rogström*, Linköping University, Sweden, *M. Johansson-Jõesaar*, Seco Tools AB, Sweden, *N. Schell*, Helmholtz-Zentrum Geesthacht, Germany, *M. Odén*, Linköping University, Sweden

Cathodic arc evaporated $Ti_{1-x}Al_xN$ is commonly used as a hard coating on metal cutting inserts. It is well known that the as-deposited unstable cubic (B1) state of $Ti_{1-x}Al_xN$ decomposes in two steps at elevated temperatures. The first, beneficial step, where coherent nanostructured cubic c-TiN and c-AlN rich domains are formed during spinodal decomposition, is followed by a detrimental transformation of c-AlN into its stable hexagonal form (h-AlN, B4).

In the present work, we have studied the decomposition of arc evaporated $Ti_{0.50}Al_{0.50}N$ and $Ti_{0.33}Al_{0.67}N$ during heat treatment in vacuum by *in-situ* synchrotron x-ray diffraction. Three isothermal temperatures (between 950 ºC and 1100 ºC) per sample have been used with a time resolution of approximately three measurements per minute. The measurements were conducted on powder of $Ti_{1-x}Al_xN$ which makes a quantitative analysis of the diffractograms possible. In addition, *in-situ* small angle x-ray scattering measurements were conducted to explore details of the wavelength evolution of the spinodal decomposition, thus providing information about the critical size of the c-AlN rich domains prior to the onset of the h-AlN transformation.

The results provide valuable information of the fractional cubic to hexagonal transformation of AlN in $Ti_{1-x}Al_xN$ as a function of time and yield an activation energy between 3.1 and 3.6 eV/at. The onset of the hexagonal transformation occurs at about 50 ºC lower temperature in $Ti_{0.33}Al_{0.67}N$ compared to $Ti_{0.50}Al_{0.50}N$. A critical wavelength of the cubic domains of about 8 nm was observed for $Ti_{0.33}Al_{0.67}N$ and about 12 nm for $Ti_{0.50}Al_{0.50}N$. Furthermore, the conversion rate from cubic to hexagonal AlN in $Ti_{1-x}Al_xN$ was significantly lower for the low Al content $Ti_{1-x}Al_xN$ powder. For example, $Ti_{0.33}Al_{0.67}N$ has completed the transformation to h-AlN after 120 min at 1000 ºC while $Ti_{0.50}Al_{0.50}N$ has only completed 40% during the same annealing time.

3:30pm **B4-2-7 Microstructural Study of Thermal Spray Pseudo-alloy Coatings Using X-ray Diffraction (XRD)**, ***E.A. Lopez Covaleda*** *(ealopezco@unal.edu.co)*, Universidad Nacional de Colombia

The grain size, residual stress and strain set some of the properties of the coatings made by thermal spray, this is due to the process and hi cooling rates, which trend to produce nano-grains with hi residual stress and strains, or even amorphous metals.

This research use the thermal spray wire arc in order to make steel coatings using the alloy Fe-W-Cr-Nb and traditional steels AISI/SAE 1020 and 420 as follows: Single layer coatings of each material and simultaneous coatings of two materials at the same time using the alloy and one of the traditional steels. That in order to create pseudo alloys. The grain size, residual stress and strain were computed using mathematical approximations of the X-ray diffraction results and transmission electron microscopy (TEM). The coatings also are characterized by using, optical microscopy, scanning electron microscopy (SEM) and micro-hardness.

It was found that the single layer coatings of the alloy had the smallest grain size, (nano grain size) also those kind of coatings have the biggest residual stress and therefore the biggest strains, this is possible due to the powder inside the original metal core can be nano-grain nucleant, increasing the nucleation rates, if that is accompanied with the cooling rates own of the process 10^7 K/s can be obtained nano structures, as well as were observed by TEM. On the other hand the traditional steel coatings have typical grain size found in the literature, also these kind of coatings have smaller residual stress and strain than the alloysingle coatings. Finally using the alloy and the traditional steels, the pseudo alloys obtained had residual stress and strain smaller than its precursors, conformably grain size were bigger than the traditional steels.

This effect may be due to changes at the direction, heat rate, thermal conductivity thermal expansion among others, details of the computation and correlation with the results are exposing at this research presentation.

3:50pm **B4-2-8 Characteristic Change of Hydrogen Permeation in Stainless Steel Plate by BN Coating**, ***M. Tamura*** *(mtamura@sangaku.uec.ac.jp)*, The University of Electro-Communications, Japan

Hydrogen cracking of high-strength steels is a major concern in steel processing and service, and occurs in several applications, such as cracking of rolled steel products, cold cracking of welds, and as a result of corrosion in H_2S environments.

Low-permeation hard coatings can be used as wear-resistant hydrogen permeation barriers. When coated on stainless steel they can reduce the rate of hydrogen transport. And they might be useful for sterling engines, tritium containment, or components of hydrogen fuel cells.

The hydrogen permeation behavior of BN-coated SUS316L stainless steel was investigated. The c-BN (cubic boron nitride) coating, deposited by magnetically enhanced plasma ion plating, was more effective to reduce the rate of hydrogen permeation through stainless steel than TiN coating. The c-BN coating can be used for high-temperature and wear-resistant applications as hydrogen permeation barriers.

4:10pm **B4-2-9 Influence of Modulation Period on Properties of TiN/Ta Multilayer Films**, ***H.F. Shang***, *T.M. Shao* *(shaotm@tsinghua.edu.cn)*, Tsinghua University, China

Multilayer films have attracted great attention in recent years because of their promising properties. Comparing to monolayer films, multilayer films usually demonstrate increased hardness and wear resistance. TiN film has been widely used in industry due to its high hardness, good wear resistance and anti-corrosion performance. However, due to the relatively large residual stress and weak fracture toughness, TiN film cannot meet the more stringent requirements in many cases. So, TiN/metal multilayer films such as TiN/Ti, TiN/Cu, TiN/W, and etc., have been extensively studied.

In this work, TiN/Ta multilayer films with different modulation periods were deposited by ion beam assisted deposition. Microstructure of the as-deposited TiN/Ta multilayer films was characterized by using Auger spectra analysis and transmission electron microscope. Mechanical properties of the TiN/Ta multilayer films were also tested. Tribological behavior and corrosion performance of the TiN/Ta multilayer films were analyzed and were compared to that of the TiN monolayer film. Results show that the TiN/Ta multilayer films demonstrated better mechanical properties, tribological behavior and corrosion resistance than the TiN monolayer films. Modulation period has a great influence on properties of the TiN/Ta multilayer films.

4:30pm **B4-2-10 Characterization, Mechanical Properties, Wear and Scratch Test Resistance of Various Commercial and Lab-developed Electroless Nickel Deposits**, *V. Vitry (veronique.vitry@umons.ac.be)*, ***F. Delaunois***, University of Mons, Belgium

Three commercial types electroless nickel phosphorous baths – low, mid and high phosphorous – and 2 lab-developed electroless nickel-boron bath – both based on borohydride but differing by their stabilizer, lead and thallium salts respectively – were used in this study. Samples were investigated in the as-deposited and heat treated condition (after treatment at 400°C for 1 hour).

The samples were fully characterized by GD-OES, SEM and x-ray diffraction in order to assess their chemistry, morphology and structure. Their hardness was assessed by Knoop microindentation and the boron-stabilized bath presented the better behavior. The same coating also presented the better properties during Taber abrasion test with CS-10 abrasive wheels. Some coatings were also submitted to pin on disc wear

test. Scratch test behavior of the various samples was also investigated with the aim of assessing the adhesion of the various coatings on the substrates and identifying the damage mechanisms of the various electroless nickel deposits.

4:50pm **B4-2-11 In-situ TiNi/Al_2O_3/Fe Functional Composite Coating Using Hybrid Centrifugal Assisted Combustion Synthesis**, *R. Mahmoodian,* Centre of Advanced Manufacturing and Material Processing (AMMP), Malaysia, ***M. Hamdi*** *(hamdi@um.edu.my)*, University of Malaya, Malaysia

The composite coating of a TiNi/Al_2O_3-Fe composite was synthesized by centrifugal-assisted self-propagating high-temperature synthesis (SHS). The in-situ TiNi-Al_2O_3-Fe with intermetallic phases of titanium aluminide (TiAl/Ti_3Al), possesses excellent metallurgical properties. This composite was produced from compacted titanium (Ti) and nickel (C) powders in the form of pellets embedded in a tube, which were exposed to very high temperature generated by the thermite Fe_2O_3 and Al reaction under centrifugal accelerations. The process took place in a graphite-steel tube mounted in a centrifugal accelerator machine purposely developed for this function. Functionally graded coating was produced under the centrifugal acceleration field and the product of the thermite reaction (Al_2O_3 and Fe) infiltrated the Ti+Ni pellet and to create a strong, titanium aluminide intermetallic layer. The centrifugal force significantly enhanced both metallurgical alloying and mechanical interlocking between different sample layers during product formation. The purpose of the research addresses the applications of pipes local reinforcement.

5:10pm **B4-2-12 Properties of Hybrid Satellite/W(WC) and Colmonoy/W(WC) Coating Systems**, *L. Vernhes,* Velan, Canada, ***M. Azzi***, Notre Dame University-Louize, Lebanon, *J.E. Klemberg-Sapieha (jsapieha@polymtl.ca)*, École Polytechnique de Montréal, Canada

In this paper, the mechanical, tribological and corrosion properties of two hydrid coating systems were evaluated. The first coating system consists of a tungsten-tungsten carbide W(WC) top layer and a laser cladded stellite interlayer deposited onto 316 stainless steel substrate, and the second one consists of the same W(WC) top layer and a HVOF sprayed and fused colmonoy C88 interlayer onto inconel 718 substrate. X-ray diffraction, energy dispersive spectroscopy and scanning electron microscopy were used to analyse the microstructure of the coating layers. Micro-indentation technique was utilised to measure the surface hardness as well as the hardness profile of the coating systems. Rockwell indentation technique was used to evaluate the adhesion of the coating as per CEN/TS 1071-8. Tribological properties were evaluated by pin-on-disk measurements and corrosion resistance was measured by potentiodynamic polarization and electrochemical impedance spectroscopy EIS.

Hardness profile measurements (on cross section) showed that W(WC) and Stellite have hardness values of 14 GPa and 7 GPa respectively while Colmonoy hardness varies between 7 GPa and 13 GPa depending on the phase under the indenter. On the other hand, W(WC) surface hardness was shown to depend strongly on the indentation load. Furthermore, W(WC) layer exhibits excellent adhesion on both stainless steel and inconel substrates with and without the use of interlayers, however the tribological measurements have shown that W(WC) wear resistance was improved by almost 30% with the use of hard interlayer. In addition, W(WC) layer showed excellent corrosion protection as no pitting was observed after potentiodynamic polarization testing.

Advanced Materials for Modern Device Applications
Room: Sunset - Session C5-1

Thin Films for Active Devices
Moderator: F. Tasnadi, Linköping University

1:30pm **C5-1-1 Recent Progress in Understanding Free-charge Carrier and Structural Properties of InN Thin Films**, ***V. Darakchieva*** *(vanya@ifm.liu.se)*, Linköping University, IFM, Sweden **INVITED**

A sustainable energy future is one of the major global challenges today pointing to the acute need for improved materials. InN(Indium Nitride)-based materials provide unique opportunities for device applications targeting both i) increasing the fraction of energy supply coming from sustainable energy sources and ii) improving the efficiency of energy conversions and end uses. The revision of the band gap energy of wurtzite InN from 1.9 eV to 0.6 eV has opened the way for the application of InGaN and InAlN alloy thin films in a new class of highly efficient solar cells and visible light emitting diodes for solid state lighting. Consequently, considerable research interest has been focused on InN, related alloys and low-dimensional structures. However, many of the fundamental properties of InN-based materials remain still controversial and the related metrology is challenging.

In this talk, the doping mechanisms, electronic and structural properties of InN-based materials will be discussed in relation to their application in photovoltaics and optoelectronics. Details on the microstructure and impurity incorporation and dynamics in InN films with different surface orientations and dopings will be given. Special attention will be paid to the phenomenon of electron accumulation at the surfaces of InN-based materials, observed or expected to occur only in very few semiconductors. The challenges in understanding and assessment of doping mechanisms in InN-based materials will be described. The effect of Mg doping on the experimentally determined lattice parameters of InN will be discussed and combined with first principle calculations of the size and deformation potential effects in order to draw conclusions about the origin of strain in the films. Finally, the precise measurement of the free-charge carrier properties (effective mass, concentration and mobility) of undoped and Mg-doped InN films by the unique Optical Hall effect will be presented.

2:10pm **C5-1-3 Carrier Transport in Undoped CdO Films Grown by Atmospheric-pressure Chemical Vapor Deposition**, ***T. Terasako*** *(terasako.tomoaki.mz@ehime-u.ac.jp), K. Ohmae, S. Shirakata*, Ehime University, Japan

Recently, cadmium oxide (CdO) films have been attracted much attention because of their relatively high Hall mobility values. Yan et al. reported that the Hall mobility value of 609 cm^2/Vs was achieved on the epitaxial CdO:Sn film prepared by pulse laser deposition (PLD) [1]. In our previous paper, we have reported the successful growth of undoped CdO films on *c*- and *r*-plane sapphire substrates (denoted hereafter by "*c*-Al_2O_3" and "*r*-Al_2O_3", respectively) by the atmospheric-pressure CVD (AP-CVD) using Cd powder and H_2O as source materials [2]. The highest Hall mobility of 178 cm^2/Vs was obtained on the CdO/*r*-Al_2O_3 film with the carrier concentration n of 4.2×10^{19} cm^{-3}. To clarify the carrier transport mechanism, we have investigated the temperature dependences of the electrical properties of the undoped CdO films in this paper.

The direct optical gap energies (E_g^{di}s) determined by extrapolating the linear portions of the $h\nu$-$(\alpha h\nu)^2$ curves were distributed in the range from 2.34 to 2.38 eV, which agree well with the reported E_g^{di} values (~2.37 eV) for the films grown by PLD [3]. It was also found that the variation of E_g^{di} as a function of carrier concentration n is well fitted by the calculated curve based on both the band gap widening caused by Burstein-Moss shift and the band gap narrowing caused by the electron-electron and electron-impurity interactions.

Hall effect measurements were performed at 90-330 K. For all the films, no remarkable changes were observed on the temperature (T) vs. carrier concentration n curves, indicating that these films were *n*-type degenerate semiconductors. According Bruneaux *et al.* [4], the barrier heights at grain boundaries can be determined from the slopes of the 1000/T vs. ln (μT) curves. The calculated barrier heights for the CdO films were smaller than the thermal energy at 300 K. This result indicates that the grain boundary scattering plays a minor role in the carrier transport compared with the intra-grain scattering. The gradients of the μ-T curves (denoted by $\Delta\mu/\Delta T$) can be divided into two regions: (1) Region I ($n<7\times10^{19}$ cm^{-3}); $\Delta\mu/\Delta T<0$ and μ increasing with increasing n, and (2) Region II ($n>7\times10^{19}$ cm^{-3}); μ independent of both T and n ($\Delta\mu/\Delta T=0$). The dependence of $\Delta\mu/\Delta T$ on n demonstrates the continuous transformation of the dominant intra-grain scattering mechanism from the phonon scattering mechanism to the ionized impurity scattering with increasing n.

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2:30pm **C5-1-4 Bipolar Resistive Switching in Zr-doped SiO_2 for RRAM Applications**, ***K.C. Chang***, *T.M. Tsai, T.C. Chang (tcchang@mail.phys.nsysu.edu.tw), G.R. Liu, Y.C. Pan*, National Sun Yat-Sen University, Taiwan, *S.M. Sze*, National Chiao Tung University, Taiwan

In this study, resistance random access memory (RRAM) was made by doping a small amount of Zr into the silicon oxide. The fitting results of current-voltage curve indicated that the carrier conduction mechanism at a high resistive state is complied with the Poole-Frenkel emission while the carrier transfer mechanism at a low resistive state is dominated by the Ohmic's conduction. This phenomenon is consistent with the filament theory. The technique of SiO_2 and Zr co-sputtering was used in this study to equip the SiO_2 with the property of RRAM.

2:50pm **C5-1-5 Investigating in Via-Contact-Type Amorphous Indium-Gallium-Zinc-Oxide Thin Film Transistors Two-Stage Rise Capacitance-Voltage Characteristics Degradation in Different Environment**, ***J.C. Jhu***, *T.C. Chang (tcchang@mail.phys.nsysu.edu.tw)*, National Sun Yat-Sen University, Taiwan, *G.W. Chang*, *Y.H. Tai*, National Chiao Tung University, Taiwan

Electrical characteristics and the effect of negative bias stress (V_{GS}-V_T=-30V) are investigated in via-contact-type a-InGaZnO thin film transistors in different environments. Current-voltage and capacitance-voltage measurements are utilized to investigate the impact of water vapor on device characteristics as well as degradation behaviors caused by a negative bias stress. We observed that threshold voltage (V_T) shifts positively with negative gate bias applied. It is also found that the gate to channel capacitance (C_{GC}) curves exhibit an anomalous two-stage rise with the first stage similar to that of initial. Negative bias stress brings about electron trapping in the etch stop layer in H_2O vapor environment, and this is further verified through modulating the water vapor partial pressure. The quantity of electron trapping in the etch stop layer was calculated from ISE-TCAD simulation. Also, the result shows good agreement with C_{GC} curve shifts phenomenon calculated by ISE-TCAD simulations.

3:10pm **C5-1-6 Deposition and Characterization of Germanium Thin Films for Active Device Applications**, *H. Mohammed, M. DeBerry, U. Obahiagbon, O. Akpa,* ***N. Korivi*** *(nkorivi@mytu.tuskegee.edu), K. Das,* Tuskegee University, US

We report on the deposition and characterization of germanium (Ge) thin films for subsequent application in active devices such as semiconductor photodetectors. A radio frequency magnetron sputtering method was used to deposit Ge thin films on silicon (Si) substrates. The deposited Ge films were characterized microscopically and electrically. Our characterization indicates that the sputtering process investigated here is a viable alternative to other methods of Ge thin film deposition including molecular beam epitaxy.

The Ge thin films were deposited on both n- and p- type Si by radio frequency magnetron sputtering from Ge targets. The Si substrates were surface prepared by the standard RCA cleaning procedure. The sputtering of Ge was done at a substrate temperature of 350 °C, following by a post-deposition annealing of the Si substrates. The thickness of the deposited films was measured using a surface contact profiler. Rutherford backscattering spectroscopy (RBS) and transmission electron microscopy (TEM) were used to analyze the films. Impurities were introduced into deposited Ge films and single crystalline Ge by ion implantation and furnace diffusion. Boron (B) was introduced as the p-type impurity, while phosphorus (P) and arsenic (As) were the n-type impurities. Hall Effect measurements were employed to determine the carrier type, carrier concentration, mobility, conductivity and resistivity of the doped Ge films. Four point probe measurements were also employed to determine the sheet resistance and resistivity of the doped Ge films. For electrical characterization, metal contact dots were deposited on Ge films and single crystalline Ge. Silver, aluminum (Al), gold (Au), and nickel (Ni), were used to form contacts on P diffused Ge samples, whereas Al and Au were used for establishing contacts onto As and B implanted Ge samples.

RBS analysis on the film indicated a Ge/Si hetero-junction with Au impurity. The RBS spectra also yielded the film thickness. TEM of cross-sectional samples established that the films were polycrystalline. It was established that all metal contacts on P diffused polycrystalline Ge samples were rectifying where the barrier heights were independent of metal work funtion as is the case with single crystal bulk Ge. These rectifying contacts appeared to be non-ideal. High dose As implantation followed by subsequent rapid thermal anneal was employed to establish low resistivity ohmic contacts to diffused n-Ge films. Boron implantation resulted in low resistance contacts to p-Ge films.

3:30pm **C5-1-7 Device Applications of Energetically Deposited Metal Oxide and Carbonaceous Thin Films**, ***J. Partridge*** *(jim.partridge@rmit.edu.au), E. Mayes, B. Murdoch, M. Kracica,* RMIT University, Australia, *S. Elzwawi, MW. Allen,* University of Canterbury, New Zealand, *M. Bilek,* University of Sydney, Australia, *D. McCulloch,* RMIT University, Australia

We report on the properties and device applications of energetically deposited metal oxide and carbonaceous thin films. Using both filtered cathodic vacuum arc and high impulse power magnetron sputtering systems, unintentionally n-doped ZnO thin films have been deposited with sufficient quality to support Schottky diodes and field effect transistors . The films exhibit high transparency, moderate carrier concentrations, and Hall mobilities up to 30 cm^2/V.s. Their properties can be further improved by post-deposition annealing. Bandgap tuning has been accomplished in energetically deposited $Zn_{1-x}Mg_xO$ films with varying Mg content and Schottky detectors sensitive to ultraviolet light in the UVB region have been formed on these films. Featuring graphitic carbon anodes, these detectors exhibit UVB-visible rejection ratios up to 10^4. Detailed micro-structural, optical and electrical characterisation of the thin films will be presented and related to the characteristics of all devices.

3:50pm **C5-1-8 Bipolar Memristive Properties of TiO_2 Thin Film on Pt/p^{++}Si**, *S. Gullulu, T. Karacali,* ***H. Efeoglu*** *(hefeoglu@atauni.edu.tr),* Ataturk University, Turkey

Current voltage characteristics of TiO_2 at nano scale have unique property under certain conditions which defined as memristor in electronics. In general Metal/Metal Oxide/Metal structures are expected to be a candidate for memristor applications. The memristive behavior is modeled with filament formation, voltage driven oxygen vacancies and Poole Frenkel emission from the electronic states. The well known and the first memristor is based on TiO_2 film having nm thickness. TiO_2 thin films fabricated using reactive RF sputtering with 20ccm Ar and 0.46ccm O_2 having 6N purity. A sequential sputter is used for 10nm Pt or Ti film on p^{++}Si and then 10nm TiO_2 grown with 0.027A/sec rate. Top Pt metallization has done onto TiO_2 using lift off technique or Al using vacuum deposition and shadow mask. I-V measurements were carried out using Keithley 2400 with current compliance. Voltage scanning rate was changed from 0.5V/sec to 0.001V/sec. In general reverse current remained several order of magnitude smaller than forward case. Abrupt switching did not observed but a gradual switching between ON and OFF states were observed during continuous cycling. In some cases ON/OFF resistances of some the samples were increased to order of 10^{12} Ohm during voltage cycling. By the time much lower resistance occurred but when cycling repeated later, the resistance goes up again. This observation indicates trapping and detrapping of electronic states may control the resistance. This proses to be activated by kT energy or carriers driven by built in electrical field at the interface. This situation require further temperature dependent measurement and time base analysis of I(t).

4:10pm **C5-1-9 Transparent Conductive and Structural Characterization of Pulsed-laser-deposited ZnO and Sn-doped ZnO Films for Nanorods Growth**, ***W.C. Hung***, *M. Chen (chenmi@must.edu.tw),* Minghsin University of Science and Technology, Taiwan

ZnO and Sn-doped ZnO (SZO) films with addition amount of 2.0 wt% SnO_2 are deposited on glass substrates at various substrate temperatures by pulsed laser deposition (PLD). Influence of substrate temperature on transparent conductive characteristics of ZnO and 2.0 wt% Sn-doped ZnO on glass substrates are demonstrated with structural, electronic, and optical measurements. Optoelectronic characteristics of Sn-doped ZnO films on glass substrates at various substrate temperatures are apparently better than those of ZnO films for optical transmittance at longer wavelengths, possibly due to the optical energy bandgap variation caused by doping and substrate temperature effects. The resistivity and mobility of resultant films initially decrease up to 300°C and then increase to $1.8x10^{-2}$ W.cm and 5.34 $cm^2V^{-1}s^{-1}$ with increasing substrate temperature. The lowest electrical resistivity (ρ), carrier mobility and the highest carrier concentration of 3.0 wt% Sn-doped ZnO films on galas substrates are $9.13x10^{-3}$ W.cm, 2.07 $cm^2V^{-1}s^{-1}$ and $3.28x10^{20}/cm^3$, respectively. Electrical and optical properties of deposited films are critically related with tin (Sn) doping and substrate temperature during deposition, and physical characteristics of Sn-doped ZnO films are suitable for the application of optoelectronics devices.

Keywords: Sn-doped ZnO; Thin films; Pulse laser deposition; Transparent conductive oxide

4:30pm **C5-1-10 Improved Multiferrioc Properties of $Bi_{0.9-x}Sm_xLa_{0.1}FeO_3$/$Pb(Zr_{0.52}Ti_{0.48})O_3$ Multilayers Prepared by Pulsed Laser Deposition**, ***R. Barman***, *D. Kaur (dkaurfph@iitr.ernet.in),* Indian Institute of Technology Roorkee, India

In this study, $Bi_{0.9-x}Sm_xLa_{0.1}FeO_3/Pb(Zr_{0.52}Ti_{0.48})O_3$ [BSLFO/PZT] multilayer thin films were fabricated on $LaNiO_3$ coated Si (100) substrates by Pulsed Laser Deposition method. All films showed the typical XRD patterns of the perovskite structure without the presence of a second phase. BSLFO/PZT multilayer films showed a uniform and small grain size rather than pure BFO and PZT films. In this multilayer structure, superior multiferroic properties were observed at room temperature. However, substantial enhancements in magnetic properties, such as saturated ferromagnetic hysteresis loop with large $2M_r$ (~70 emu/cm^3) and $2H_C$ (~15 kOe), as well as moderate ferroelectric properties, such as $2P_r$ (~50 μC/cm^2) with low leakage current density (~5 $x10^{-9}$A/cm^2 at 100 kV/cm), were observed in the BSLFO/PZT multilayer films at room temperature. The observed changes in the electric and magnetic behavior of the systems were related to an increased degree of disorder for electric dipoles and magnetic moments, due to the increased number of layers and crystallization treatments.

4:50pm **C5-1-11 Large Polarization in Lead Free Ferroelectric Thin Films Fabricated by Pulsed Laser Deposition**, ***Y. Kolekar*** *(ydkolekar@gmail.com)*, University of Pune, India, *A. Bhaumik*, Missouri State University, US, *C.V. C. V. Ramana*, University of Texas at El Paso, US, *K. Ghosh*, Missouri State University, US

We report ferroelectricity with a large remnant and saturation polarization close to a morphotropic phase boundary (MPB) lead (Pb) free $(0.5)BaTi_{0.8}Zr_{0.2}O_3$-$(0.5)Ba_{0.7}Ca_{0.3}TiO_3$, (BZT- 0.5 BCT), thin films. High quality thin films of Pb free BZT- 0.5BCT were grown on $Pt/Ti/SiO_2/Si$ substrate using pulsed laser deposition (PLD). The structural and ferroelectric properties have been studied using X-ray diffraction (XRD), Raman spectroscopy, and polarization switching measurements. The Raman spectroscopic data in combined with the XRD data confirm the high quality BZT- 0.5 BCT thin films on $Pt/Ti/SiO_2/Si$ substrate. Polarization versus electric field data shows a square hysteresis loop with a large remnant and saturation polarization and a small coercive field (~1.5 kV/cm) which is essential for practical device applications. We found that the thin films of BZT-0.5BCT close to MPB exhibits a large remnant polarization of 118 m C/cm^2 and a saturation polarization of 120 m C/cm^2, which are much higher than any previously reported values for any ferroelectric thin film. The polarization switching dynamics are well correlated with structural distortion and phonon vibration observed in XRD and Raman spectroscopy. The observed results may stimulate to develop new Pb free ferroelectric thin films for future non-volatile random access memory and many other high-tech applications.

5:10pm **C5-1-12 Structural, Optical and Electrical Properties of Transparent p-NiO/n-FTO Hetero-junction**, ***D. Tatar*** *(demettatar@atauni.edu.tr)*, Atatürk University, Turkey, *F. Bakan*, Sabancı University, Turkey, *K. Cınar, E.E. Sukuroglu, Y. Totik, B. Duzgun*, Atatürk University, Turkey

In this study, we obtained p-NiO /n-FTO hetero-junction performing p-type NiO (nickel oxide) films by the dip-coating method on n-type FTO (flourine doped tin oxide) films deposited on optical glasses by the spray pyrolysis. The structural, optical and electrical properties of p- NiO/n-FTO hetero-junction was achieved by different measurement techniques in details. The structural characterization of the films was carried out by X-ray diffraction (XRD) measurements using a Rigaku D/Max-IIIC diffractometer with CuKα radiation (λ=1.5418 Å), at 30 kV, 10 mA. Surface morphology of the resulting films was examined by SEM. The electrical characterization of p-NiO/n-FTO heterojunction was carried out at room temperature. We calculated that band gap of an n-type FTO thin films is 3.37 eV and also 4.00 eV for p-type NiO thin films at room temperature, respectively. We investigated with help I-V (current-voltage) and C-V (capacitance-voltage) measurements to the electrical properties of p-NiO/n-FTO hetero-junction. When the ideality factor and barrier height values of this hetero-junction were calculated from I-V measurements and built-in potential, barrier height values from C-V measurements, respectively. The aim of this study have been obtained the preparation of doped tin oxide thin films because of its simple and inexpensive experimental arrangement, ease of adding various doping material, reproducibility, high growth rate, and mass production capability for uniform large area coatings. In addition, it is demostrated that these values of p-NiO/n-FTO hetero-junction applied to Thermionic Emission theory (TE).

Tribology & Mechanical Behavior of Coatings and Engineered Surfaces
Room: California - Session E2-3

Mechanical Properties and Adhesion

Moderator: J. Michler, EMPA (Swiss Federal Laboratories for Materials Science and Technology), R. Chromik, McGill University, D.F. Bahr, Purdue University

1:50pm **E2-3-2 High Temperature Creep of Gas Turbine Coatings**, ***J. Davenport*** *(jrd49@cam.ac.uk)*, University of Cambridge, UK, *M. Hancock*, Rolls-Royce plc, UK, *R. Stearn, W. Clegg*, University of Cambridge, UK

MCrAlYs (where M = Ni/Co) are used throughout gas turbine engines, as oxidation resistant coatings, bond coats for thermal barrier coatings and more recently, to hold abrasive particles onto the tip of shroudless turbine blades. In the latter; the MCrAlY must have sufficient strength to hold the abrasive particles in place as the abrasive tip cuts a track in the abradable on the casing. The temperatures that these abrasive tips see are some of the hottest within the engine, and they are not protected by thermal barrier coatings. Existing work on MCrAlYs extends up to 1050 ^oC, although the abrasive tips may have to withstand temperatures higher than this.

In this paper we present a method to study the mechanical properties of thin free standing MCrAlYs at temperatures as high as 1200 ^oC. This method avoids the use of large specimens or substrate coatings couples, so that the results are representative of the materials that are seen within the engine. Coatings of different compositions and different fabrication techniques have been characterised and correlated with the microstructures of the MCrAlY.

2:10pm **E2-3-3 High Temperature Yield Stress of Hard Coatings**, ***J.M. Wheeler*** *(jeffrey.wheeler@empa.ch)*, *R. Raghavan, V. Chawla*, EMPA (Swiss Federal Laboratories for Materials Science and Technology), Switzerland, *M. Morstein*, PLATIT AG, Switzerland, *J. Michler*, EMPA (Swiss Federal Laboratories for Materials Science and Technology), Switzerland **INVITED**

In order to evaluate the performance of hard coating materials used in aggressive cutting operations such as end milling or high speed machining, it is necessary to investigate the materials properties at the high temperatures generated in service. However, the small length scale of the coatings limits the utility of conventional high temperature techniques. The recent extension of nanoscale techniques such as nanoindentation and nanoimpact to elevated temperatures has recently made this a possibility, and recent work using these techniques has demonstrated the utility of these techniques [1, 2]. The development of vacuum techniques for high temperature nanoindentation [3, 4] has recently also allowed measurement at temperatures where oxidation of the indenter or sample may be problematic.

Micropillar compression at high temperature offers several attractive advantages over hardness testing [5]. Indentation is highly dependent on tip geometry for accurate measurements, and indenter geometry variation due to erosion by oxidation and abrasive wear or plastic deformation of the tip is a serious concern at high temperatures. Using a flat punch indenter avoids any such geometric variation. Also, the micropillar geometry offers a uniaxial stress state in contrast to the triaxial stress state of indentation. This provides a direct measurement of the yield stress.

The elevated temperature performance of a wide range of Chromium Nitride-based hard coatings was evaluated using *in situ* micro-compression at temperatures up to 500°C. This allows the first direct measurement of the uniaxial high temperature yield strength, rather than the hardness, of such coatings. The microstructure of the coatings was analysed using X-ray diffraction, Raman spectroscopy and focused ion beam cross sectioning followed by electron microscopy. Micropillars were examined using electron microscopy before and after compression. Trends in deformation behaviour and yield stress with temperature are discussed in relation to the coatings' microstructures.

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2:50pm **E2-3-5 Temperature Dependent Energy Loss and Internal Friction Measurement in Nanocrystalline Metal Thin Films**, *Y.-T. Wang, Y.-C. Cheng, F.-J. Hsu,* ***M.-T. Lin*** *(mingtlin@nchu.edu.tw)*, National Chung Hsing University, Taiwan

This study uses a temperature controlled capacitance-based system to measure the mechanical behaviors associated with temperature dependent energy loss in ultra-thin metal films. Cu, Al and Ag thin film are widely used in electronic interconnections and MEMS structures; however, most studies have focused on their temperature dependent mechanical properties at larger scales. This study designed a paddle-like test specimen with metal films deposited on the upper surface in order to investigate the in-situ temperature dependent mechanical properties of metal thin films at elevated temperature up to 200C under high vacuum conditions at very small scales. In-Situ Energy loss was measured according to decay in the oscillation amplitude of a vibrating structure following resonant excitation. Film thickness and grain size were closely controlled with respect to the mechanical properties of the films. We also determined that the temperature dependent internal friction of thin and ultra-thin metal films is less strongly dependent on film thickness than on grain boundaries during annealing.

3:10pm **E2-3-6 Ni-Bi Composite Coatings Produced by Ionic Co-discharge Electrodeposition**, ***S.L. Tay***, *C.Z. Yao*, The University of Auckland, New Zealand, *W. Chen*, Beijing Institute of Technology, China, *W. Gao (w.gao@auckland.ac.nz)*, The University y of Auckland, New Zealand

Composite coating is widely used in applications due to its good mechanical properties and long service life. A variety of coating processes or technologies are used in industries. However, the most common process is electroplating, one of the simplest and cheapest methods to produce coatings. Most of the recent studies are conducted by deposition of metal with oxide or ceramic particles to produce composite coatings. However, there are lacks of studies for the deposition of two insoluble metals. In this research, a mixture of two different insoluble metals, Ni-Bi, were synthesized by co-ionic discharge method. Direct current and pulse electricity have also be used to produce Ni and Ni-Bi coatings for comparison purpose. Results showed that the hardness of the coatings is increased with the incorporation of Bi into the Ni coating. Pulse electroplating produced a higher hardness value than direct current electroplating. Ni-Bi coating also has an enhanced wear resistance. The morphology, microstructure and electrochemical properties of this type of composite coatings are also discussed in this paper.

3:30pm **E2-3-7 Synthesis and Thermal Stability of Gold-Zinc Oxide Nano-Composite Thin Films for Electrical Contacts**, ***R.S. Goeke*** *(rsgoeke@sandia.gov), J. Mogonye, N. Argibay, S.V. Prasad*, Sandia National Laboratories, US

Gold coatings that are ideally suited for low electrical contact resistance (ECR) applications are mechanically soft and exhibit unacceptable amounts of adhesion and friction. To mitigate these problems gold for ECR applications is typically alloyed with Ni, Co or Fe which increases the film hardness and wear resistance. A key limitation of hard gold coatings is the propensity for the non-noble alloying metal species to diffuse to the surface and form non-conductive oxide films that can severely impact the electrical contact behavior. These traditional hard gold films, which are fabricated via electro-deposition, have been limited to electrochemical compatible materials. Using co-deposition by physical vapor deposition (PVD) methods we have eliminated the material limitations and generated a new class of hard gold thin films. We have synthesized a thin film via PVD co-deposition comprised of gold and 0.1 – 2 vol% ZnO zinc oxide using a Triad e-beam evaporation system with capability for co-depositing three elements or compounds,. The ceramic phase is used to strengthen the composite via grain refinement. The resulting film can replace typical hard gold films and exhibits enhanced thermal stability as the ceramic phase has no thermodynamic driving force to migrate the surface. The results from accelerated aging studies and the role of ceramic inclusions on the stability of these nano-grain structures will be discussed.

* Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000

3:50pm **E2-3-8 In Situ Biaxial Mechanical Testing of Metallic Thin Films on Stretchable Substrate: Synchrotron Diffraction Versus Image Correlation Analyses**, ***P.O. Renault*** *(pierre.olivier.renault@univ-poitiers.fr), E. Le Bourhis, R. Guillou*, University of Poitiers, France, *P. Goudeau*, CNRS, France, *D. Faurie*, University of Paris 13, France, *G. Geandier*, CNRS/Universite Lorraine, France, *C. Mocuta, D. Thiaudiere*, SOLEIL Synchrotron, France **INVITED**

Complex in-plane strain paths are often applied to thin films during elaboration and use processes. Hence, the elastic-plastic-failure behaviour of the composite metallic film - polymeric substrate need to be investigated both under equi-biaxial and non-equi-biaxial loading conditions. This paper reports on the mechanical behaviour of nanostructured metallic thin films deposited on a polyimide substrate under controlled biaxial loadings thanks to a biaxial testing device developed on DiffAbs beamline at SOLEIL synchrotron (France). The in-situ tensile tests were carried out combining synchrotron X-ray diffraction (XRD) and digital-image correlation (DIC) techniques. The two techniques can accurately measure deformations at two different scales, namely the in- grain scale or lattice strain and the macroscopic scale. In the elastic domain, our results show that the two strain measurements, i.e. lattice strain in the crystalline part of the metallic components of the film measured by XRD and macroscopic strain in the substrate measured by DIC, match to within $1x10^{-4}$. This result clearly demonstrates that the applied strain in the elastic domain is transmitted unchanged through the metal-polymer interface. The elastic limit of the nanostructured metallic composite (W/Cu) thin films was determined at the bifurcation point between the XRD lattice strain and the DIC macroscopic strain. Such an experimental combination allows to determine the yield surface of a polycrystalline thin film deposited on a stretchable substrate, and to scrutinize their mechanical behavior. As for example, the results show the brittle behavior of the W/Cu nanocomposite film.

4:30pm **E2-3-10 Effect of Plasma Spraying Parameters on Microstructure and Mechanical Properties of Titania-doped Yttria-stabilized Zirconia**, ***S. Liscano***, *L. Gil (lindaegil@gmail.com)*, UNEXPO, Venezuela (Bolivarian Republic of)

The properties of thermal barrier coatings system (TBCs) are dependent not just on the material being used but also on the process parameters. **NiCoCrAlY** bond coat, and titania doped YSZ (ZrO_2–10% Y_2O_3–18% TiO_2) coatings were deposited on AISI **A36 steel**coupons by atmospheric plasma spraying (APS) using an 2^2 factorial experimental design by varying spraying parameters: torch power and spraying distance. The main goal of this work was to evaluate the microstructure and mechanical properties of plasma-sprayed titania-doped yttria stabilized zirconia (YSZ) TBC. The mechanical properties of the coating were evaluated using microindentation hardness and scratch test. The microstructure and phase composition of the coating were characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD). The results of microindentation hardness and microstructural characteristics indicated that the best coatings properties were obtained for spraying condition with 38000 W of torch power and 100 mm of spraying distance.

Key Words: titania- doped YSZ, Plasma-sprayed, torch power, spraying distance, microhardness

4:50pm **E2-3-11 Effect of Plasma Nitriding Species on the Surface Properties of Tool Steels**, ***P. Abraha*** *(petros@meijo-u.ac.jp)*, Meijo University, Japan, *J. Miyamoto*, Toba National College of Maritime Technology, Japan

In this study, tool steel surfaces are nitrided by primarily nitrogen atoms that maintained the as-finished surface conditions of the specimen. The nitriding of the tool steels was performed in electron beam excited plasma specifically geared to differentiate and use the neutral nitrogen atoms. For comparison, the charged nitrogen ions are used separately. Nitrogen concentrations of the treated specimen were varied in both neutral (atom) and ion nitriding to study the effect on the surface properties of the tool steels.

The results of our experiments show that in neutral nitriding the tool steel specimen for 6 hours, a mirror finish surface (Ra=14nm) with a diffusion layer of up to 80 µm and a surface hardness of more than two times (1300 Hv) that of the untreated specimen (600 Hv) were produced. On the other hand, in ion nitriding the tool steel specimen for 6 hours, surface finish of Ra=83 nm with a diffusion layer of up to 95 µm, a compound layer of about 7 µm and a surface hardness of 1350 Hv were produced. The obvious difference was that the mirror surface finish was retained on the specimen treated by neutral nitriding while a rough compound layer was formed on the specimen surfaces treated by ion nitriding. In consideration of the above results, neutral nitriding could be a good candidate for duplex treatment of cutting tools, punch and dies and precision mechanical components that require high hardness and wear resistance without altering the as-finished dimensional accuracy, surface roughness and appearance.

New Horizons in Coatings and Thin Films
Room: Royal Palm 4-6 - Session F4

New Oxynitride and Oxide-based Coatings
Moderator: W. Kalss, Oerlikon Balzers Coating AG, M. Stüber, Karlsruhe Institute of Technology

1:50pm **F4-2 Effect of Oxygen Incorporation on the Structure and Elasticity of Ti-Al-N-O Coatings Synthesized by Cathodic Arc and High Power Pulsed Magnetron Sputtering**, ***M. Hans*** *(hans@mch.rwth-aachen.de), M. to Baben, D. Music, J. Ebenhöch*, RWTH Aachen University, Germany, *D. Primetzhofer*, Uppsala University, Sweden, *D. Kurapov*, Oerlikon Balzers Coating AG, Liechtenstein, *M. Arndt, H. Rudigier*, OC Oerlikon Balzers AG, Liechtenstein, *J. Schneider*, RWTH Aachen University, Germany

Ti-Al-N-O coatings were synthesized by cathodic arc and high power pulsed magnetron sputtering. The effect of substituting nitrogen by oxygen on structure and mechanical properties was investigated. The chemical composition of the coatings was determined by means of elastic recoil detection analysis and energy dispersive X-ray spectroscopy. Lattice parameters and Young‘s moduli were obtained by X-ray strain analysis and nanoindentation, respectively. Both, the decrease of lattice parameter and Young’s modulus with increasing oxygen content can readily be understood based on ab initio calculations: The substitution of nitrogen by oxygen is

enabled by formation of metal vacancies, preserving thereby charge neutrality.

2:10pm **F4-3 Magnetron Sputtering of p-type $AgFeO_2$ Thin Films with the Delafossite Structure Using a Combinatorial Approach**, ***U. Jansson*** *(ulf.jansson@kemi.uu.se), F. Mao, T. Nyberg, T. Thersleff,* Uppsala University, Sweden

Delafossites AMO_2 (A= Cu,Ag, Pd, Pt; M=Fe, Co, Ni, Cr, Al, Mn, etc) have interesting potential applications as transparent p-type conducting oxides, photocatalysts, luminescent materials, batteries and thermoelectric materials. Recently, high temperature superconductivity was also suggested for doped members of this type of oxide compounds. The delafossites can be described as natural nanolaminates with MO_2 layers separated by A planes. The chemical stability of these compounds is defined by the linear O-A-O bonds. Copper-based delafossites have been synthesized using solid-state reactions, hydrothermal synthesis methods, sol-gel methods and, in a few cases, reactive sputtering with high temperature post-annealing ($\geq 700^oC$). Very few studies, however, have previously been published on silver-based delafossite films deposited by sputtering. The main challenge is that the silver-based delafossites are easy to decompose at high temperatures ($>400^oC$) due to the less stable O-Ag-O bonds. Furthermore, the synthesis of Ag-based delafossites by reactive sputtering is usually restricted to a narrow parameter window.

In this work, we have deposited delafossite $AgFeO_2$ thin films with reactive magnetron sputtering using a combinatorial approach with gradient films. Rapid screening combined with XRD, XPS and XRF were used to determine the chemical composition and phase composition. The most interesting films were studied by TEM. Optical and electrical properties have also been investigated. Our results show that the $AgFeO_2$ successfully can be deposited without post-annealing using a pulsed Ag target. The process window is very narrow and strongly dependent on deposition temperature, sputtering power, pulse frequency, O_2 flow rate, working pressure, etc. An optimum temperature is 400 ^oC and a pulsing frequency of 150 kHz. The XRD and TEM showed that the $AgFeO_2$ films were textured with the (*00l*) planes perpendicular to the growth direction also on an amorphous SiO_x substrate. A very strong substrate dependence was observed with good quality films on Si and a poor crystallinity on glass. Furthermore, the films were p-type and transparent. Further post-annealing in air improved the electric properties.

2:30pm **F4-4 Influence of Si Doping on Process Stability and Coating Properties During Arc Deposition of $(Al, Cr)_2O_3$**, ***L. Landälv*** *(ludla@ifm.liu.se),* Linköping University, IFM, Thin Film Physics Division and Sandvik Coromant R&D, Sweden, *E. Göthelid, M. Ahlgren,* Sandvik Coromant R&D, Sweden, *L. Hultman, B. Alling, P. Eklund,* Linköping University, IFM, Thin Film Physics Division, Sweden

α-Al_2O_3 made by PVD-processes has been a long sought goal in coating development for the cutting tool industry. Different approaches have been taken throughout the years, such as alloying with materials stabilizing the corundum phase, i.e. Cr, as reported in [1, 2, 3]. Having achieved α-$(Cr, Al)_2O_3$ phase from compound targets, there are still many problems to solve with respect to process stability and coating quality. The reactive arcing of mixed AlCr targets in oxygen creates a large amount of droplets as well as target poisoning [4], which leads to a reduced film quality and uneconomical use of target material, especially on an industrial scale. A recent discovery shows that Si can be added to the AlCr-material in order to stabilize the process, creating a more even erosion of the cathode [5]. However, the Si-content in the target need to be balanced carefully in the light of another study indicating that Si in the coating stabilizes the cubic phase instead of the desired corundum phase [6]. It remains to be found with which Si content the improved erosion of the targets may result in better film integrity, that is, fewer droplet and voids while retaining hardness, E-modulus, crystal structure, and improving the machining properties of the original AlCr oxide.

Thus, this work aims to study the influence of adding different amounts of Si to AlCr-target material with increasing Al/Cr ratio respect to erosion rate of the target as well as the resulting coating properties. SEM, XRD, TEM, and XPS among other techniques showed that some Si is incorporated into the coating when having 10 at% Si in the target with Al/Cr=1. The α-$(Cr, Al)_2O_3$ coating, free from silicon, change phase to possibly cubic-$(Cr, Al)_2O_3$ upon incorporating silicon. The hardness is also reduced when adding Si in the coating. The questions of where the silicon is incorporated in the coating is also further investigated in this work.

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2:50pm **F4-5 Synthesis-structure-property Relations of Al-oxide-based Coatings**, ***J. Paulitsch*** *(joerg.paulitsch@tuwien.ac.at), C.M. Koller,* Vienna University of Technology, Austria, *R. Rachbauer, J. Ramm,* Oerlikon Balzers Coating AG, Liechtenstein, *P. Polcik,* PLANSEE Composite Materials GmbH, Germany, *D. Holec,* Montanuniversität Leoben, Austria, *P.H. Mayrhofer,* Vienna University of Technology, Austria **INVITED**

Many investigations already indicated that alloying Al to ceramic-like nitride coatings, such as CrN or TiN, increase their mechanical and thermal properties. Especially the formation of dense alumina (Al_2O_3) outer layers during high temperature oxidations is highly acknowledged due to its chemical inertness and passivating character. However, synthesizing crystalline corundum-type alumina itself indicated to be challenging, especially when using deposition temperatures <700°C.

Within this study we present results on selected alloying materials, obtained from first principle calculations, which not only influence the crystallographic appearance of Al-Cr-O coatings but also enhance the target evaporation characteristic during cathodic arc evaporation, hence the process itself. Furthermore architectural optimized Al-O-based multilayer coatings were deposited using low and high ionizing deposition techniques, like conventional direct current magnetron sputtering or cathodic arc evaporation, respectively, to indicate the possibility of stabilizing preferential crystallographic configurations by tailoring the bi-layer thickness.

Our results demonstrate the advantages of a combined computational and experimental investigation as well as of a sophisticated layer arrangement to deposit high performance coatings.

3:30pm **F4-7 Structure and Electronic Properties of $AlCrO_xN_{1-x}$ Thin Films Deposited by Reactive Magnetron Sputtering**, ***H. Najafi*** *(hossein.najafi@epfl.ch), A. Karimi,* EPFL, Switzerland, *M. Morstein,* PLATIT AG, Switzerland

Metal oxynitride thin films, a novel class of mixed anionic solid structures, have gained an intense interest during recent years related to the unique interplay of oxygen (O) and nitrogen (N) with metals in the material structure. In this regard, we studied the structure and electronic properties of Cr-rich oxynitrides (Cr/Al~1) showing a cubic (B1) structure in the nitride regime, O/(O+N) < 0.6. The obtained films in this growth regime exhibited a well-developed columnar structure and high nanohardness values ranging from 30 to 33 GPa. Our results show the incorporation of oxygen into the films without any oxide region segregation results in the development of a strong (002) crystallographic preferred orientation and a decrease of the cubic lattice parameter, which allows to suggest the formation of a substitutional $AlCr(O_xN_{1-x})$ solid solution. Material system electronically behaves like nitrides; however, the higher charge transfer between metals and oxygen, as compared to less electronegative nitrogen, favors the formation of an iono-covalent solid structure. In the range of oxygen content from 0.6 < O/(O+N) < 0.97, transition regime, coatings with diffuse columnar structure and high values of metal vacancies were formed. However, the cubic lattice survives despite the large proportion of oxygen. According to the structural and electronic properties of corresponding layers, we assign this region to the formation of metastable monoxides with B1 structure, which are stabilized by the presence of a high amount of vacancies. The nanohardness decreased to about 21-25 GPa as a consequence of the formation of vacancies and changes in chemical bonding states as well as in the coating microstructure. Coatings in the oxide regime with nitrogen contents close to or even below the detection limit of chemical composition analysis, O/(O+N)>0.97, consisted of a solid solution of $(Al,Cr)_2(O_{0.97},N_{0.03})_3$ with corundum lattice and finer columnar structure. It was verified that the incorporation of even small amounts of N in the corundum lattice results in the development of hard coatings with proper wear resistance and less brittle nature.

3:50pm **F4-8 Stoichiometry Gap in MF Sputtered CrON Thin Films**, ***M. Renzelli*** *(m.renzelli@stm.uniroma3.it), M. Sebastiani, E. Bemporad,* University of Rome "Roma Tre", Italy, *H. Kappl, M. Fenker,* FEM Forschungsinstitut Edelmetalle & Metallchemie, Germany

Oxynitrides of transition metals are an important scientific and technological topic. Some of them exhibit tunable properties according to the O/N ratio, but not all the metals can form them, and their properties are dependent on the growing conditions, if prepared as thin films. The authors found a lack of knowledge in the literature on the production of CrON by

medium frequency (MF) magnetron sputtering, so this is a report on the synthesis and characterization of MF sputtered CrON thin films on silicon and M2 high speed steel substrates. Temperature control was employed, together with substrate biasing to influence the coatings microstructure. X-ray diffraction (XRD) and glow discharge optical emission spectroscopy (GDOS) analysis point to a stoichiometry gap between an oxygen doped CrN-like film and a nitrogen doped CrOx one. Frequency and duty cycle variation of the DC pulses on the chromium target shifted the oxygen flow threshold between the two compositions. Polarization tests for corrosion test, stress measurements and instrumented micro and nanoindentation were employed to fully characterize the coatings produced.

4:10pm **F4-9 Influence of the Power Supplied in the Optical Properties of ZrO_xN_y/ZrO_2**, ***J.E. Alfonso*** *(jealfonsoo@unal.edu.co), M.J. Pinzón, J.J. Olaya, G. Cubillos*, Universidad Nacional de Colombia Bogotá, Colombia

The zirconium oxynitride has physical-chemistry properties that allow be used in different applications such as a temperature sensor device, as a corrosion resistance coating and recently, ZrO_xN_y thin films have been proposed for decorative and biological applications. For these reasons, we study the influence of power supplied to the target on the structure, in the morphology and optical properties of ZrO_xN_y/ZrO_2 thin films deposited on common glass using RF reactive sputtering technique, in atmosphere of N_2/O_2, with a flow ratio $\Phi N_2/\Phi O_2$ of 1,25. Structural analysis was carried out through X-ray diffraction (XRD); morphological analysis was done through scanning electron microscopy (SEM) and the optical response was evaluated through transmittance measurements. DRX analysis show that the ZrO_xN_y/ZrO_2 films were grown with monoclinic crystalline structures and preferentially oriented along the (-111) plane. The SEM analysis, evidence that the films grew with homogeneous morphology and exhibit a columnar growth, and used the transmittance values and through Swanepoel method we calculated the refractive index, thickness and absorption coefficient of the crystalline films, additionally the energy gap was determined used the Urbach's formula.

4:30pm **F4-10 Influence of the Annealing in the Corrosion Resistance of $Bi_xTi_yO_z$ Coatings Deposited on Ti6Al4V**, ***M.J. Pinzón*** *(mjpinzonc@unal.edu.co), J.E. Alfonso, J.J. Olaya*, Universidad Nacional de Colombia Bogotá, Colombia

The ferroelectric and optical properties of family of compounds bismuth titanate ($Bi_xTi_yO_z$) have been focus of many researches, of which have generated applications as opto-acoustic devices, photocatalytic activity in degradation of several compounds and non-volatile ferroelectric memories, inter alia. Nevertheless, the studies of other properties of this compounds as eg its behavior in corrosive environments or its use as protective layer against attack by degrading agents, have been very few. Taking in account this situation, and based in before works made for us, which show that these compounds in amorphous phase are potentially useful as protective layer against corrosion, we propose in this work, evaluate the effect of crystalline evolution of bismuth titanate by means annealing to several temperatures, on its corrosion resistance. For this purpose, bismuth titanate thin films were grown on titanium alloy (Ti6Al4V) substrates, through RF magnetron sputtering. In order to observe the evolution the crystallinity of the coatings, these were submitted to an annealing at temperatures in the range among 298 K and 973 K in step of 100 K, The structure crystalline were characterized by X-ray diffraction (XRD) and the corrosion resistance of the coatings was studied by Potentiodynamic polarization test (Tafel extrapolation). The coatings annealed, revealed a change in its microstructure, since they evolve from a completely amorphous phase to a polycrystalline phase. The preliminary results shows that the corrosion resistance of the coating is much better in the amorphous phases of bismuth titanate than in the polycrystalline phases, this is probably due to that low temperatures favors the formation of passive TiO_2 films over the substrate and reinforced the protective of the bismuth titanate coating, while to high temperatures the passive TiO_2 film is reduced.

4:50pm **F4-11 Characterization of Microstructure and Basic Properties of Plasma Sprayed Oxides Coatings Modified by Submicrocrystalline Powders of Different Oxides**, *G. Moskal (grzegorz.moskal@polsl.pl)*, Silesian University of Technology, Poland, ***S. Polis***, SUT, Poland

Microstructural characterization and basic properties description of atmospheric plasma spraying oxide coatings modified by nano- and submicro-crystalinne different types of oxides will be presented in this article. In first part the short characterization of nano- and submicro-crystalinne oxides powders will by showed, especially theirs characterization form grain size and phases composition point of view. Analyzed powders were as follow: RE_2O_3 (RE=Sm, Eu, La), ZrO_2, 3YSZ, Y_2O_3, CeO, α-Al2O3 and γ-Al2O3. Those powders will by described by STEM, XRD and laser diffractions methods. In second part of investigations microstructural characterization of APS coatings of 8YSZ, Al_2O_3 and Al_2O_3 x 13 TiO_2 with addition of nano- and submicro-crystalinne oxides powders will be showed. The morphology of the coatings will be described, their hardness and results of erosion tests in different conditions. The value of K_{Ic} parameters will be estimated as well.

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Topical Symposia
Room: Tiki - Session TS2-1

Advanced Characterization of Coatings and Thin Films

Moderator: M. Sebastiani, University of Rome "Roma Tre", R. Ghisleni, EMPA (Swiss Federal Laboratories for Materials Science and Technology), S. Korte-Kerzel, RWTH Aachen University

1:30pm **TS2-1-1 Synchrotron Nanodiffraction and X-TEM on Al-Ti-N based Hard Coatings with Different Morphologies**, ***M. Bartosik*** *(matthias.bartosik@tuwien.ac.at)*, Vienna University of Technology, Austria, *R. Rachbauer*, Oerlikon Balzers Coating AG, Liechtenstein, *C. Krywka*, University of Kiel and Helmholtz Zentrum Geesthacht, Germany, *C.M. Koller, J. Bernardi*, Vienna University of Technology, Austria, *J. Keckes*, Montanuniversität Leoben, Austria, *P.H. Mayrhofer*, Vienna University of Technology, Austria

Cross-sectional synchrotron nanodiffraction allows the volume-averaged characterization of property-depth gradients in hard coatings with submicron resolution [1]. The approach is based on wide angle X-ray diffraction and is performed in transmission geometry along the cross-section of thinned film/substrate lamellas. The small beam size of about 100 nm in diameter and the high brilliance of modern synchrotron sources make it a powerful tool for the advanced thin film characterization. Al-Ti-N is used as a model system to explore the potential of cross-sectional synchrotron nanodiffraction of hard coatings with different architectures and morphologies. The investigated samples comprise a bilayer with different grain sizes, nanograined Al-Ti-N and a combination of monolithic and multilayer film design. Comparative studies for detailed discussions have been conducted by transmission electron microscopy and selected area diffraction.

[1] J. Keckes, M. Bartosik, et al., Scripta Mater. 67 (2012) 748.

1:50pm **TS2-1-2 Predictive Power of First-principles Calculations for the Electron Energy Loss Spectroscopy**, ***D. Holec*** *(david.holec@unileoben.ac.at)*, Montanuniversität Leoben, Austria, *L. Zhou, P.H. Mayrhofer*, Vienna University of Technology, Austria

Electron energy loss near edge structure (ELNES) analysis provides a tool to experimentally probe unoccupied density of states taking the advantage of high spatial (down to atoms) and energy resolution in modern transmission electron microscopes. In order to understand and interpret the experimental results, a comparison with simulations is necessary. This paper presents a density functional theory based technique facilitating a statistical approach with supercells and partial core hole charges for calculating the ELNES.

The predictive power of our approach is demonstrated by comparing the calculated spectra with available experimental data for a wide variety of nitride-based material systems. Specifically, we will discuss the evolution of the N K-edge in $Ti_{1-x}Al_xN$ exhibiting cubic-to-wurtzite and conductor-to-semiconductor transitions and the impact of magnetism on Cr $L_{2,3}$ and N K-edges in CrN_x and Cr_2N.

2:10pm **TS2-1-3 Local Lattice Strain as Stabilizing Factor of Metastable fcc-(Ti,Al)N in Nanoscaled TiN/(Ti,Al)N/AlN Multilayers**, ***U. Ratayski*** *(ulrike.ratayski@iww.tu-freiberg.de), D. Chmelik, C. Wüstefeld, F. Hanzig, M. Motylenko*, Institute of Materials Science , TU Bergakademie Freiberg, Germany, *C. Baehtz*, Helmholtz-Zentrum Dresden-Rossendorf, Germany, *M. Šíma,* SHM s.r.o., Germany, *D. Rafaja*, Institute of Materials Science , TU Bergakademie Freiberg, Germany

Titanium aluminum nitride coatings are objects of many research activities that are focused on the stabilization of the metastable solid solution of fcc-(Ti,Al)N. The (Ti,Al)N coatings are prevalent for high temperature applications such as metal cutting at high cutting speeds or dry cutting, where the thermal stability of fcc-(Ti,Al)N is the limiting factor for the lifetime of the coatings. At high temperatures, the supersaturated fcc-(Ti,Al)N is known to undergo spinodal decomposition into Ti- and Al-rich

fcc-(Ti,Al)N, which is followed by the transformation of the Al-rich regions into the thermodynamically stable w-Al(Ti)N, that contains a very low amount of Ti. Although the effect of the lattice strains on the spinodal decomposition is basically known, the experimental studies of the interplay between the local concentration gradients and lattice strains are extremely rare.

In this study, the interplay between the concentration gradients and lattice strains was investigated with the aid of TiN/(Ti,Al)N/AlN multilayer coatings, deposited by simultaneous reactive cathodic arc evaporation of Ti and Al in N_2 atmosphere. The multilayers consisted of a periodic TiN/(Ti,Al)N/AlN motif with the thickness of about 2.7nm. The average [Al]/([Ti]+[Al]) ratio in the multilayers was about 0.3. The in situ high-temperature synchrotron experiments performed at the ROBL BM20 beamline at the ESRF have shown that up to 800°C, the amplitude of the original concentration undulations decreases simultaneously with the decreasing magnitude of the lattice strain. The periodic multilayer structure was preserved up to the maximum annealing temperature of 950°C (hold for 1h). In Ti-rich (Ti,Al)N, a significant decrease of the compressive residual stress occurred at annealing temperature above 850°C as expected for the intermixing of Ti and Al between Ti- and Al-rich layers. During cooling the samples from ≥ 850°C to 100°C, concurrently the decomposition of fcc-(Ti,Al)N into the isostructural Ti- and Al-rich compounds and the transformation of Al-rich (Ti,Al)N into w-Al(Ti)N appeared. The transformation from Al-rich fcc-(Ti,Al)N to w-Al(Ti)N was evidenced by the increase of the multilayer periodicity, which was driven by the unit cell expansion during the phase transition.

The in situ synchrotron experiments combined glancing-angle X-ray diffraction to determine of residual stresses and stress-free lattice parameter and X-ray reflectivity to obtain the thickness of the periodic motif, the modulation of the electron density and/or interface roughness. Analytic transmission electron microscopy was used to characterize the interface quality and to quantify the composition profiles.

2:30pm **TS2-1-4 Nucleation and Initial Growth of sp^2-BN Thin Films by Chemical Vapor Deposition**, ***M. Chubarov*** *(mihails.cubarovs@liu.se)*, Linköping University, IFM, Thin Film Physics Division, Sweden, *H. Pedersen*, Linköping University, Sweden, *Z. Czigany*, Hungarian Academy of Sciences, Research Centre for Natural Sciences, Hungary, *H. Högberg*, *A. Henry*, Linköping University, IFM, Thin Film Physics Division, Sweden

Boron nitride (BN) is an interesting material due to its electrical and mechanical properties and close similarities to crystalline carbon. The atoms in BN can be sp^2 or sp^3 hybridized and in the sp^2 hybridized state (sp^2-BN) BN can form hexagonal (h-BN) or rhombohedral (r-BN) lattices, which both bare close structural similarities to graphite. sp^2-BN exhibits wide bandgap (~ 6 eV) and can be doped both p- and n-type in addition being chemically and thermally stable. A wide range of applications within electronics and optoelectronics are envisioned for BN. However, BN is the least investigated material among III-N materials, mainly due to the difficulty in deposition of high quality epitaxial thin films. Another difficulty is the determination of the crystalline structure of sp^2-BN; h-BN and r-BN differ only in stacking sequence. In-plane lattice constants are the same – 2.504 Å and spacing between basal planes is around 3.333 Å for both crystal structures. This makes it impossible to distinguish between c-axis oriented h-BN and r-BN thin films by using X-ray diffraction (XRD) in Bragg-Brentano geometry and requires atomic resolution investigation by cross-section transmission electron microscopy (TEM)

In previous work, we presented deposition of high quality r-BN thin films on a-Al_2O_3 by Chemical Vapor Deposition [1]. Here we present study of the nucleation and film development at the early stages of the growth of sp^2-BN thin films on (0001) a-Al_2O_3, (0001) 4H-SiC, (0001) 6H-SiC and (111) 3C-SiC. We have observed in scanning electron microscope that the initial growth starts by formation of triangular features. These features are observed with two orientations rotated 60° with respect to each other. This observation is in-line with our XRD measurements which suggests that the sp^2-BN films are epitaxially grown twinned r-BN with 60° rotation between twins. Our TEM results suggest that the growth on a-Al_2O_3 with an AlN buffer layer starts with around 10 initial basal planes of h-BN and that the stacking sequence then changes to r-BN. Albeit, it is not possible to observe contribution from h-BN in XRD. Moreover, SiC substrates are found to be highly suitable for the direct deposition of c-axis oriented crystalline sp^2-BN and epitaxy of r-BN is observed on 4H-SiC.

[1] M. Chubarov, H. Pedersen, H. Högberg, J. Jensen, A. Henry, *Cryst. Growth Des.***12** (2012), 3215

2:50pm **TS2-1-5 Recent Advances in Glow Discharge Optical Emission Spectrometry GD-OES for Material Characterization**, ***P. Hunault*** *(philippe.hunault@horiba.com)*, *C. Morin*, HORIBA Scientific, US, *P. Chapon*, Horiba Jobin Yvon S.A.S., France

Functional multilayered coatings often feature layers down to nanometer scale. Reference surface techniques as ESCA, AES, SIMS offer very high surface sensitivity but are limited for depth profiling of thin layers. For embedded nanometer layers or interface observation, cross section and SEM EDX or TEM characterization are usually used. However, there is a technique capable to give the chemical composition as a function of depth, with nanometer resolution for thin and thick coatings. Rf GD-OES, Radio Frequency Glow Discharge Optical Emission Spectrometry, relies on the sputtering of a large area of the material of interest (conductive or not) by a high density (10^4) and low energy Rf plasma and offers a very fast sputter rate (typically 2-10nm/sec.). Various applications taken from different fields from high temperature corrosion in metallurgy to Photovoltaic, coatings on glasses to Li-ion batteries will be presented. Feature and benefit of a recent patented development allowing ultra fast sputering of thick polymer layers with an excellent in-depth resolution will be described. In addition, it will be explained how GD-OES can be used with great profit for SEM sample preparation to access and reveal enbedded inclusion in stainless steel or enhance surface preparation prior to EBSD measurements of Tungsten Carbides.

3:10pm **TS2-1-6 New Insights into the Contribution of Auger Spectroscopy Towards Energy Applications: Auger Recent Performance Improvements, Complementarity with XPS and ToF-SIMS, "Imaging Cluster" Approach**, ***E. De Vito*** *(eric.de-vito@cea.fr)*, *S. Jouanneau*, *E. Radvanyi*, *W. Porcher*, *A. Bordes*, *J.P. Barnes*, CEA Grenoble, France, *P. Marcus*, Chimie ParisTech (ENSCP), France

Minatec Nanocharacterization Center, located at Minatec Campus, has a unique cluster of surface analysis investigation tools, with transfer modules allowing multiprobing characterization. Cross-analysis of small objects is supposed to allow a more precise description of the chemical arrangement of the observed structures, though difficulties quickly appear in this approach. Among our instruments, the new Auger nanoprobe opens new perspectives for Auger spectroscopy. Though spatial resolution is still far behind what can be reached with newest microscopy methods, it keeps the convenience and versatility of scruting an amorphous material without any surface modification or sample manipulation. Complementarity with other surface techniques such as XPS or ToF-SIMS is also a key point that must be underlined. Studies will be presented there as illustrative examples, among them the study of Li mechanism in Si negative electrodes [1].

[1] *Study of lithiation mechanisms in silicon electrodes by Auger Electron Spectroscopy*, J. Mater. Chem. A, 2013, 1, 4956-4965

3:30pm **TS2-1-7 Microstructure Control of Metal Thin Films by Ion Irradiation**, ***R. Spolenak*** *(spolenak@mat.ethz.ch)*, ETH Zurich, Switzerland **INVITED**

The microstructure of thin films can be partly controlled by deposition parameters and thermal treatments. Both, however, are usually limited by the deposition method and the substrate properties. This paper focuses on ion irradiation from the keV to the MeV range of thin fcc and bcc metal films. The microstructure can then be tuned by phenomena as preferential sputtering, non-selective and selective grain growth, grain rotation and phase transformation. Even in refractory metals significant grain growth can be achieved at room temperature, which due to substrate limitations is virtually impossible by thermal means. The phenomena are illustrated by analytical models and applications in microelectronics.

4:10pm **TS2-1-9 A Novel Instrument and Methodology for the In-Situ Measurement of the Stress in Thin Films**, ***D.M. Broadway*** *(david.m.broadway@nasa.gov)*, NASA Marshal Space Flight Center, US, *M.O. Omokanwaye*, Massachusetts Institute of Technology, US, *B.D. Ramsey*, NASA Marshal Space Flight Center, US

We introduce a novel methodology for the in-situ measurement of mechanical stress during thin film growth utilizing a highly sensitive non-contact variation of the classic spherometer. By exploiting the known spherical deformation mode of the substrate the value of the curvature is inferred by measurement of only one point on the substrate's surface—the sagittal. From the known curvature the stress can be calculated using the well-known Stoney equation. Based on this methodology, a stress sensor has been designed which is simple, highly sensitive, compact, and low cost.

The technique employs the use of a double side polished substrate that offers good specular reflectivity and is isotropic in its mechanical properties, such as <111> oriented crystalline silicon, for example. The measurement of the displacement of the uncoated side during deposition is performed with a high resolution (i.e. 5nm), commercially available, inexpensive, fiber optic sensor which can be used in both high vacuum and

high temperature environments (i.e. 10^{-7} Torr and 480°C, respectively). A key attribute of this instrument lies in its potential to achieve sensitivity that rivals other measurement techniques such as the micro cantilever method but, due to the comparatively larger substrate area, offers a more robust and practical alternative for subsequent measurement of other characteristics of the film that might be correlated to film stress.

We present measurement results of nickel films deposited by magnetron sputtering which show good qualitative agreement to the know behavior of the stress in polycrystalline films with deposition rate as previously reported by Thornton and Hoffman.[1]

[1]John A. Thornton, David W. Hoffman, "Internal stresses in titanium, nickel, molybdenum, and tantalum films deposited by cylindrical magnetron sputtering" J. Vacuum Science Technology., Vol. 14, No.1, Jan/Feb. 1977

4:30pm **TS2-1-10 New Approach for Tailoring Mechanical Properties and Residual Stress of a-C:H:W Coatings**, ***C. Schmid***, TU Darmststadt, Physical Metallurgy, Germany, *H. Hetzner*, *F. Hilpert*, University of Erlangen-Nürnberg, Germany, *K. Durst (k.durst@phm.tu-darmstadt.de)*, TU Darmststadt, Physical Metallurgy, Germany

Proper variation of process parameters during deposition of a-C:H:W allows to produce coatings with tailored properties. In this work a-C:H:W coatings were deposited by unbalanced reactive magnetron sputtering of a WC target using acetylene as reactive gas. The process parameters like reactive gas flow, sputter power and bias voltage were varied according to a central composite experimental design and their influence on coating properties (determined by nanoindentation) like hardness and modulus of elasticity were observed. It turned out that bias voltage and acetylene gas flow affect the hardness of the coatings most. Subsequently, five coatings with predefined mechanical properties were deposited according to the generated model. The mechanical properties were selected in such a way that two coatings exhibit the same i.e. hardness values, using however different process parameters. These 5 coatings were investigated in terms of microstructure, chemical composition, mechanical properties and residual stresses by focused ion beam (FIB), atomic force microscopy, auger electron and Raman spectroscopy and nanoindentations. Residual stresses of these amorphous coatings were determined by means of FIB and digital image correlation (DIC). For this purpose a double slit was milled in the coating which causes the residual stresses to relax. By determining the resulting displacements with DIC the residual stresses can be quantified. It was observed that both the residual stresses and the hardness of the coatings increase with bias voltage whereas with raising acetylene gas flow the hardness decreases by simultaneous increasing residual stresses. The obtained results can be helpful for a tailored coating design considering not only hardness and modulus, but also residual stress level of the a-C:H:W coatings.

4:50pm **TS2-1-11 Process Control of TiCN Thin Films Deposited by Cathodic Arc Evaporation with Combined Raman and Optical Emission Spectroscopy**, ***G. Leach*** *(mdu.aurora@gmail.com)*, Simon Fraser University, Canada, *M.H. Shih*, MingDao University, Taiwan, *T. Burai*, Simon Fraser University, Canada, *B.H. Hsiao*, MingDao University, Taiwan, *X.Z. Zhang*, *A.S. Schiffer*, Simon Fraser University, Canada, *J.H. Hung*, Aurora Scientific Corp, Canada, *D.Y. Wang*, MingDao University, Taiwan

TiCN thin films h ave been widely us ed as protective coatings for various industrial applications f or their superior properties of high hardness, low friction coefficient, high wear resistance and chemical inertness. Due to the high miscibility between TiN and TiC, the two main constituents of TiCN, there is the necessity to quantify further the correlation between the synthesizing plasma conditions and the tribological properties of the resulting TiCN thin films for the purpose of reliable process control. In this study, TiCN thin films were synthesized using the cathodic arc evaporation process under different C_2H_2 / N_2 flow ratios of 08/40, 16/32, 24/24, 24/36, 26/32, 36/32 sccm at a balanced working pressure of 2 Pa. An *in-situ* optical emission spectrometer probe recorded the variation of Ti neutral, radical, and ion emission intensity as a function of C_2H_2 / N_2 flow ratio. The evolution of TiN and TiC phases in TiCN corresponding to various C_2H_2 / N_2 flow ratios was assessed by using post-deposition Raman analysis. The morphology, microstructure and chemical composition of the resulting TiCN thin films were also characterized using scanning electron microscopy (SEM), x-ray diffraction (XRD), and x-ray photoelectron spectroscopy (XPS). The micro-hardness and tribological properties were assessed using a nano-indenter and ball-on-disk tribometer, respectively. Preliminary results indicate a strong correlation between the OES signal of the C_2H_2 / N_2 plasma and the tribological properties of TiCN. A control mechanism for precision deposition of TiCN across a wide spectrum of C:N ratios can be devised accordingly.

Coatings for Use at High Temperatures
Room: Sunrise - Session A1-3

Coatings to Resist High Temperature Oxidation, Corrosion and Fouling
Moderator: M. Weaver, The University of Alabama, V. Kolarik, Fraunhofer Institute for Chemical Technology ICT, D. Litton, Pratt & Whitney

8:00am **A1-3-1 High Temperature Oxidation Behavior of Al2O3/ Al Composite Coating on γ-TiAl**, ***Y. Xu***, Nanjing University of Aeronautics and Astronautics, *Q. Miao (miaoqiang@nuaa.edu.cn)*, Nanjing University of Aeronautics and Astronauticsg, China, *W. Liang, X. Yu, L. Wang, Q. Jiang, B. Ren, J. Yang*, Nanjing University of Aeronautics and Astronautics, China

A composite coating system, which consisted of an Al interlayer and an Al_2O_3 surface layer, was introduced on the substrate γ-TiAl alloy by magnetron sputtering. The isothermal oxidation behavior of the coated γ-TiAl alloy was investigated at 1000°C. X-Ray diffraction (XRD), scanning electron microscopy (SEM) with energy dispersive X-ray spectrometer (EDX) technique were employed to characterize the coatings and the oxide scales. The results indicated that the Al_2O_3/Al composite coatings improved the oxidation resistance of γ-TiAl alloy at 1000°C air exposure. No spallation or crack was observed in the oxide scales which were composed of α-Al_2O_3 and $TiAl_3$ after the oxidation test. The outward Al diffusion from interlayer provided sufficient Al source for the formation of Al_2O_3 layer in the coating surface. The oxidized coating showed good adhesion strength with the substrate during the scratch test. Due to inward and outward diffusion, the Al interlayer was consumed after 100 h oxidation test and a Ti-Al interdiffusion zone was formed.

8:20am **A1-3-2 High-Temperature Oxidation of Al-Hf and Al-Hf-O Coatings**, *X. Maeder*, CSEM SA, Switzerland, *M. Döbeli*, ETH Zurich, Switzerland, *A. Dommann*, EMPA, Switzerland, *A. Neels*, CSEM SA, Switzerland, *P. Polcik*, PLANSEE Composite Materials GmbH, Germany, *H. Rudigier, B. Widrig*, ***J. Ramm*** *(juergen.ramm@oerlikon.com)*, Oerlikon Balzers Coating AG, Liechtenstein

Al-Hf and Al-Hf-O coatings were synthesized by cathodic arc evaporation. The depositions were performed onto sapphire substrates utilizing composite targets with compositions of $Al_{0.75}Hf_{0.25}$, $Al_{0.70}Hf_{0.30}$ and $Al_{0.67}Hf_{0.33}$, respectively. The Al-Hf coatings were produced in non-reactive processes (without gas addition), while pure oxygen was utilized for Al-Hf-O coatings. The chemical composition was analyzed by EDX and RBS. For the Al-Hf coatings, it deviates distinctively from target composition. This was not the case for Al-Hf-O. XRD phase analysis proves the synthesis of Al_3Hf and Al_2 Hf intermetallic compounds for the Al-Hf coatings while the oxide coatings indicates the monoclinic HfO_2 phases in an amorphous matrix.

The coatings were annealed in ambient up to 1290°C to study the oxidation process. *In-situ* XRD analysis of the coatings was performed during annealing. Depending on composition, the intermetallic phases undergo phase transformations at temperatures between 690° and 850°. After a transition period charcterized by the evolution of characteristic phases, coatings stabilized at about 1100°C forming two oxide phases: alumina (corundum) and monoclinic HfO_2. Applying the same treatments to the Al-Hf-O coatings result in an improvement of crystallinity for the monoclinic HfO_2 phase starting at about 860°C. After a transition period to 1100°C, the corundum and monoclinic HfO_2 phases are formed.

The oxidation processes for the Al-Hf intermetallic phases and the Al-Hf-O oxides are compared placing particular emphasis on the transition region. The parameters of the deposition process and their influence on the stabilization of the oxides at already lower temperatures are discussed.

8:40am **A1-3-3 Hard Wear-resistant Mo-Si-B-(N) Coatings with Oxidation Resistance up to 1400^{0}C**, ***Ph.V. Kiryukhantsev-Korneev*** *(kiruhancev-korneev@yandex.ru)*, *A. Meurisse, A. Bondarev, E.A. Levashov, D.V. Shtansky*, National University of Science and Technology "MISIS", Russian Federation

MoN and MoB(N) coatings demonstrate relatively high hardness and wear resistance, low friction coefficient and good adhesion to the steel substrates but their working temperatures are limited by 500-600^{0}C. It's well known that oxidation resistance and thermal stability of nitride and boride coatings can be enhanced by Si alloying. The goal of this work is a complex study of the Mo-Si-B-N coatings, including the investigation of high-temperature tribological characteristics, thermal stability, oxidation resistance, and diffusion barrier properties.

The multicomponent $MoB_{0.3}Si_{0.1}$ and $MoB_{0.2}Si_{0.4}$ composite cathodes produced by self-propagation high-temperature synthesis technology were subjected to magnetron sputtering either in a pure Ar or N_2 atmosphere, or in a gaseous mixture of $Ar+N_2$. Molybdenum, silicon, alumina, NiCrAlW and WC-Co alloys were used as substrate materials. To evaluate the high-temperature oxidation resistance, diffusion-barrier properties, and thermal stability, the coatings were annealed in air at various temperatures range from 500 to 1500^{0}C. The structure of as-deposited and heat-treated coatings was studied by means of X-ray diffraction, scanning and transmission electron microscopy, glow discharge optical emission spectroscopy, X-ray photoelectron spectroscopy, Raman and FTIR spectroscopy. The mechanical properties of the coatings were measured using nanoindentation and scratch-testing. The tribological properties were evaluated in air using a high-temperature ball-on-disc tribometer. The properties of Mo-Si-B-N were compared with those of the MoN and Mo-B-(N) reference coatings.

The results obtained show that the Mo-Si-B-N coatings contained nanocrystalline nc-$MoSi_2$ and nc-MoB grains surrounded by amorphous a-SiN_x phase. The Mo-Si-B-N coatings with high concentration of Si and N demonstrated the following characteristics: high adhesion strength (critical load > 40 N), hardness up to 35 GPa, elastic recovery up to 65%, elastic modules less than 350 GPa, and wear rate less than 10^{-5} $mm^3N^{-1}m^{-1}$. The decreasing of friction coefficient from 0.8 (room temperature) to 0.3 (500^{0}C) was observed and can be explained by the formation of MoO_3 phase acted as a solid lubricant. When the Si content was raised from 4 to 50 at.%, the oxidation resistance of the Mo-Si-B-N coatings was showed to increase from 600 to 1400^{0}C and attributed to the formation of a SiO_2 top-layer, which protected the coatings from an intensive oxidation at high temperatures. The combination of relatively high hardness, wear, and high-temperature oxidation resistances makes the Mo-Si-B-N coatings promising candidates for high-temperature tribological applications.

9:00am **A1-3-4 On the Mechanisms and Mitigation of CMAS Attack on YSZ Thermal Barrier Coatings**, *K.-I. Lee*, The University of Manchester, UK, ***R. Wu***, National Institute for Materials Science, Japan, *P. Xiao (p.xiao@manchester.ac.uk)*, The University of Manchester, UK

Yttria stabilized zirconia (YSZ) made thermal barrier coatings (TBCs) have been widely applied to aero engines for decades. During the engine operation, airborne particles, dusts and ashes could be injected into engine, which then melt and deposit on turbine blades, forming calcium-magnesium-alumino-silicate (CMAS). This substance penetrates into TBCs, both chemically and mechanically damaging the integrity of the YSZ top-coat. For the state-of-the-art TBC technology, two major techniques have been developed to mitigate the CMAS attack: 1) modifying the YSZ topcoat chemistry by elemental doping, 2) fabricating a protective overlay on top of YSZ. With these two techniques, alumina is the most common material chosen to prevent CMAS attack. In this study, the relationship between chemical reaction and temperature is investigated for two systems: YSZ topcoat/CMAS and Al_2O_3/CMAS systems. Real volcanic ash is utilized to better simulate CMAS. In YSZ/CMAS system, differential thermal analysis (DTA) results show that the reaction between the two began at 490°C, during which, yttria is depleted, and the melting temperature of the simulated CMAS (volcanic ash) decreased from the original 1250°C to 1160°C when mixed with YSZ powder. Furthermore, the result of XRD semi quantitative analysis indicates that the ratio of tetragonal to monoclinic phase in YSZ decreased after heat treatment. In contrast, in the absence of CMAS, the ratio of pure YSZ increased after the same heat treatment procedure. In the case of Al_2O_3/CMAS system, reactions between the two occurred when the temperature reached 410°C, forming anorthite ($CaAl_2Si_2O_8$) as a reaction product and the melting temperature increased to around 1450°C with the addition of alumina. All these results demonstrate that reactions of CMAS with both YSZ and alumina start far below its melting point. Alumina prevents CMAS penetration by increasing the melting temperature beyond the materials operating temperature

9:20am **A1-3-5 On the Ways to Improve the Oxidation Resistance of the Nb-Si Composites System**, ***S. Mathieu*** *(stephane.mathieu@ijl.nancy-universite.fr)*, Université de Lorraine, France, *S. Knittel*, Snecma, SAFRAN Group, France, *L. Portebois*, Université de Lorraine, France, *N. Adkins, M. Wickins*, University of Birmingham, UK, *C. Seemüller, M. Heilmaier*, Karlsruhe Institute of Technology (KIT), Germany, *M. Mulser*, Fraunhofer Institute for Manufacturing Technology and Advanced Materials, Germany, *S. Drawin*, Onera, France, *R. Braun*, DLR, Germany, *M. Vilasi*, Université de Lorraine, France **INVITED**

Refractory alloys such as Nb-Si intermetallic composites exhibit low density and high strength above the operating temperature range of nickel-

based superalloys. Due to these advantageous properties they have been investigated as replacement for nickel-base superalloys in structural components for high-temperature applications, such as aircraft or land-based turbines. However those alloys are not ready to withstand the higher-temperature hostile environments (high combustion gas flow rates, with presence of aggressive elements such as water vapor, oxygen and CMAS, component temperatures of more than 1150°C). Indeed they suffer from rapid degradation (pesting) in air and severe metal recession that hindered their industrial use.

Several strategies are developed to limit the oxidation rate of these compounds:

- Modification of the composition (Al, Si, Ti and Sn additions),

- Microstructure design using powder metallurgy processes,

- Manufacturing of a protective bond coat,

- Deposition of a bond coat plus an environmental/thermal barrier coating (E/TBC).

The research efforts made in these four directions allow obtaining Nb-Si intermetallic composites less susceptible to pesting at moderate temperature and with improved oxidation resistance at higher temperature. Moreover, protective coatings based on $Ti_3X_3CrSi_6$ (with X = Fe, Co and Ni) have been developed allowing their use up to 1200°C in air or air + steam. Finally, recent investigations evidenced the compatibility of these coating materials with TBC system like yttria partially stabilized zirconia (YSZ). From first results, an increase of the operating temperature for the Nb-Si based system can be expected.

10:00am **A1-3-7 Protection of Nb-Si Alloys by Diffusion Coatings Manufactured by the Halide Pack-cementation Technique: Influence of the Ti and Si Activities on the Coating Microstructure**, ***L. Portebois*** *(leo.portebois@univ-lorraine.fr), S. Mathieu, M. Vilasi*, Université de Lorraine, France

Extensive work has been undertaken to develop structural material able to work at higher temperature than nickel based superalloys, currently operating at 90 % of their melting point [1]. Among potential candidates, refractory alloys based on the Nb-Si system would allow a jump of 200°C of the operating temperature and a decrease by 25% of density in comparison to temperature capabilities and densities offered by current nickel based superalloys. However, their oxidation resistance is too low for a use as structural material without any protective coating, just like current nickel superalloys. Diffusion coatings based on ternary [2] of quaternary [3] complex silicides have been developed, but both systems presented limitation regarding their thermal stability at high temperature. As a consequence, the coating has to be made more refractory. Titanium silicides diffusion coatings could be good candidates for the protection of Nb-Si alloys as (i) they form a slow growing SiO_2 layer serving as a barrier against oxygen penetration (ii) they are perfectly and uniformly adherent with the substrate [4].

In the present work, halide activated pack cementation technique (HAPC) was applied to coat the Nb-Si alloys. Chlorides ($CrCl_3$) were used as activator and four compositions of masteralloy were employed : Ti_5Si_3 + Ti_5Si_4, $TiSi_2$ + Ti_5Si_4, $TiSi_2$ + TiSi, Si + $TiSi_2$. Deposits were performed for 9 h at 1200°C in vacuum (10^{-6} mbar). Each subsequent coating was characterized by X-ray diffraction and scanning electron microscopy. Results allow the determination of the nature of the successive layers formed during the coating process at the surface of the substrate. Phase successions were considered regarding the available thermodynamic data of the system.

Then, oxidation tests were performed in air to assess the coating performances in a large range of temperature (isothermal oxidation at 1300°C and 1400°C, thermal cycling at 815°C and 1100°C). Regarding results, the coating formed using the pack with the higher silicon activity exhibited the best oxidation resistance both at 815°C and 1300-1400°C. However, limitations appear at 1100°C in cyclic conditions.

[[1]] DIMIDUK D. M., PEREPEZKO J. H., *MRS Bull.* 2003, *28*, 639 .

[2] KNITTEL S., MATHIEU S., VILASI M. *Surface and Coatings* (2013) in press

[3] KNITTEL S. MATHIEU S., PORTEBOIS L., DRAWIN. S, VILASI M. *Surface and Coatings* (2013) in press

[4] BV COCKERAM, RA RAPP, *Metallurgical and Materials Transactions* A, 1995 - Springer

10:20am **A1-3-8 NiCrN Coatings for Forming and Moulding Applications**, ***P. Navabpour*** *(parnia.navabpour@miba.com), H. Sun, K. Cooke*, Teer Coatings Limited, Miba Coating Group, UK

The dies used for moulding and forming require excellent mechanical properties in order to withstand the high levels of stress applied to them during the processing. Another requirement is low release forces to allow for the separation of the moulded/formed product from the surface of the die without fouling of the die surface or damaging the processed components.

Closed Field UnBalanced Magnetron Sputter Ion Plating (CFUBMSIP) is a well-known process capable of producing hard, wear resistant coatings such as CrN. Whilst CrN has been successfully used in a number of forming and moulding applications to enhance the hardness and wear resistance of dies, the release properties are not always sufficient. The addition of Ni in the coating can enhance the release properties against a number of polymers such as low-density polyethylene and epoxy resins.

This presentation reports on NiCrN coatings deposited using reactive CFUBMSIP from elemental Cr and NiCr alloy targets using nitrogen as the reactive gas. The variation of process parameters, such as Ni and N content has been carried out in order to obtain the desired mechanical and non-stick properties. Coatings have shown excellent results in practical moulding applications by reducing the release force and fouling of the die.

10:40am **A1-3-9 Chemical Inertness of Ta–Si–N Coatings with Lanthanum Borosilicate Glasses in Glass Molding Process**, *Y.I. Chen (yichen@mail.ntou.edu.tw),* ***Y.R. Cheng***, National Taiwan Ocean University, Taiwan, *L.C. Chang*, Ming Chi University of Technology, Taiwan, *Y.H. Chen*, Young Optics Inc., Taiwan

Lanthanum borosilicate glasses, B_2O_3-SiO_2-La_2O_3 based, are widely used as optical glass materials for lens utility in glass molding technology. To evaluate the feasibility of protective coatings on glass molding dies, Ta –Si–N coatings were sputtered on cemented tungsten carbide substrates. Lanthanum borosilicate glasses were placed on the surface of coatings and heat-treated in a glass molding atmosphere of 15 ppm O_2 – N_2 in a thermal cycling annealing at 270 and 600 °C. Up to 2,000 thermal cyclic annealing tests were performed and the holding time at the molding temperature was set at 1 min for each cycle. The variations in crystalline structure, nanohardness, surface roughness and chemical composition profiles in depth after various annealing durations were investigated.

11:00am **A1-3-10 Control of Bon Coat Microstructure in HVOF Process for Thermal Barrier Coatings**, ***S. Myoung***, *Z. Lu, M. Kim, H.-S. Kim, Y. Jung (jungyg@changwon.ac.kr),* Changwon National University, Republic of Korea

The thermal durability of TBCs is closely related to their microstructure, determining thermo-mechanical properties and failure mechanism. Therefore, the control of microstructure in the top and bond coats is proposed as a new strategy for advanced TBCs. The TBC system consists of heat-resistant ceramic top coat, intermetallic bond coat, and nickel-based substrate. The nickel-based superalloys used as the substrate are well known for their excellent mechanical properties in high temperature applications, especially for gas turbines. However, the substrate should be protected by MCrAlY (where M= Co, Ni or Co/Ni) bond coat, due to their lack of the oxidation and corrosion resistances. The bond coat plays an important role in ensuring structural effectiveness and affording extra adhesion of the top coat to the substrate, which also prevents and/or delays oxidation of the substrate. Many techniques have been developed and employed to prepare the bond coat, such as low-pressure plasma spray, air plasma spray (APS), and high velocity oxy-fuel (HVOF) spray. Among these techniques, HVOF process is a promising technique for forming the bond coat in TBCs, owing to its good microstructure, better adhesive strength, and low operating costs compared with APS process. In this study, various deposition conditions, such as gun distance, powder feeding rate, and ratio of fuel/oxygen/air, were controlled to optimize the microstructure of bond coat in HVOF process. In order to understand the effects of microstructural design on mechanical properties in the bond coat, the mechanical properties with feedstock powder and coating parameter were investigated using various techniques and the optimized microstructure for the bond coat prepared by HVOF process was proposed.

11:20am **A1-3-11 Multi-Component High-Entropy Alloy Coatings for Use in High Temperature Environments**, ***J. Alfano*** *(jpalfano@crimson.ua.edu), M. Weaver*, The University of Alabama, US

Equiatomic or near equiatomic alloys, often called High-Entropy Alloys (HEAs), are a new class of materials that are currently being studied for a broad range of applications because of their high hardness, high temperature stability, and slow diffusion. These alloys lack a principal component and are composed of five or more metallic elements, each constituent having between 5 and 35 at.%. The unique properties of HEAs make them an ideal candidate for high temperature environments, but little research has been performed on the use of HEAs as a wear or oxidation resistant coating. Based on oxidation behavior and characterization of a bulk NiAlCrCoSi HEA, a similar coating was created using co-sputtering via DC Magnetron sputtering. The coating was deposited on pure Ni and on the Ni-based

superalloy CMSX-4. After coating deposition, the coatings were heat treated and isothermally oxidized to determine phase formation and oxidation behavior. Heat treatment at 600°C resulted in a fine multi-phase microstructure that varied little with aging time. The isothermal oxidation test revealed significant improvement when comparing mass change of pure Ni to that of the Ni plus coating. Further improvement in mass gain was observed for the coating on CMSX-4. The mass gain results were then compared to those obtained previously for β-NiAl+Cr+Zr/Hf coatings. The multi-component alloy coating was found to have a lower parabolic mass curve than the β coatings.

12:00pm **A1-3-12 Performance of HVOF Sprayed Al_2O_3-CoCrAlTaY Coating on 12Cr-1Mo steel to Combat Hot Corrosion at 800°C**, *N. Jegadeeswaran*, RITM, India, *M. Ramesh*, NITK, Surathkal, India, ***B. Udaya*** *(udayabhatk@gmail.com)*, NITK Surathkal, India

12Cr-1Mo steel is a candidate material for use in the hot section of the gas turbines. To protect the components from degradation and prolong their life in a high temperature salt environment, coatings are being used. In the present investigation, a special steel, namely MDN-121, with 12Cr and 1Mo as major alloying element is used as substrate material. The steel is coated with fused oxide alloy powder (10wt% Al_2O_3-90(CoCrAlTaY)) using high velocity oxy-fuel (HVOF) method. The substrate material as well as coated material is investigated for hot corrosion resistance at 800°C in presence of 50vol % Na_2SO_4+V_2O_5. Hot corrosion behaviour is investigated under cyclic conditions which involved 1 hour holding at 800°C followed by 20 minutes of air cooling. Total 50 thermal cycles are used in this investigation. Gravimetric analysis is done to investigate weight gain during each cycle and to estimate the parabolic rate constant. It is observed that coated material exhibits less weight gain. Also, the parabolic rate constant is one order less for the coated substrate. Scanning electron microscopy and x-ray diffraction study indicated that the surface of uncoated substrate consisted of FeO and Cr_2O_3, where as the surface of the coated substrate consists of Cr_2O_3 and CoO. The oxide scale on the surface of uncoated substrate was peeling off where as the scale on the coated surface was intact. Cross sectional microscopy and compositional mapping of the scale on the coated surface indicated that the coating is free of cracks and only small portion of the coating is affected during hot corrosion under cyclic thermal conditions. Based on the experiments and results it is concluded that high velocity oxy fuel sprayed fused oxide alloy powder coating on MDN-121 steel is effective in combating hot corrosion in presence of a mixture of Na_2SO_4 and V_2O_5 at 800°C.

Key words: Hot corrosion, Special steel, HVOF, Thermogravimetric analysis, Fused oxide alloy powder.

Hard Coatings and Vapor Deposition Technology
Room: Golden West - Session B2

CVD Coatings and Technologies
Moderator: E. Blanquet, SIMaP CNRS/Grenoble INP/UJF, M. Shiratani, Kyushu University

8:00am **B2-1 Pulsed Direct Liquid Injection CVD: a High Potential Process for Advanced and Nanostructured Carbide and Nitride Coatings**, ***F. Maury*** *(francis.maury@ensiacet.fr), A. Douard, G. Boisselier*, CIRIMAT, France, *F. Schuster*, CEA, France **INVITED**

The pulsed direct liquid injection (DLI) of precursors is an emerging technology to feed CVD reactors with high vapor flow rates. This allows for example to increase the size of the CVD reactors or to develop deposition processes for continuous scrolling treatments. This technique has been especially developed to deposit functional oxides with applications in microelectronics. The molecular precursors are generally dissolved in a solvent and the use of an oxygen partial pressure prevents contamination of the films by carbon. More recently, solutions were found to control the carbon incorporation into the films and new DLICVD processes were proposed for the deposition of non-oxide coatings. In this paper, it is demonstrated that this technology offers new opportunities for the deposition of metallurgical coatings as carbides and nitrides as well as multilayer nanostructured coatings, as required for high protective performances under extreme environment. For nanostructured coatings each component should grow at the same temperature and pressure, and the multilayer architecture is achieved by controlling alternatively the composition of the gas phase. Examples of DLICVD processes operating either under atmospheric or low pressure are described. This includes hard chromium based coatings (Cr, Cr_xC_y, CrN) and refractory coatings SiC and HfC_x. Furthermore nanostructured multilayer coatings as Cr/CrN and CrN/CrC_x with a bilayer period as low as 50 nm have been grown at 500 °C . HfC/SiC multilayer coatings 5 µm thick were deposited at 750 ° C with a bilayer period of 100 nm, *i.e.* thickness of individual layer was 50 nm. Preliminary properties of these advanced coatings and some interesting effects as self-healing of microcracks occurring during the growth of multilayers and surfactant effect induced by the solvent vapor are discussed.

8:40am **B2-3 Niobium Nitride Thin Films Deposited by High Temperature Chemical Vapor Deposition**, ***F. Mercier*** *(frederic.mercier@simap.grenoble-inp.fr)*, SIMaP CNRS/Grenoble INP/UJF, France, *S. Coindeau*, CMTC-SIMaP, France, *M. Benz*, SIMaP CNRS/Grenoble INP/UJF, France, *A. Crisci, T. Encinas*, CMTC-SIMaP, France, *G. Riado, R. Boichot, A. Mantoux*, SIMaP CNRS/Grenoble INP/UJF, France, *C. Jimenez, F. Weiss*, LMGP CNRS/Grenoble INP, France, *E. Blanquet, M. Pons*, SIMaP CNRS/Grenoble INP/UJF, France

Niobium nitride (NbN) is a well-known superconductor and is considered to be one of the promising cryoelectronic materials. Till now, the thin films necessary for superconductive devices are mostly synthesized by physical vapor deposition methods. The aim of this study is to introduce chemical vapor deposition technique, CVD, as an alternative technique to process superconducting niobium nitride thin films.

In this work, NbN thin films have been grown by CVD from ammonia NH_3 (99.999 %) and Nb chlorides species $NbCl_x$, in situ produced via chlorination of high purity Nb wire (99.999%) with chlorine gaz Cl_2 (99.999%). Substrates are C-plane (0001) monocrystalline hexagonal sapphire, A-plane (11-20) monocrystalline hexagonal sapphire, (111) monocrystalline cubic silicon carbide. Deposition temperature has been varied between 900°C and 1300°C. Without any post-deposition treatments, the thin films have been characterized by means of SEM (Scanning Electron Microscopy), XRD (X-Ray Diffraction), XRR (X-Ray Reflectometry), Raman spectroscopy and EPMA (Electron Probe Micro Analysis). In this presentation, the influence of experimental parameters (temperature, composition of the gas phase, substrate) on the composition of the thin film and its structural properties (crystal structure, growth direction, lattice parameter, orientation relation between the substrate and the thin film) will be given. In particular, the stability of the cubic structure, the only structure which has the superconductive properties, will be discussed regarding the growth parameters. Finally, the potentiality of the CVD technique to synthesize high quality niobium nitride thin films and multilayers structures will be presented.

9:00am **B2-4 Diamond Coatings for the Machining of Composite Materials used in Aerospace Industry**, ***B. Mesic*** *(Biljana.Mesic@CemeCon.de), M. Frank, M. Woda, W. Koelker, O. Lemmer, C. Schiffers*, CemeCon AG, Germany

Due to the characteristic and attractive combination of the high strength and low weight (high strength-to-weight ratio), the composite materials - carbon reinforced fiber plastics (CFRP) and CFRP stacked with aluminum and titanium - are used as construction material in aerospace industry. The machining of these extreme abrasive composite and sandwich materials brings new challenges for the modern cutting tools. These are the surface quality of the workpieces without fiber delamination or uncut fibers and the rapid tool wear. It has been demonstrated that diamond coated cutting tools are the proper choice for such applications, due to their outstanding hardness and reduced tendency to stick of the workpiece material.

The multilayer CVD diamond coating on cemented carbide tools developed by CemeCon AG is specially designed to resist wear, prolong the tool lifetime and enhance the machining performances. The remarkable good properties of these CVD diamond coatings produced by a special hot filament chemical vapor deposition (HFCVD) process combine the advantages of an adhesive layer with the fracture toughness of nano-crystalline diamond. The performances of these multilayer diamond films in CFRP are excellent. The much finer and smoother diamond coating on cutting tool enables the vibration free drilling which results in high surface quality of the workpiece without chatter marks.

9:20am **B2-5 CVD Titanium Aluminum Nitride Coatings for Cutting Applications**, ***D. Stiens*** *(dirk.stiens@walter-tools.com), T. Manns, S. Ruppi*, Walter AG, Germany

The first reports on aluminum-rich, fcc-phase $Ti_{1-x}Al_xN$ coatings by thermal CVD were published in 2006. These coatings, which were produced in laboratory scale deposition equipment, were reported to outperform state-of-the-art CVD and TiAlN PVD coatings in cutting tests. Current research and development in industry therefore focuses on the scale-up of the deposition process. For the present work $Ti_{1-x}Al_xN$ coatings were produced by thermal CVD in production scale equipment from the precursors $TiCl_4$, $AlCl_3$, and NH_3. The coatings were characterized by X-ray diffraction, scanning electron microscopy and microhardness measurements. Coatings with h-AlN/fcc-TiN or fcc-$Ti_{1-x}Al_xN$ structure were obtained. Milling tests against grey cast iron and steel show that dramatic tool lifetime increases

are possible when phase content and structure of the coatings are properly controlled.

9:40am **B2-6 Functionalization of Aluminium Nitride Grown by High Temperature Chemical Vapor Deposition**, ***M. Pons*** *(michel.pons@simap.grenoble-inp.fr)*, Grenoble Institute of Technology, France

Functionalization of aluminium nitride grown by high temperature chemical vapor deposition

M. Pons[1*], R. Boichot[1], E. Blanquet[1], S. Lay[1], F. Mercier[1], D. Pique[2]

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The application of AlN films in optoelectronics, sensors and high temperature coatings is strongly dependent on the nano- micro-structure of the film, impurity level and defect density. AlN epitaxial thin (0.5 – 10 µm) and thick polycrystalline (> 10 µm) films were grown on different foreign substrates (sapphire, silicon carbide, graphite) and single AlN crystals by Chemical Vapor Deposition (CVD), also called Hydride Vapor Phase Epitaxy (HVPE), at high temperature (1200-1750 °C). In the first part of this paper, polycrystalline growth of thick films (>10 µm) prepared at high growth rate (>100 $\mu m.h^{-1}$) was performed on graphite substrates to study the preferential orientation of the films. AlN/W multilayers were deposited on silicon carbide composites to increase their performance at high temperature in aggressive conditions. Such multilayer materials can be used for the cladding of nuclear fuel. The second part of this paper concerns the characterization of epitaxial films, including their crystalline state, surface morphology, and inherent and thermally induced stress which inevitably leads to high defect densities and even cracking. The full-width at half-maximum (FWHM) of X-Ray rocking curves of the grown AlN layers exhibited very large values (several thousand arcsec), and they became steeply deteriorated with increasing growth rate. To improve the crystalline quality of AlN layer, well-known growth techniques, such as multi-step growth using buffer layers, were used at temperatures above 1200 °C in order to lower the disorientation to 300 arcsec. The applications of such "templates" for deep UV light emitting diodes (UV LED) and surface acoustic wave sensors (SAW) are discussed.

10:00am **B2-7 Diagnostics of SiH4/H2 Plasma and Surface Reaction in Microcrystalline Silicon Deposition**, ***K. Ishikawa*** *(ishikawa@plasma.engg.nagoya-u.ac.jp), Y. Abe, A. Fukushima, Y. Lu, S. Kawashima, K. Miwa, K. Takeda, H. Kondo, M. Sekine, M. Hori*, Nagoya University, Japan **INVITED**

The tandem solar cell was commonly fabricated by stack of hydrogenated micro-crystalline silicon (µc-Si:H) thin film for the bottom cell and amorphous silicon (a-Si:H) thin films for the top cell. The µc-Si:H can absorb light in higher wavelength towards the infrared region of the solar spectrum and has excellent stability against light soaking. However, the indirect optical transition of µc-Si:H is not efficiently absorbed sunlight, film thicknesses greater than 2 µm. To realize low-cost fabrication of solar cell with the plasma-enhanced chemical vapor deposition (PECVD) processes at low temperature, the high-rate growth of high-quality µc-Si:H films is required.

To date, the growth rate of approximately 2 nm/s was realized using a capacitively coupled plasma (CCP) system with a very high frequency (VHF)-power source and a high working pressure (ca. 1000 Pa) with a narrow electrode gap. In particular the relatively high working pressure, the high electron density is demanded on achievement effectively the SiH_4 depletion. Moreover, the H radicals are recognized as a key factor that influences the crystallinity of Si thin films. Sufficient supply of H radicals to a growing Si thin film surface induces crystallization.

The SiH_4/H_2 gas mixture ratio was 3% with a total gas flow rate of 1000 sccm, and the total pressure was kept at 1200 Pa. The distance between the VHF and lower GND electrodes was 10 mm, and that between the VHF and upper GND electrodes was 5 mm.

The electron density in the SiH_4/H_2 plasma region was measured using a 35 GHz microwave interferometer. A multi-channel spectrometer was used to observe the optical emission intensity of the Si* (288 nm) and SiH* (414 nm) lines. The absolute density of H radicals was measured by vacuum ultraviolet laser absorption spectroscopy (VUVLAS).

The crystallinity factor, preferential orientation, defect density, micro-structure, and the post-deposition oxidation of deposited Si thin films were investigated by Raman spectroscopy, XRD, ESR, TEM, and FTIR, respectively. For the fabrication of Si thin films for solar cell devices to achieve selective enhancement of the H radical densities for crystallization of the films under low depletion of SiH_4. From these results, we will discuss effects of those radicals on surface reaction in µc-Si:H deposition.

10:40am **B2-9 In-situ Measurements of Volume Fraction of cDusters in Films During Plasma CVD**, ***M. Shiratani*** *(siratani@ed.kyushu-u.ac.jp), S. Toko, K. Koga, N. Itagaki, H. Seo*, Kyushu University, Japan

We have developed an in-situ measurement method of volume fraction Vf of clusters (nanoparticles) in films during deposition using quartz crystal microbalances with a cluster-eliminating filter [1, 2]. The cluster volume fraction has been determined by comparing deposition rates of the films with and without clusters. The cluster volume fraction gives useful information to control the incorporation of clusters into films [1-3]. We applied this measurement method to a-Si:H deposition by rf capacitively coupled discharge plasma CVD and obtained the following results. 1) Vf is the highest in 2 s after discharge plasma initiation and then decreases to a steady state value with a characteristic time of 50 s. This long characteristic time depends on gas composition change due to dissociation of molecules in the discharges and a rise of electrode temperature mainly due to ion flux to the electrodes. 2) Contributions of negatively and positively charged species to film deposition rate are less than a few %, namely, they are minor deposition species. 3) Typical size of clusters incorporated into films is less than 2 nm, deduced from force balance. 4) Amplitude modulated discharges with sine wave bing about lower initial Vf, shorter initial transient duration of Vf, and lower steady state Vf value. These results give insights into film deposition processes. Based on the insights we can improve significantly stability of a-Si:H films, which is the key to high efficiency Si thin film solar cells.

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[1] Y. Kim, et al., Jpn. J. Appl. Phys., 52, 01AD01 (2013).

[2] Y. Kim, et al., MRS Proc. 1426, 307 (2012).

[3] Y. Kim, et al., Surf. Coat. Technol. 228, S550 (2012).

11:00am **B2-10 Microstructure and Wear Mechanisms of Texture-controlled CVD α-Al_2O_3 Coatings**, *R. M'Saoubi (rachid.msaoubi@secotools.com)*, ***T. Larsson***, Seco Tools AB, Sweden

The microstructure and wear mechanisms of texture controlled CVD α-Al_2O_3 layers with (0001), (01-12), and (10-10) growth textures were investigated in single point turning of AISI 1045. A wide range of cutting speed conditions and tool geometries were investigated to achieve broad combination of mechanical and thermal loads on the cutting tools that were also assessed experimentally.

The experimental coatings were investigated by FEG-SEM, EBSD and a combination of FIB and analytical TEM techniques prior to and after machining. Significant texture effects on wear performance of the α-Al_2O_3 coating layers were observed, confirming results from previous wear studies in the context of machining AISI 4140 carbon steel (Ruppi 2007, M'Saoubi and Ruppi 2009). The wear mechanisms of the coating layers are further interpreted in the light of thermal, mechanical and frictional conditions occurring at the tool–chip contact interface. In particular, it is suggested that the enhanced near surface deformation (0001) Al_2O_3 modifies the frictional conditions and heat dissipation at the tool-chip contact thus reducing the overall deformation of the cutting edge.

11:20am **B2-11 Grain Boundary Engineered α-Al_2O_3 Coatings**, ***S. Ruppi*** *(sakari.ruppi@walter-tools.com), D. Stiens, T. Manns*, Walter AG, Germany

The introduction of texture-controlled deposition processes is one of the most important recent developments in CVD of α-Al_2O_3. Consequently, today it is possible to deposit α-Al_2O_3 coatings with several preferred growth directions e.g. (012), (110), (001) and (100). α-Al_2O_3 layers with 001 texture have been shown to be superior to all the other textures and randomly oriented α-Al_2O_3 coatings in many metal cutting applications and several manufacturers have introduced products based on this technology.

Grain boundary engineering is a promising way to further enhance the performance of the textured α-Al_2O_3 coatings and grain boundaries in CVD a-alumina have attained growing interest during the last few years. By controlling the preferred growth direction in the α-Al_2O_3 during deposition the grain-boundary distribution and morphology can be modified and controlled.

In this paper experimental α-Al_2O_3 coatings with different grain boundary structures and textures will be presented and discussed. The experimental α-Al_2O_3 were deposited on Ti(C,N) coated cemented carbide inserts to identical thickness for comparative cutting tests. In addition to the cutting tests, the coatings were analyzed in detail by using SEM, TEM, XRD and EBSD.

11:40am **B2-12 Growth Mechanism of Amorphous Phase Mixed α-Al2O3 Hard Coatings**, ***S. Tatsuoka*** *(shotatsu@mmc.co.jp), K. Sato, N. Iwasaki, K. Yamaguchi, A. Osada*, Mitsubishi Materials Corporation, Japan

Chemical Vapor Deposition (CVD) method has been used for the industrial production of wear resistant coatings on cutting tools and Al_2O_3 coatings have been widely used to maintain high hardness and excellent oxidation resistance under such a severe cutting condition. It is well known that Al_2O_3 exhibits a number of crystalline polymorphs, such as α, κ, δ, θ, etc. However, there are few reports on crystalline-amorphous phase mixed Al_2O_3 thin films as wear resistant coatings.

In this work, we investigated growth mechanism of amorphous phase mixed α-Al_2O_3 thin films deposited using gas mixtures of trimethylaluminium, as aluminum precursor, O_2, and Ar instead of conventional gas mixtures, such as $AlCl_3$, CO_2, and H_2. The deposited Al_2O_3 layer is composed with high aspect ratio columnar-like α-Al_2O_3 grains and the amorphous Al_2O_3. The amorphous phase mixed α-Al_2O_3 thin films were prepared with several interface layers to control orientation and morphology of the α-Al_2O_3 grains. The α-Al_2O_3 grains show anisotropic growth enhanced along a-axis and suppressed along c-axis depending on the prepared interface layers.

12:00pm **B2-13 Chemical Vapor Deposition of Epitaxial sp^2-Boron Nitride Thin Films**, *M. Chubarov (mihails.cubarovs@liu.se),* Linköping University, IFM, Thin Film Physics Division, Sweden, *H. Pedersen,* Linköping University, Sweden, *H. Högberg,* ***A. Henry***, Linköping University, IFM, Thin Film Physics Division, Sweden

Thin films of boron nitride in the sp^2-hybridized state (sp^2-BN) is promising material for electronic and optoelectronic devices to be operated at high temperatures and in chemically demanding environments. This is due to high thermal and chemical stability, a wide band gap (~ 6 eV), low dielectric constant and the possibility of both p- and n-type doping.

A further advantage for sp^2-BN is that the hexagonal basal plane exhibits the same structure as graphene, where the carbon atoms have been replaced by half nitrogen and half boron atoms. As a result the lattice mismatch between sp^2-BN and graphene is only 2%. The structural similarity to graphene suggests additional applications as a dielectric substrate and gate dielectric in graphene electronics.

Despite the promising properties, sp^2-BN is still the least investigated material among the III-nitrides, mainly due to limitations in depositing thin films with necessary quality.

In this study, we present results from growth of sp^2-BN films by Chemical Vapor Deposition (CVD) focusing on the quality of sp^2-BN films as a function of process temperature, precursor mixture as well as the effect of adding silicon during growth. .

The deposition of the films was conducted in a horizontal hot-wall CVD reactor using triethyl boron (TEB) and ammonia (NH_3) as boron and nitrogen precursors. As substrate 0001 oriented a-Al_2O_3, 0001 oriented hexagonal silicon carbide (SiC) and 111 oriented cubic SiC were used. We have previously shown that an AlN buffer layer is necessary for the growth of rhombohedral BN (r-BN) of good quality on a-Al_2O_3 [1]. Our recent results obtained on SiC substrates suggest opposite behavior, when AlN is *in-situ* deposited on SiC prior to the BN deposition, *i.e.* AlN buffer layer is not necessary but even makes it impossible to obtain high quality sp^2-BN on SiC. Our results show that successful deposition of epitaxial r-BN is confined to a narrow process parameters window: T = 1500 °C, nitrogen-to-boron ratio of 600-700, hydrogen as carrier gas at a process pressure of 70-100 mbar [2]. In addition, we found that presence of a few parts per million (ppm) of Si is needed for the epitaxial growth of r-BN on sapphire [3] and that it improves quality of the sp^2-BN on the SiC substrate.

[1] M. Chubarov, H. Pedersen, H. Högberg, V. Darakchieva, J. Jensen, Per O. Å. Persson, A. Henry,*Phys. Stat. Sol. RRL***5** (2011), 397

[2] M. Chubarov, H. Pedersen, H. Högberg, J. Jensen, A. Henry, *Cryst. Growth Des.***12** (2012), 3215

[3] M. Chubarov, H. Pedersen, H. Högberg, A. Henry, *CrystEngComm***15** (2013), 455

Hard Coatings and Vapor Deposition Technology
Room: Royal Palm 1-3 - Session B4-3

Properties and Characterization of Hard Coatings and Surfaces

Moderator: C. Mulligan, US Army ARDEC, Benet Laboratories, J. Lin, Southwest Research Institute, U. Beck, BAM Berlin

8:00am **B4-3-1 Ion Beam Induced Damages on Metastable Nitride Coatings**, ***E. Lewin*** *(erik.lewin@kemi.uu.se)*, Empa, Swiss Federal Laboratories for Material Science and Technology, Switzerland, *J. Patscheider*, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland

There is in the thin film and coating community a continuously growing interest in metastable phases and microstrucures, which are synthesised through low temperature deposition and are proposed for use in various fields of applications. A commonly used technique to analyse these coatings with regards to chemical composition and bonding is X-ray photoelectron spectroscopy (XPS) coupled with sputter etching using an ion gun to attain information below the outermost surface, which most commonly is oxidised. The use of sputter-etching may however affect the analysed material, which becomes more important to take into account as also metastable materials are studied.

We here present a study on AlN-based coatings, alloyed with Si, Ge or Sn, thus producing more or less metastable materials. These materials are hard multifunctional coatings with tuneable optical properties [1,2]. Through the use of in-situ UHV transfer of samples from the deposition chamber to the analysis instrument we can compare undamaged (and non-oxidised) surfaces with those resulting from sputter-etching to depth typically used in analysis of samples exposed to atmosphere. Our results show that standard XPS techniques can be used to analyse also metastable materials, but the utmost care must be taken, as extensive ion-beam induced damages are observed for some materials when ion Ar^+ ion energies of 1 keV or above are used to sputter-etch the samples prior to analysis. For the here studied materials, sensitivity to ion beam damage (for Ar^+ energies of 200 eV to 4k eV) is found to increase for the different alloying elments Si, to Ge to Sn; as well as with alloying content. Damages mainly manifest themselves as preferential nitrogen sputtering and subsequent metallisation of the alloying element. The observed trend agrees with the general nitrogen affinity of these elements.

These results are also relevant for other hard coating materials that include less stable nitride or carbide forming elements. Together with a previously published study on carbide materials [3], this underlines the importance of evaluating the possible presence of ion-beam induced damages, introduced during analysis when working with complex and (at least partly) metastable coating materials.

1. A. Pélisson, et al., **Surface and Coatings Technology** 202, 884 (2007)

2. E. Lewin, et al., **Journal of Materials Chemistry** 22, 16761 (2012)

3. E. Lewin et al., **Surface and Coatings Technology** 204, 455 (2009)

8:20am **B4-3-2 Residual Stress Gradients in α-Al_2O_3 Coatings Determined by Pencil X-ray Nanodiffraction: the Influence of Blasting Media**, ***M. Tkadletz*** *(michael.tkadletz@mcl.at)*, Materials Center Leoben Forschung GmbH, Austria, *J. Keckes, N. Schalk,* Montanuniversität Leoben, Austria, *C. Czettl*, CERATIZIT Austria GmbH, Austria, *C. Mitterer*, Montanuniversität Leoben, Austria

Post-deposition blasting treatments are widely used to introduce compressive residual stresses into CVD hard coatings, which usually exhibit tensile stresses after deposition on cemented carbide substrates. Within this work, α-Al_2O_3 coatings grown by thermally activated CVD on TiCN base-layers were dry-blasted using a globular as well as an edged blasting medium. The as-deposited and blasted samples were characterized using X-ray nanodiffraction in transmission geometry. Since the point focus nanodiffraction [1] did not provide sufficient diffraction, a pencil X-ray beam with a size of 10 µm x 200 nm was implemented. The beam was aligned parallel to the interface and the cross-sections of the samples were scanned in order to analyze depth gradients of strains, phases and microstructure with a resolution of 100 - 200 nm.

The results document that the maximum compressive stresses of ~4 GPa are much higher for the samples blasted with the edged medium compared to those blasted with the globular material, which showed maximum compressive stresses of ~2 GPa. The stress gradient obtained with the edged medium is steeper, while the affected zone of the sample blasted with the globular material reaches deeper into the coating. The results obtained from the synchrotron experiments are supplemented by laboratory XRD

experiments. In addition, the observed stress gradients could be corroborated by the particle impact using a contact mechanics approach.

[1] J. Keckes, M. Bartosik, R. Daniel, C. Mitterer, G. Maier, W. Ecker, J. Vila-Comamala, C. David, S. Schoeder, M. Burghammer, X-ray nanodiffraction reveals strain and microstructure evolution in nanocrystalline thin films, Scripta Mater. 67 748 (2012).

8:40am **B4-3-3 Investigation on Interfacial Adhesion of Ti-6Al-4V/Nitride Coatings**, ***L. Jin***, *A.R. Riahi (ariahi@uwindsor.ca), K. Farokhzadeh, A. Edrisy*, University of Windsor, Canada

Adhesion tendency of Ti-6Al-4V titanium alloys to three different types of coatings namely TiN, ZrN, and TiAlN was investigated after one pass sliding of a coated ball on a Ti-6Al-4V disc at 3N load, and sliding distance of 0.01m. The same testing conditions were performed for uncoated AISI 52100 steel balls for comparison purpose. After each test the sliding surfaces of the coated balls and the titanium discs were investigated using analytical microscopy techniques e.g. scanning and transmission electron microscopy (SEM, TEM), and energy dispersive spectroscopy (EDS). Microstructural analysis revealed that titanium adhered to the contact surfaces at the early stages, which, attributed as the main reason for an increase in the friction force. The microstructural investigations from cross sections of the transferred material to the ball surfaces obtained by focused ion beam milling showed a solid interface between the transferred Ti-6Al-4V and the coatings/uncoated steel ball. Transmission electron microscopy analysis and corresponding electron diffraction patterns revealed an embedded nanocrystalline structure for transferred Ti-6Al-4V close to the interface with the steel ball. Electron energy loss spectroscopy (EELS) mapping also displayed titanium oxides that were distributed in between the layers of transferred Ti-6Al-4V. These observations were used to determine the mechanisms of adhesion of Ti-6Al-4V to steel and nitride coatings.

9:00am **B4-3-4 High Resolution Electron Microscopy Structure Determination of the Metastable Cubic SiNx Phase**, *A. Fallqvist, L. Hultman,* ***P. Persson*** *(perpe@ifm.liu.se)*, Linköping University, IFM, Thin Film Physics Division, Sweden

The TiN-SiN_x system is subject to intense research, mainly as a model system for superhard nanocomposite materials.[1] Although the elements are commonly deposited together, the TiN-SiN_x nanocomposite formation is a consequence of phase separation of the immiscible components. Many similar composites are investigated for such applications and exhibit transition metal carbide, nitride or boride crystallites embedded in a thin, 1-2 monolayer(s), matrix of a covalent material.[2] As a consequence of the small dimensions, dislocation glide is prevented while also the thin matrix prevents grain boundary sliding due to its high cohesive strength.[3] While the structure of the crystallites is well known, e.g. B1 (NaCl) TiN in the TiN-SiN_x system, the structure of the TiN-SiN_x interface and the intergranular SiN_x matrix has been debated for some time. The spatially constrained dimensions makes it challenging to just "look at it and see".[4] Partially to limit the complexity, but also to investigate the hardening mechanisms a number of studies have reported successful growth of transition metal nitride-SiN_x multilayers and that these ML also exhibited increased hardness for thin SiN_x layers.[5,6] Depending on thickness of the SiN_x layer, the ML structure can be grown epitaxially, indicating a crystalline nature of the SiN_x. Constituting an epitaxial nature, these multilayers are the key towards understanding the nanocomposite TiN to SiN_x interface. Through the significance of the TiN-SiN_x (001) interface, it's nature has been subject to theoretical studies.[7,8] In contrast, few results have been published by high resolution electron microscopy methods.

In this contribution, the structure of a 13 Å thick SiN_x layer, epitaxially stabilized on TiN(001), is determined by atomically resolved scanning transmission electron microscopy ((S)TEM), annular bright field (ABF)-(S)TEM and spatially resolved electron energy loss spectroscopy (EELS) of the nitrogen (N-K) near edge fine structure (ELNES) in combination with full potential calculations and image simulations.

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9:20am **B4-3-5 Phosphorus Content Effect on the Chemical Reaction and Mechanical Properties of the Sn/Ni-*x*P Metallurgical System**, *C.E. Ho (ceho1975@hotmail.com),* ***C.W. Fan***, *C.H. Yang, L.H. Hsu*, Yuan-Ze University, Taiwan

The Ni(P) films are superior con-tenders for corrosion and wear resistant coatings. Deposition of Ni(P) via electroless plating might possess a P content ranging from 2 at.% and 20 at.%. Electroless Ni(P) deposit is crystalline at low P contents (< 9.5 at.%), while at high P levels (> 9.5 at.%), the deposit is amorphous. It has been shown that the P content in the electroless Ni greatly influences the interfacial reactions with solders and the solder joint characteristic must also be closely related to the P content. Thus, the P content effect on the solderability of the Ni(P) film must be investigated as far as microelectronic packaging reliability is concerned.

In the present study, the chemical reaction and mechanical properties of the Sn-3Ag-0.5Cu/Au/Ni(P)/Cu joint system were investigated using a field-emission electron probe microanalyzer (FE-EPMA), field-emission scanning electron microscope (FE-SEM) equipped with an electron backscatter diffraction (EBSD) analysis system, and high-speed ball shear (HSBS) test machine. The P contents (*x*) in the Ni(P) films were 6 wt.% (10.8 at.%), 8 wt.% (14.1 at.%), and 10 wt.% (17.4 at.%), respectively, and all of them possessed a typically amorphous Ni(P) structure, as reflected its high P content in the Ni matrix.

After reaction at 250 ^{o}C for 2 min, the surface layer of Au was eliminated from the Sn/Ni(P) interface, where three distinct intermetallic species, including Ni_3Sn_4, Ni_2SnP, and Ni_3P, formed. The morphology/thickness of the intermetallics strongly depended on the P content in the Ni(P) films, especially for the former (i.e., Ni_3Sn_4). As the P content was low (6 wt.%), Ni_3Sn_4 displayed a layered structure with a facet-type morphology over the Ni_2SnP/Ni_3P structure. With increasing the P content to 10 wt.%, the phase (Ni_3Sn_4) nearly disappeared from the interface by spalling itself into the Sn matrix and the Ni_2SnP became dominant intermetallic species grew at the interface. These P-dependent reactions were dictated by thermodynamics and can be rationalized using the Ni-Sn-P isotherm. The HSBS testing showed that the microstructural change arising from various P contents in the Ni(P) films significantly affected the mechanical properties of solder joints. These findings revealed that the P content is a very important factor of solderability. Detailed descriptions regarding the P effects on the above issues, i.e., chemical reaction and the mechanical properties, were addressed in this study.

9:40am **B4-3-6 Mechanical Property Characterization of Coatings and Surfaces within the Nano- and Micro-Scale**, ***T. Chudoba*** *(t.chudoba@asmec.de)*, ASMEC Advanced Surface Mechanics GmbH, Germany **INVITED**

The field of industrial applications of coatings is steadily increasing and more and more coatings are used in applications where their mechanical strength comes to a limit. Apart from their primary properties for the intended use (optical, electrical, chemical, biological) also mechanical properties have to be considered and tested to guarantee the lifetime of the components. The preferred mechanical measurement technique for thin coatings is nanoindentation. It is an established and precise technique with high local resolution and provides typically hardness and modulus of the uppermost layer. However there are more mechanical properties responsible for lifetime and wear behaviour like adhesion, internal stresses, tensile strength, Poisson's ratio, fatigue behaviour, friction against a certain counterpart, roughness and defect density of all layers and the substrate in a multilayer. Therefore only a combination of several measurement techniques can deliver a more comprehensive view of the mechanical properties of coatings. Additionally several of these techniques can be used to investigate the mechanical behaviour of bulk materials in small volumes (grains, pillars, micro beams) which can be different from that of large samples.

The talk will give an overview of the state of the art of different mechanical characterization methods for coatings. It will mainly focus on nanoindentation in combination with the measurement of lateral force-displacement curves. Additionally other methods like ultrasonic surface waves, centrifuge test, scratch test or atomic force acoustic microscopy are mentioned and compared. Further it will be shown that it may be very helpful to combine tests with advanced stress calculations to extract more mechanical properties and to come from a more qualitative comparison of coatings to a quantitative comparison which allows an optimization of coated systems.

10:20am **B4-3-8 Growth of 3C-SiC Films on Si Substrates by Vapor-Liquid-Solid Tri-phase Epitaxy**, ***H.Y. Lee***, *Y.L. Liang, J.L. Huang, X.D. Qi (xqi045@mail.ncku.edu.tw)*, National Cheng Kung University, Taiwan

Epitaxial 3C-SiC films were deposited on Si substrates by the vapor-liquid-solid (VLS) tri-phase growth method. We show that such a technique was able to overcome some drawbacks encountered in the epitaxial growth of

3C-SiC films by sole physical or chemical vapor deposition methods. In the VLS method a metallic thin layer, which was evaporated on the Si substrate prior to the growth, was melted at high temperature as the flux and then, methane gas (carbon source) was diffused into the liquid layer to react with Si, leading to the epitaxial growth of 3C-SiC on the substrate surface. The VLS-grown films were characterized by a wide range of techniques including high-precision X-ray diffraction, energy dispersive X-ray spectroscopy, X-ray photoelectron spectroscopy, scanning electron microscopy, and transmission electron microscopy. We will report on the effects of the growth parameters, such as flux thickness, substrate temperature, methane flow rate, etc., on the microstructures of the grown films, as well as the growth mechanisms of the VLS process.

Keywords: SiC, thin film, epitaxy

10:40am **B4-3-9 Effect of Zwitterioinic Surfactants on the Coating Efficiency and Properties of Electroless Ni-P Coatings**, ***M. Rajaraman*** *(muralimechraja@gmail.com)*, *E. Rasu*, Pondicherry Engineering College, India, *T. Balaji*, M. Tech, SRM University, India

The major drawback in electroless coating is high cost because the coating efficiency and nickel recovery efficiency are considerably low. It reflects in cost of the final product. Surfactant (Surface active agent) is an additive to reduce the surface tension into the electrolyte bath. There are 4 types of surfactant anionic, cationic, zwitterionic, Nonionic. However no researchers were concentrated in zwitterionic surfactant in electroless coating process. Zwitterionic (amphoteric) surfactant consists of two charges (positive and negative) in its head group called hydrophilic and negative charge in its tail group called hydrophobic. Influence of both positive and negative (hydrophilic effect) charged particles in head group shows effective changes in electroless coating process. The problem occurs during coating is that the H2 bubbles floats as the reaction starts, while floating the H2 bubbles carries the Ni particles along with it and as the H2 bubbles bursts the Ni particles become turbulent and coat other than the substrate. Role of surfactant is to reduce the surface tension energy in the EN bath and clears the interfacial bonding energy between Ni particles. Coating was carried out on mild steel specimens. Coating was done for two hours and volume of bath was fixed as 200ml. Nickel chloride, sodium hypophosphite, ammonium chloride and tri sodium citrate were used as source of nickel, reducing agent, complexing agent and stabilizer respectively. The coating parameter pH was maintained at 8-9.The effect of surfactants on the surface roughness, hardness and microstructure of electroless nickel – phosphorus (ENi-P) surface protective coating obtained from an alkaline bath and its mechanism is presented in this paper. In this study the influence of zwitterioinic surfactant 3-(n,n-dimethylmyristylammonio)propanesulfonate on the surface roughness, hardness and microstructure of electroless Ni–P coated samples has been investigated. The variation on surface morphology was examined using scanning electron microscope (SEM), surface roughness values were measured using a stylus instrument and surface hardness values were measured using a hardness tester. It was observed that t he surface roughness, surface hardness and surface morphology of Ni-P coating were clearly influenced by the addition of zwitterioinic surfactant. The complete experimental details, results obtained and their analysis are presented in this paper.

Keywords: electroless coating, zwitterionic surfactant, coating efficiency, surface roughness, surface hardness and surface morphology

11:00am **B4-3-10 High-resolution Transmission Electron Microscopy of Hard Zr-B-C-N Films**, ***M. Zhang***, *J. Jiang*, *P. Kroll*, University of Texas at Arlington, US, *J. Vlcek*, *P. Steidl*, *J. Kohout*, *R. Cerstvy*, University of West Bohemia, Czech Republic, *E. Meletis (meletis@uta.edu)*, University of Texas at Arlington, US

Nanostructured multifunctional Zr-B-C-N films with high-temperature oxidation resistance and stability have attracted great attention due to the potential applications in coating technology and high-temperature industry. In the present work, nanocomposite Zr-B-C-N films were deposited onto Si substrates using pulsed magnetron co-sputtering of a single B4C-Zr target (45% Zr fraction in the target erosion area) in four different nitrogen-argon gas mixtures with the nitrogen fraction of 0%, 5%, 10% and 15%. High-quality defect-free films (thickness range from 4.0 to 4.2 μm) with smooth surfaces (the average roughness Ra ≤ 4 nm) and good adhesion to substrates were produced. The chemical information, microstructures and mechanical properties of the Zr-B-C-N films were studied using X-ray photoelectron spectroscopy, X-ray diffraction, cross-section and plan-view high resolution transmission electron microscopy and nano-indentation. The film with a composition of Zr41B30C8N20 (in at.% without 1 at.% of hydrogen) deposited in the 5%N2+95%Ar gas mixture exhibits a high hardness of 37 GPa and high oxidation resistance in air up to 550°C. Structure simulations using density-functional methods show rapid formation of distinct geometric fragments in Zr41B30C8N20 at the nano-scale. 6-membered B-rings capped by Zr resemble ZrB2, while Zr atoms form closest packed arrangements with interstitial C and N atoms resembling ZrC and ZrN. The effects of the atomic structure on the hardness of the Zr-B-C-N films are discussed. This work is supported by the National Science Foundation under Award NSF/CMMI DMREF- 1335502.

11:20am **B4-3-11 Enhancement of Scratch Resistance and Hydrophobicity on Polycarbonate via a Multifunctional Hybrid O/I Coating**, ***N. Le Bail***, Ecole Centrale de Lyon, France, *B. Toury (berangere.toury-pierre@univ-lyon1.fr)*, Université Claude Bernard Lyon 1, France

The polycarbonate is a widespread polymer material, highly appreciated for its low density, its transparency and its good mechanical properties. This material is used for divert applications (automotive, medical, optical...) and is very competitive in terms of quality and prices. However, it displays some weaknesses, essentially due to its poor abrasion and scratch resistance and its possible degradation under UV or hydrolysis, releasing the Bisphenol A molecule known as an endocrine disruptor. Therefore, the paper "Le Monde" announces on December the 13th, 2012 that : "a measurement of Bisphenol A interdiction on food packaging will be applied on July the 1st, 2015".

In this context, I started my Ph-D with the aim to design and develop a new hybrid O/I protective coating with silica and zirconia prepared by the sol gel process, which allow a cure compatible with the polycarbonate's glass transition (145°C). In this presentation, I propose to describe the solutions retained to obtain a scratch resistant, hydrophobic transparent coating, with good adhesion properties. In a first part, my presentation demonstrates the influence of synthesis parameters (organo-silane nature, pH, T°...) on the final functional coating properties characterized among others by infrared spectroscopy and energy-dispersive x-ray spectroscopy. It also defines the best conditions and the most performing process to obtain a homogenous coating with controlled thickness. In a second part, it presents the result of the scratch resistance of the thin film with scratch test and nano-indentation. Finally, film adhesion on polycarbonate is discussed by demonstrating the beneficial effect of an atmospheric plasma treatment.

Advanced Materials for Modern Device Applications
Room: Sunset - Session C5-2

Thin Films for Active Devices
Moderator: F. Tasnadi, Linköping University

8:00am **C5-2-1 Characteristics of PECVD SiO_xN_{1-x} for Resistive Memory Application**, ***F. Zhou*** *(essenonvidare@gmail.com)*, *YF. Chang*, University of Texas at at Austin, US, *B. Fowler*, Privatran LLC, US, *J.C. Lee*, University of Texas at at Austin, US

Resistive switching materials have been intensively studied for nonvolatile memory applications. Among them, SiO_2 stands out and is well studied due to ready availability of the material and minimum infrastructure modification. In this work we characterized the PECVD SiO_xN_{1-x} based resistive devices and discuss the important role of oxygen and oxygen vacancies in device performance.

Resistive Memory devices were fabricated on N^{++} Si prime wafer cleaned with BOE for 1min to remove native oxide. A 50nm SiO_xN_{1-x} layer was PECVD deposited at 300C using NH_3, N_2O, and SiH_4 as reactive species. Refractive index of SiO_xN_{1-x} layer was measured using ellipsometry immediately after deposition. Using the SOPRA database for PECVD SiO_xN_{1-x}, the oxygen concentration x was determined. Different recipes with varying gas flow rate were used to achieve 5 different oxygen concentrations (10%, 32%, 49%, 66%, 80%) in the SiO_xN_{1-x}. Then 200nm tantalum nitride was deposited by sputtering followed by lithography and CF_4-based dry etch to define the top electrodes. After removing photoresist, all samples were wet etched in BOE for 3min to remove SiO_xN_{1-x} from field regions.

Devices were then tested in vacuum using substrate as ground and top electrode to apply bias. Ten devices with each oxygen concentration condition were measured and device yield was determined. It was found that device yield increases with increasing oxygen concentration. And HRS and LRS current level measured at 1V, set voltage and reset voltage were all extracted from DC IV data of each working device. Their respective cumulative distribution shows that devices with more oxygen have a steeper slope in HRS state, indicating a tighter distribution and better device stability; whereas for LRS state such trend is not clear. For set and reset voltage, all devices have a minimum of 0.5V variation due to its random nature of filamentary switching. $SiO_{10}N_{90}$ devices have the largest variation, up to 2V, showing the worst device stability.

Electron Spin Resonance (ESR) study on E' center has shown that nitridation of SiO_xN_{1-x} would lower oxygen vacancy concentration in the

film. Those works were used to explain our result that devices with higher oxygen concentration have higher oxygen vacancy concentration and more robust conductive filament, which results in better endurance characteristics and improved stability.

In conclusion, we demonstrated the switching behavior of PECVD SiO_xN_{1-x} resistive memory device, and show the impact of oxygen atom concentration in SiO_xN_{1-x} on device performance. The result suggests that reversible switching phenomenon may arise from the oxygen in $SiO_xN_{1-x.}$

8:20am **C5-2-2 Investigation of Temperature-Dependent Asymmetric Degradation Behavior Induced by Hot Carrier Effect in Oxygen Ambiance in In-Ga-Zn-O Thin Film Transistor**, ***B.W. Chen***, *T.C. Chang (tcchang@mail.phys.nsysu.edu.tw)*, National Sun Yat-Sen University, Taiwan

The effects of oxygen ambiance on electrical characteristic degradation phenomena in a-InGaZnO thin film transistor with different biases and temperatures are investigated. It can be found that oxygen is substantially adsorbed on the backchannel and results in device instabilities during positive gate bias stress. However, visible light irradiation is found to desorb the adsorbed oxygen ions and this verifies that oxygen dominates the degradation behavior. Moreover, comparing with that in vacuum, hot-carrier stress in oxygen ambiance leads to an extra potential barrier height near the drain side due to oxygen adsorption and causes asymmetric degradation. Furthermore, the asymmetric degradation behavior after hot-carrier stress in oxygen ambiance is suppressed at high temperature due to temperature-induced oxygen desorption.

8:40am **C5-2-3 Investigating Characteristics and Reliabilities of Dual Gate a-InGaZnO Thin Film Transistor with an Etch Stop Layer**, ***P.Y. Liao***, *T.C. Chang (tcchang@mail.phys.nsysu.edu.tw)*, National Sun Yat-Sen University, Taiwan

Dual gate amorphous-InGaZnO thin-film transistors (TFTs) with a bottom-gate that covers the whole channel and a top-gate that covers only a portion of the channel are investigated. The degree of degradation between top- and bottom-gate structured amorphous InGaZnO TFT is compared with each other. Under hot-carrier stress (HCS), the degradation of dual gate TFT is more significant than that of bottom-gate. This HCS-induced degradation phenomenon is dominated by electron-trapping in the etch stop layer (ESL). In addition, under negative gate bias illumination stress (NBIS), the threshold voltage of bottom-gate TFT monotonically shifts in the negative direction, whereas top-gate TFT exhibits on-state current increases without V_T shift. Such anomalous degradation behavior under top-gate NBIS is due to hole-trapping in the ESL above the central portion of channel. These phenomena can be ascribed to the screening of electric field by redundant source/drain electrodes.

9:00am **C5-2-4 Wide Band-gap $CuInAlS_2$ Thin Film and Its Application to UV Detectors**, ***D.C. Perng*** *(dcperng@ee.ncku.edu.tw)*, National Cheng Kung University, Taiwan, *T.T. Kao*, National Kaohsiung First University of Science and Technology, Taiwan, *R.P. Chang*, National Cheng Kung University, Taiwan

The $Cu(InAl)S_2$(CIAS)thin films, direct and band-gap adjustable chalcopyrite materials, have attracted much interest in recent years for optoelectronic, photovoltaic as well as bio-imaging applications. The widest band-gap $CuAlS_2$ film has potential to be used for building blue and green light emitting devices. Most of the previous researches were focus on material synthesis and/or characterizations. In this paper, we propose a novel approach to form a good quality wide band-gap CIASfilm and present its application to ultraviolet (UV) photodetector (PD).

Silicon wafer with 100nm-thick SiO_2 film was used as substrate. A 400nm-thick Mo film was deposited on top of the SiO_2 film followed by co-sputter deposition of 500nm-thick Cu/In/Al metallic precursors (Small amount of In was added to minor adjust the band-gap). The Mo film was used to avoid any reaction of Cu, In or Al with the substrate during the subsequent high temperature process and also serve as an electrode when the device is fabricated.

Sulfurization of Cu/In/Al precursors directly to form wide band-gap CIAS film usually leads to a small grain-sized film with minor cracks. XRD results indicate that many Cu-S phases exist when the sulfurization temperature was lower than 700^{o}C. A rapid thermal annealing process was adopted to anneal the Cu/In/Al precursors at 600^{o}C for one hour to form a single phased Cu_9Al_4 compound. Good quality CIAS film can be successfully formed by sulfurizing the Cu_9Al_4 film at 700^{o}C for 100 min. The XRD patterns show that the post-sulfurized film is a single-phased CIAS film with (112)-preferred orientation, the medium grain size is approximately 400-500 nm and no cracks was found under scanning electron microscopy observation.

$CuIn_{1-x}Al_xS_2$ samples with x >0.85 were prepared to fabricate UV PDs. Two sensing schemes, metal-semiconductor-metal (MSM) and ZnS/CIAS pn junction, were tested for the PDs. The 5-μm finger spacing MSM scheme obtained a 12x magnification in photocurrent with UV illumination. The photo response data suggests that the UV PDs have cut-off frequency near 380 nm. However, there is a clear 423nm peak under photoluminescence measurement. The luminescence peak shifted to a longer wavelength is related to the defect structure of the CIAS film. The UV testing using pn junction scheme is more sensitive than MSM when the grain size of the film is small. Wide band-gap CIAS film is a good candidate as a UV sensing material.

9:20am **C5-2-5 Room Temperature Acetone Sensing of Sulfonated Copper Phthalocyanine (TsCuPc) Modified ZnO Films**, ***A. Bal*** *(amandeep27@rediffmail.com)*, Amritsar College of Engineering and Technology, India, *M. Kahlon*, DAV Institute of Engineering and Technology, India

Sulfonated copper phthalocyanine (TsCuPc) surface modified Zinc Oxide (ZnO) films were fabricated and structural as well as room temperature acetone sensing characteristics were investigated. Based on X-ray diffraction results it was observed that modification of pure ZnO by TsCuPc precursor enhanced the c-axis orientation of pure ZnO films. Field emission scanning electron micrographs of pure and surface modified ZnO film indicated dendrites and agglomerated grains respectively. The electrical resistance measurements of modified ZnO films also show increase in resistance as compared to pure ZnO film. It has been demonstrated that these films were more sensitive to acetone compared to pure ZnO film. The response for 50 ppm acetone reached to -162% for ZnO film modified by 1 M of TsCuPc. Negative value of response was attributed to p type character incorporated in ZnO film by p type TsCuPc. However, for concentrations >100 ppm, the response was saturated.

9:40am **C5-2-6 Influence of Supercritical CO_2 Fluid Treatment on Resistive Switching Behaviors of Ti-doped SiO_2 Thin Film**, ***T.M. Tsai***, *K.C. Chang, T.C. Chang (tcchang@mail.phys.nsysu.edu.tw), G.R. Liu, J.P. Jiang*, National Sun Yat-Sen University, Taiwan, *S.M. Sze*, National Chiao Tung University, Taiwan

In this work, the Ti-doped SiO2 (Ti:SiO_2) thin film was treated by supercritical carbon dioxide ($SCCO_2$) fluid mixed with pure water. After $SCCO_2$ fluid treatment, the resistive switching qualities of the Ti:SiO_2 thin films are carried out by x-ray photoelectron spectroscopy (XPS), fourier transform infrared spectroscopy (FTIR), and current-voltage (IV) measurement. The fitting results of IV curve indicated that the carrier conduction mechanism at a high resistive state transfer from Poole-Frenkel emission to Hopping conduction mechanism. Furthermore, the carrier transfer mechanism at a low resistive state changes from Ohmic's conduction to Hopping conduction. Based on the electrical analysis, a molecular reaction model is proposed to explain the resistive switching behaviors of Ti-doped SiO_2 thin film with $SCCO_2$ fluid treatment, verified by material analyses of XPS and FTIR.

10:00am **C5-2-7 Surface Decoration using Pd Nanoislands for YBCO Superconducting Thin Film using Pulsed Laser Deposition**, ***M. Ertugrul*** *(ertugrul@atauni.edu.tr), D. Tatar, E. Sonmez, M.T. Yurtcan*, Ataturk University, Turkey

Due to their outstanding features, superconductors give the opportunity to develop technology available in many areas and to improve the performance of the devices. Superconducting materials are used in many fields particularly in industry, transport, electronics, generation and storage of electricity and transport of electrical current. They are used in industry in the construction of powerful superconducting magnet and superconducting motor and transformer, in transportation, in levitation trains and superconducting motor boats, and in electronics, in the construction of the SQUID, superconducting transistors, particle accelerators, microchips, sensors, detectors, resonators and filters. Rapid developments in the field of electronics make it necessary to increase performances of electronic devices. Because of features such as high speed, low loss, and high resolution, superconductors are preferred in electronics more than the conventional devices. However, studies on superconducting devices have not been completed yet and the physics behind these devices has not been fully understood.

Micro-wave resonator improved in terms of quality and performance is used in many areas such as aerospace, communication, television technology, radar, medicine, industry and military. While superconducting devices are made of low-temperature super-conductors such as Nb and NbSn3, high-temperature superconductors are preferred in recent years because of their working capacity at liquid nitrogen temperature and their high critical current and field values. Among high-temperature superconductors, YBCO stands out for microwave applications.

Pd nano-dots have been formed on the substrates and, in YBCO, non-superconducting BZO nano-columns have been formed spontaneously on these nano-dots. These nano-columns in YBCO strip act as artificial pinning center. On the studies of use of the Pd to form nano-columns in YBCO, we have shown that artificial pinning centers significantly enhance the performance of the superconducting strip in magnetic field.

10:20am **C5-2-8 Abnormal Temperature-dependent Floating-body Effect on Hot-carrier Degradation in PDSOI n-MOSFET**, ***K.J. Liu***, *T.C. Chang (tcchang@mail.phys.nsysu.edu.tw)*, National Sun Yat-Sen University, Taiwan

This letter investigates the abnormal degradation behavior after hot-carrier stress (HCS) in partially depleted silicon-on-insulator n-channel metal–oxide–semiconductor field effect transistors. HCS (Ib,max) shows that the floating-body (FB) device degrades more than body-contact (BC) device at room temperature. However, the degree of degradation has no significant difference between BC and FB devices at high temperature. Furthermore, unlike the degraded drain current measured by conventional characterization method after HCS, ultra-fast measurement shows that transient rising drain current becomes unobvious at elevated stress temperature on FB device. This behavior can be attributed to faster recombination rate of accumulated holes at the body at high temperature. Hence, the floating body effect is obviously reduced at high temperature.

10:40am **C5-2-9 Anomalous V_t Shifts after PBTI Stress by Fast I-V Measurement in Input/Output High-k/Metal Gate Stack**, ***S.H. Ho***, National Chiao Tung University, Taiwan, *T.C. Chang (tcchang@mail.phys.nsysu.edu.tw)*, National Sun Yat-Sen University, Taiwan

This letter investigates anomalous V_t shifts after PBTI stress by fast I-V measurement in Input/output high-k/metal gate stack. With fast I-V measurement, it shows that V_t shift in negative direction after PBTI. In addition, gate current is insignificant under initial. Hence, this phenomenon indicates that electrons discharge from high-k bulk traps to metal rather than that charge to high-k bulk traps from channel. Through a change in high level and low voltages by double sweep fast I-V measurement, it indicates that ΔV_t increases with a rise in high level voltage and a decrease in low level voltage. Furthermore, in comparison of SiO2, high-k/1nm and high-k/3nm devices in double sweep fast I-V measurement, it evidences that anomalous V_t shift after PBTI due to electrons discharging from pre-existing high-k bulk traps.

11:00am **C5-2-10 Investigation of Carrier Transport Behavior in Amorphous In-Ga-Zn-O Thin Film Transistors**, ***T.Y. Hsieh***, *T.C. Chang (tcchang@mail.phys.nsysu.edu.tw), P.Y. Liao*, National Sun Yat-Sen University, Taiwan

Behaviors of carrier transport in amorphous In-Ga-Zn-O thin film transistor are investigated. It is found that the electron mobility is higher at elevated temperature, which is contrary to that in crystalline Si devices. Drain current enhancement with regard to temperature at corresponding gate voltage follows Arrhenius equation. This implies that carrier transport is limited by the potential barrier heights induced by trap states within In-Ga-Zn-O, and therefore current conduction is heat-activated to overcome those barriers. In addition, the extracted activation energy decreases with increasing gate voltage, indicating the effective potential barrier height is lowered when abundant electrons are injected into the channel. Furthermore, the relationship between carrier mobility and carrier concentration is also investigated, with the carrier mobility monotonically increasing with carrier concentration. Such behavior can be ascribed to lowered effective barrier above conduction band when the Fermi-level rises.

Tribology & Mechanical Behavior of Coatings and Engineered Surfaces
Room: California - Session E3-1

Tribology of Coatings for Automotive and Aerospace Applications

Moderator: S. Dixit, Plasma Technology Inc., A. Gies, Oerlikon Balzers Coating AG, Liechtenstein, G. Doll, University of Akron

8:00am **E3-1-1 Boundary Lubrication of W-DLC Coatings – from Laboratory to Real Engine**, ***T. Polcar*** *(T.Polcar@soton.ac.uk)*, University of Southampton, UK, *M. Evaristo*, SEG-CEMUC, University of Coimbra, Portugal, *P. Mutafov*, Czech Technical University in Prague, Czech Republic, *A. Cavaleiro*, SEG-CEMUC, University of Coimbra, Portugal

The increasing demand for more energy efficiency and environmental friendly products leads to more severe conditions to which the surfaces are subjected. Carbon-based coatings with excellent wear resistance are regularly used in lubricated sliding conditions to protect bulk materials in combustion engines. However, the chemical interaction of the coating surface with oil additives is often limited, which results in relatively high friction. To decrease friction, particularly in boundary lubrication, is still an engineering challenge. In this study we summarize our recent work on tribological behaviour of various tungsten doped DLCcoatings in lubricated conditions.

C-based coatings with different W and H content (W-DLC/H) were deposited by DC magnetron sputtering in reactive and non-reactive atmospheres. All deposited coatings have compact morphologies with amorphous or nanocrystalline structures with tungsten carbide nanograins embedded into amorphous carbon matrix. The tungsten content was in range 2-20 at.%, hydrogen content 0-36 at.%. Pure DLC coatings, both hydrogenated and non-hydrogenated, were deposited as reference. The hardness of the coating increased from 10 to 15 GPa with increasing W content. The coatings were tribologically tested in lubricated contact using pin-on-disc with base (PAO), modified (different amount of additives) and fully formulated oils. Selected coating was then applied on valve lifters and tested in real combustion engine. The coated surfaces almost did not show any wear mark, which was in contract with scratched non-coated steel lifters. Raman spectroscopy, HR-TEM and TOF-SIMS was used to identify coating structure, sp2 /sp3 ratio, and particularly tribolayer formed on the coating surface. We can conclude that the surface of W-DLC/H coatings does react with oil additives and form very thin chemisorbed tribolayer with a thickness 2-4 nanometrs.

8:20am **E3-1-2 Catalytic Cracking of Lubricating Oils to Extract DLC Boundary Films at Sliding Interfaces**, ***A. Erdemir*** *(erdemir@anl.gov)*, *O.L. Eryilmaz*, Argonne National Laboratory, US

In this study, we report the formation of diamondlike carbon (DLC) boundary films on lubricated surfaces which contain catalytically active metallic species in a nanocomposite coating. These catalytically active nanocomposite coatings were produced on steel samples using magnetron sputtering. The hard phase or matrix of the coating was made of MoNx and/or VNx and constituted of at least 95% of the total coating, while catalytically active metals (such as Cu, Ag, Ni, etc.) accounted for 2 to 5%. When tested in pin-on-disk and block-on-ring test machines under severe boundary conditions under lubricated conditions, such films reduced friction by as much as 50% and the amount of wear on sliding surfaces was difficult to measure. UV Raman and a variety of other surface and structure analytical techniques used in our study confirmed the presence of a DLC-like boundary film on rubbing surfaces. Based on the results of these experimental and analytical studies, we will provide further insight into the structural and chemical nature of these boundary films and explain their fundamental lubrication mechanisms under severe operating conditions.

8:40am **E3-1-3 Lubricated Tribological Behavior of VN-Cu Coatings**, ***G. Ramirez*** *(jramirez@anl.gov)*, *O.L. Eryilmaz*, *A. Erdemir*, Argonne National Laboratory, US

VN-Cu composite coatings were prepared by using a reactive magnetron sputtering technique. A pure vanadium and copper target sputtered at different power levels to achieve different ratios of vanadium and copper in the film. Along with argon, nitrogen gas is used as a reactive gas during deposition. A High power impulse magnetron sputtering power supply is used to sputter Vanadium and for metal ion etching purposes to improve the adhesion of the composite coatings. The films are grown on 440C stainless steel flat and 3/8" diameter ball samples for tribological tests and Si wafer samples are coated for other coating characterization studies. XRD and XPS

techniques were used to characterize the coatings before and after tribological testings; also nanoindentation technique is used to determine the mechanical properties of the coatings. Using fully formulated 5W30 engine oil and pure poly-alpha olefin (PAO 4) oil, a series of tribological tests were run with a ball-on-disk and high-frequency reciprocating test machines under boundary lubricated test conditions and at temperatures up to 100 C. Test results revealed much reduced friction coefficients for the VN-Cu coated substrates and the amount of wear on both the substrate and ball side was hard to measure as opposed to very significant wear on uncoated surfaces. XPS is used to elucidate the friction and wear mechanisms of VN-Cu surfaces.

9:00am **E3-1-4 Composite Coatings with Ceramic Matrix Including Nanomaterials as Solid Lubricants for Oil Free Automotive Applications**, *A.. Posmyk, J. Myalski,* ***B. Hekner*** *(bartoszhekner@gmail.com)*, Silesian University of Technology, Poland

The analysis of tribological systems in machine parts shows that the greatest mechanical and thermal loads are applied to the surface layer (SL). Therefore, it is essential to form such a SL, which would carry any required loads. A homogeneous (bulk) SL on currently used engineering materials fails to carry such loads. Hence, composite coatings are the latest trend in machine parts production, with properties changing from those of the base material to those of an SL directly exposed to tribological loads. As the construction of the SL with changing properties is not possible to be obtained, the intermediate layers have to be made. They must be capable of accepting transfer of loads, absorbing vibration, extracting heat and, in particular cases, collecting impurities and wear debris. The role of the SL is to reduce friction and wear via formation of a permanent boundary lubricant layer. The role of SL is very important by automotive machine parts made of aluminum alloys possessing ability to adhesive taking with most engineering materials.

The producing technology principles and selected properties of composite coatings with ceramic matrix including nanomaterials as solid lubricants (glassy carbon nanotubes and metal nanowires) will be presented in proposed paper. The matrix of the coatings is the anodic oxide coating. Due to the porous structure of anodic oxide layer a synthesis of carbon nanotubes in the pores of oxide cells is possible. The synthesis has been conducted due to bringing of substance including carbon into the pores and its carbonization. Result of these is a composite coating including very hard, wear resistant oxide coating in that are regular distributed glassy carbon nanotubes which serve as grease reducing friction and wear. Such coating can be used in machinery's pairings acting under conditions in which using of lubricants is not allowed, for example in electronic and aerospace industry. The elaborated composite coating - short named AHC+GC - has been formed on machinery's part destined for oil free pairings. These investigated parts in form of disc have been made of aluminium alloy EN-AW-6061. As sliding partner has been chosen cast iron EN-GJL-350, used for piston rings manufacturing. The investigations have been carried out on tribological tester T11 in ambient temperature and air with relative humidity 60%. To have the possibility to evaluate the investigated layer the comparative investigations of anodic hard coating (AHC) without glassy carbon nanotubes have been carried out. Friction coefficient during sliding of cast iron against AHC+GC was lower than the one in pairing cast iron/AHC.

9:20am **E3-1-5 DLC Coating to Lower Friction Loss of Piston Rings in Internal Combustion Engines**, ***R. Lammers*** *(ralf.lammers@federalmogul.com), M. Kennedy, S. Hoppe*, Federal-Mogul Corporation, Germany

DLC coatings on piston rings offer a significant potential to reduce mechanical friction losses and therefore fuel consumption and CO_2 emissions of internal combustion engines, as piston rings contribute to 25% of friction loss. The challenge is to still master the thermo mechanical and tribological load conditions that piston rings must endure owing to smoother cylinder bores, reduced lubrication, and the use of alternative fuels. This is why the coating robustness described by wear resistance and scuff resistance plays an increasing role.

Federal-Mogul´s DuroGlide coating meets in an emerging way these demands. It is the first full DLC coating which can fulfill lifetime requirements even in high loaded Diesel engines. Due to the high amount of sp3-hybridized carbon (tetragonal structure) it can be applied with a layer hardness of up to 5000 HV0.2. In contrast to state of the art hydrogen-free DLC coatings, the intrinsic stress of DuroGlide is reduced during the coating process, which makes coating thicknesses of up to 25 microns with an excellent adhesion to cast iron or steel surfaces possible. A coating topography that is already close to the final design as well as optimized manufacturing processes result in very smooth piston ring surfaces.

Performance investigations started with Rig tests which were tailored to determine friction, wear and scuff resistance under overload conditions. Additionally, results out of a so-called floating liner single cylinder gasoline engine are presented with regards to friction losses in comparison to other coatings. Further, robustness studies out of engine tests with more than 500h running time are shown to confirm the lifetime capability of DuroGlide coated piston rings, applied in different engines and different piston grooves.

9:40am **E3-1-6 Improving Adhesion of Diamond Like Carbon (DLC) and its Tribological Properties**, ***D. Romagnoli*** *(romagnoli.denis@sts-group.it)*, STS srl, Italy

Carbon-based materials play an important role in science and technology today . Carbon is a very versatile element that can crystallize in the form of diamond and graphite. In recent years , there have been continuous and significant progress in the science of carbon, such as chemical vapor deposition of diamond , the discovery of fullerenes , carbon nanotubes and single-layer graphene . There have also been important developments in the field of disordered carbons . In general, an amorphous carbon system can be any mixture of sp^3 (diamond) and sp^2 (graphite) . The management of these fractions allows to enhance the hardness or contain the deleterious effects of friction generating different types of DLC.

The request for the application of DLC on engine components (pins , valves , camshafts) and mechanical parts in general is increasingly growing because it has been demonstrated how this coating is able to increase the surface hardness and reduce friction ; for the racing this means an improvement in the overall performance of the engine for the automotive improvement in yield resulting in the possibility to observe the dictates relating to emissions into the atmosphere.

The need to have a layer well bonded and tribological characteristics of hardness and friction coefficient is crucial to the performance of the component.

The deposition process under consideration is a hybrid technology PVD-PaCVD (physical vapor deposition and plasma - assisted chemical vapor deposition) . The preparatory stages of degassing and etching to enhance the adhesion of the coating to be evaluated with the aid of the scratch test and the test Mercedes . To improve the adhesion will be used several types of interlayers and act on the conditions of preparation dell'etching (gas flows and potential difference) .

The change in the conditions of deposition (reactive flows , applied potential difference , evaporation conditions) allows the optimization of the tribological properties of hardness and friction coefficient , respectively, with measurable nanoindenter and tribometers to contact. The change of the tribological characteristics will be related with the fraction sp2 - sp3 .

10:00am **E3-1-7 Few Layer Graphene: The Next Solid Lubricant?**, ***A. Sumant*** *(sumant@anl.gov), D. Berman,* Center for Nanoscale Materials, Argonne National Laboratory, US, *A. Erdemir*, Energy Systems Division, Argonne National Laboratory, US **INVITED**

Minimizing friction and wear-related mechanical failures remains as one of the greatest challenges in today's moving mechanical systems, and the search for new materials, coatings, and lubricants that can potentially avoid such failures continues around the globe. We demonstrate that few layer graphene not only helps in slowing down tribo-corrosion process but also drastically reduces wear (4 orders of magnitude) and friction (4-5 times) in the case of the most commonly used tribo-pairs, in particular, steel against steel sliding under 1 N load regardless of the surrounding environments (i.e., humid air or dry nitrogen) [1-2]. In addition, we show that graphene application as well as re-application does not require any additional processing steps other than just sprinkling a small amount of ethanol solution containing graphene flakes on the surface of interest making this process simple, cost effective, and environmental friendly. Most of all, unlike conventional solid lubricants which are all sensitive to environmental conditions, graphene offers the possibility of being effective regardless of the operating environment.

References:

[1] D. Berman, A. Erdemir, A.V. Sumant: "Few layer graphene to reduce wear and friction on sliding steel surfaces". Carbon, 54, 454-459 (2013)

[2] D. Berman, A. Erdemir, A.V. Sumant: "Reduced Wear and Friction Enabled by Graphene Layers on Sliding Steel Surfaces in Dry Nitrogen", Carbon, 59, 167-175 (2013)

10:40am **E3-1-9 Gold-Ceramic Nanocomposite Thin Films: The New Gold Standard**, ***N. Argibay*** *(nargiba@sandia.gov), R.S. Goeke, S.V. Prasad, C.C. Battaile, M.T. Dugger*, Sandia National Laboratories, US

More than two centuries after the first account of its use, electroplated gold alloy thin films remain an essential class of materials for engineers and tribologists designing electrical contacts for extreme environments, where low and consistent friction coefficients, wear, and electrical contact

resistance are typically all requirements. Modern advances and refinement in physical deposition techniques have enabled practical fabrication of multi-layer and graded thin film topologies better suited to mitigate the common failure modes exhibited by traditional electroplated metal films, such as through-film solid diffusion of underlayer and codeposited species to the contact surface. The use of zinc oxide in a gold matrix as a friction and wear modifier via dispersion strengthening (Au-ZnO nanocomposites), alumina diffusion barrier layers, and gold-alumina multilayer films, and their effect on tribological and electrical contact behavior will be discussed.

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11:00am **E3-1-10 Novel Nano-impact Techniques for Determining the Onset of Fracture in Brittle Films**, ***J.E. Mogonye***, *S.V. Prasad (svprasa@sandia.gov)*, Sandia National Laboratories, US

Pendulum based nanoindention platforms have been previously developed to perform multiple or rebounding single-impact tests at a single location. In the current study, we developed a single-impact test with microsecond temporal and nano-scale force and displacement resolution. The test was designed to isolate the sample surface from rebound impacts to allow for the quantification of plastic and total work during high strain rate impacts. The technique was applied to evaluate the performance of several diamond-like carbon (DLC) coatings and nanolaminate thin films under the impact loading conditions. The initial impact energy was incrementally increased until the onset of non-plastic permanent deformation (i.e., generating new surfaces) was obtained as determined by the change in restitution of kinetic energy in the pendulum. Dynamic hardness values, coefficients of restitution, and static hardness to modulus (H/E) ratios were calculated for each DLC and nanolaminate thin film. Resultant subsurface damage was visualized by scanning electron microscopy of focused ion beam prepared cross sections. The onset of non-plastic permanent deformation, i.e. fracture, and its relation to dynamic hardness and the H/E ratio in high strain rate impacts will be presented.

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New Horizons in Coatings and Thin Films
Room: Royal Palm 4-6 - Session F3

New Boron, Boride and Boron Nitride Based Coatings

Moderator: A. Inspektor, Kennametal Incorporated, A. Henry, Linköping University, IFM, Thin Film Physics Division

8:00am **F3-1 BN Nanotubes and Nanosheets and their Utilization for Structural and Medical Applications**, ***D.V. Shtansky*** *(shtansky@shs.misis.ru), A. Matveev, M. Kovalskii, I. Batenina, K. Faerstein, A. Steinman,* National University of Science and Technology "MISIS", Russian Federation, *D.M. Tang*, National Institute for Materials Science, (NIMS),Japan, *Y. Bando, M. Yamaguchi, D.V. Golberg*, National Institute for Materials Science, (NIMS), Japan **INVITED**

Boron nitride nanomaterials (nanoparticles, nanotubes, nanofibers, and nanosheets) represent an innovative class of materials with intriguing prospects of their utilization for structural and medical applications. Boron nitride nanomaterials (BNNs) have long been in a shadow of their famous rivals - carbon nanotubes (CNTs) and graphenes. While both nano-systems revealed equally excellent mechanical properties, boron nitride nanotubes (BNNTs) possess chemical and thermal stability superior to those of CNTs. The large throughput fabrication of BN nanotubes and nanosheets, which was successfully developed in a number of scientific laboratories over the last years, allowed us to initiate advanced studies focused on their exploitation for the reinforcement of lightweight metallic matrices. In this presentation, the most recent achievements in the high-temperature CVD synthesis of BNNs are summarized. The mechanical properties of individual BNNTs are described. Different approaches concerning the surface functionalization of BNNs to improve their wettability and control interfacial interactions at the nano-BN metal matrix interface are considered. Available data in regards of the nature of BNNs binding with a variety of functional groups are highlighted. Fabrication and characterization of different metal/BNNs composite materials are presented. Application of BNNs as lubricants is demonstrated. The latest data concerning biological interaction between BNNs and living systems are also analyzed. Particular attention is paid to the fabrication of BNNs-based mesoporous structures for the transportation of medical agents. The range of confirmed and expected mechanical and functional properties makes BNNs an unprecedentedly interesting topic for the modern structural materials science and biotechnology.

8:40am **F3-3 Effect of Boron Potential in the Mechanical Properties of the Borided Layers Obtained by Boron Diffusion at the Surface of AISI 316L Stainless Steel**, ***E. Hernández-Sánchez*** *(enhernandezs@ipn.mx), Y. Domínguez-Galicia,* Instituto Politecnico Nacional-UPIBI, Mexico, *J. Hernández-Sánchez,* Instituto Politecnico Nacional, *R. Carrera-Espinoza,* Instituto Politécnico Nacional-ESIME, Mexico, *C. Orozco-Álvarez,* Instituto Politécnico Nacional-UPIBI, México

The mechanical properties as well as the thickness of the borided layers obtained by boriding at the surface of the steel alloys are strongly related with three parameters: temperature of treatment, exposure time and boron potential.

In this study the effect of the boron potential in the thickness and in the mechanical properties of the borided layers was evaluated. The boron potential was established by means of the available atoms of boron, content in a control volume inside of a cylinder. The cylinders were manufactured of AISI 316L stainless steel and the boriding treatment was carried-out by using the powder pack technique at a temperature of 1273 K and 6 h of exposure. Four different internal diameters of the cylinders were evaluated (3.17, 4.76, 6.35 and 7.93 mm). The mechanical properties such as hardness, Young´s modulus and fracture toughness, were evaluated by the Berkovich instrumented indentation technic. The volume of the different diameters in the inner of the cylinders allowed controlling the available boron content for the formation of the layers with accuracy. The results showed a clear dependence of the mechanical properties of the borided layers in relation with the boron potential and also the layer thickness increased as the diameter of the cylinders were increased.

Finally, the influence of the boron potential in the constant of parabolic growth (k) was established as a function of the internal diameter of the cylinders.

9:00am **F3-4 Thermal Radiative Properties and Behavior at Very High Temperatures of Pyrolytic Boron Nitride Coating on C/C Composites for the Heat Shield of Solar Probe Missions**, ***E. Brodu*** *(etienne.brodu@promes.cnrs.fr), M. Balat-Pichelin, C. Morin, J-L. Sans*, PROMES-CNRS, France

SPP (NASA) and PHOIBOS (ESA) are two incoming missions of space exploration designed to make comprehensive measurements in the never-observed region of the heliosphere. They will both plunge directly into the solar corona, and respectively get as close as 9.5 and 4 Rs (solar radii) from the Sun surface into a region that no other spacecraft has ever encountered, in order to understand the heating of the solar corona and the acceleration of the solar winds.

For both missions, a main thermal protection system (TPS) will protect the payload within its umbra from the thermal radiations and solar winds. For this purpose, pyrolytic Boron Nitride (pBN) thin films deposited by CVD on carbon/carbon composites were studied as a potential candidate. Materials used as the outer layer of such TPS must show the following three mandatory features: 1- a low ratio of the solar absorptivity α to the total hemispherical emissivity ε in order to keep the equilibrium temperature as low as possible at a given distance from the Sun; 2- it must also be able to withstand simultaneously the high temperatures and two specific features of the Sun environment: the ion bombardment from the solar winds and the Vacuum Ultra Violet (VUV) radiation and 3- this material must present a low mass loss rate to avoid the pollution of the measurements of the scientific on-board instrumentation.

pBN coatings on C/C composites are currently under study at PROMES laboratory. To simulate the conditions that the materials will face near the Sun, the MEDIASE facility implemented at the focus of the 1 MW solar furnace at Odeillo has been developed. Samples can be heated up to 2500 K using the concentrated solar energy, in high vacuum (10-7 hPa), and with or without addition of proton bombardment and VUV radiation. This facility is also instrumented to perform several in-situ measurements: pressure, temperature via a pyro-reflectometer developed at PROMES, mass loss rate via a QCM, qualitative nature of the ejected species with an open source mass spectrometer, and directional total, spectral, or in narrow ranges emissivity via a radiometer. Experimental results of the degradation of the pBN films in this severe environment will be presented together with the evolution of its thermal radiative properties at high temperature. Different pBN coating thicknesses (100 to 300 microns) and also bulk pBN samples are studied to identify a possible thickness dependence of the thermal radiative properties. Our results have shown that a pyrolytic BN coating tends to reduce the α/ε ratio in comparison to uncoated C/C composites, which will help reduce the heat shield temperature.

9:20am **F3-5 Cubic Boron Nitride Coatings - Fundamental Aspects During Film Growth And Challenges In Industrial Utilization**, ***S. Ulrich*** *(sven.ulrich@kit.edu), J. Ye, H. Leiste, M. Stueber*, Karlsruhe Institute of Technology (KIT), Germany **INVITED**

Cubic boron nitride is a promising material for numerous applications due to its outstanding property profile. With its extreme hardness, excellent thermal conductivity, as well as chemical inertness at high temperatures, it is, for example, superior to diamond as a protective coating of tools for use in various high-temperature and ferrous-metal machining. Coatings based on cubic boron nitride can be produced nowadays already by almost every physical vapor deposition or plasma enhanced chemical vapor deposition method. However, such coatings usually exhibit unacceptably high compressive residual stresses resulting from the intense yet obligatory ion bombardment during the nucleation and growth process and, therefore, are still inadequate for the anticipated applications. In recent years many concepts and techniques have been actively explored in attempt to reduce the undesired coating stress, such as incorporation of a third element e.g. hydrogen, carbon, oxygen or silicon in the cubic boron nitride system, reduction of ion energy after the cubic phase nucleation, post-deposition thermal annealing, high-energy ex-situ ion implantation, fluorine-based surface chemistry, and composition-graded bond layer for enhanced adhesion. Different coating concepts and processes leading to low-stress, thick cubic boron nitride based coatings, results of modeling, microstructure and properties in relation to the process parameters as well as the challenges in industrial up-scaling will be discussed.

10:00am **F3-7 Methanol Wetting Enthalpy on Few-layer Graphene Decorated Hierarchical Carbon Foam for Thermal Cooling Applications**, ***R. Paul***, *DN. Zemlyanov, RN. Reifenberger*, Purdue University, US, *A.A. Voevodin*, Air Force Research Laboratory, Materials and Manufacturing Directorate, *T. Fisher (timothy.fisher@gmail.com)*, Purdue University, US

Vertical few-layer graphene petals are grown on macro-porous carbon foam surfaces having an intrinsic open porosity of 75%. This provides a hierarchical porous structure with a significant potential for surface adsorption/desorption or wetting/dewetting energy storage applications. Carbon foams have a combined advantage of large surface area and high thermal conductivity critical for thermal energy storage, but they are prone to oxidation and exhibit low adsorption enthalpies for lightweight hydrocarbons. Our previous work [Adv. Func. Mater, 22 (2012) 3682] on BN domain formation on carbon foam surfaces through microwave heating assisted chemical modification showed considerable increases in methanol wetting/dewetting enthalpy and thermal stability. Dewetting enthalpy of methanol on carbon foam increases from 460 to 780 J per gm of carbon foam and thermal stability against oxidation is found to increase from 570° to 780°C on BN modification. Here we report on graphene petal decoration of carbon foam surface and subsequent chemical modification through BN incorporation. The resulted hierarchical structure is characterized with XPS, XRD, TEM, FESEM and Raman measurements. Methanol wetting enthalpy and thermal stability of this three-dimensional hierarchical material is analyzed using a modified solution calorimeter and thermo-gravimetric analyzer, respectively. Influences of petal decoration on surface morphology of carbon foam, chemical modification and the stochiometry of the material surface, methanol wetting enthalpy and thermal stability against oxidation are discussed in details. The applicability of this hierarchical porous material for thermal and electrochemical energy applications is established.

Topical Symposia
Room: Tiki - Session TS2-2

Advanced Characterization of Coatings and Thin Films

Moderator: M. Sebastiani, University of Rome "Roma Tre", R. Ghisleni, EMPA (Swiss Federal Laboratories for Materials Science and Technology)

8:00am **TS2-2-1 Atomic Force Microscopy: A Powerful Tool for Ultrathin Metal/Polymer Assemblies Characterization**, ***D. Siniscalco*** *(david.siniscalco.etu@univ-lemans.fr)*, Université du Maine, France

Metal-polymer thin assemblies (h <100 nm) are now increasingly used in many devices such as micro - components in micro- and nano-electromagnetic (MEMS and NEMS) and on flexible printed circuit. To ensure the high reliability of such devices, it is essential to control the mechanical holding and heat dissipation of assemblies. We know that these properties are strongly dependent of the characteristics of the metal/polymer interface which depends itself on several parameters such as the nature of the metal and polymer, the roughness of the polymer and experimental conditions of gold deposit (temperature, speed…).

To study the structural properties and electrical resistivity performance of nanothick metal/polymer assemblies, we used a combination of X-ray reflectivity (XRR) and AFM analysis. X-ray (XRR) analysis was used to elucidate details of the structural modifications induced by the deposition temperature increase. Clearly, the structure of nanometric metallic layers deposited on polymer films is complex and the representation of polymers with coatings as two layered systems with a well pronounced interface depends of the deposition temperature. We have shown the progressive embedment of the gold particles into the polymer film when the deposition temperature increases above the T_g of the polymer film. The effect of the structural evolution of the assembly is then emphasized by measuring the increase of electrical resistivity of the assembly with a conductive-probe atomic force microscopy.

For the first time, we used a new system to make electrical resistance measurements, using AFM ((Resiscope®).

After applying a voltage between the tip and the surface we recorded AFM images of the surface resistance which allowed us to confirm the diffusion of the gold in the polymer when the temperature is higher than the T_g of the polymer.

AFM images can provide information on the internal structure of a thin film but it can also be used to study the characteristic dimensions of a mounded surface when they are combined with a new statistical analysis method. The interfacial differential function (IDF) is an efficient method to extract characteristic dimensions such as grain size, inter-grain lengths and periodicity.

We have demonstrated that for model mounded surfaces, the method is the most effective one to determine the different characteristic lengths. This method was thus applied to study the evolution of the surface morphology of ultrathin gold film deposited on silica. We have demonstrated that the roughness increase with deposition temperature is mainly due to a grain height increase and not to a grain coarsening phenomena as it claimed before.

8:20am **TS2-2-2 Optimized Design of Surface Mechanical Testing Procedures**, ***G. Favaro*** *(gregory.favaro@csm-instruments.com), N. Randall*, CSM Instruments, Switzerland, *J. Kohl*, University of San Diego, US, *N. Bierwisch, N. Schwarzer*, Saxonian Institute of Surface Mechanics, Germany

Since the early 1990s, coatings have been routinely characterized using nanoindentation, scratch testing and tribology testing in order to optimize them for their applications.

Most of the current international standards were written during the same period and unfortunately most users of mechanical testers only compare values between hardness, elastic modulus, critical loads, friction and wear but these may be insufficient for a good understanding of a coating design.

Optimization of a coating remains a challenge due to the many influencing variables such as coating adhesion, yield and wear mechanism, thermal and mechanical stresses, etc.

By the use of measured data from a nanoindentation test, a physical calculation of spatial stress profiles is simulated considering realistic material properties.

This analysis allows the user to perform real dimensioning of sophisticated scratch and tribology tests so that they are focused at specific regions in the coating design architecture.

This procedure allows more specific investigations of critical interfaces, transition layers and substrate regions with adjusted depth resolution.

Due to roughness and surface structure such optimized scratch, groove or tribology tests sometimes even need to take into account the true topography of the sample surface before and after the test. Such 3D scratch or tribology tests can provide much more information about the material stability and reliability than do classical approaches.

Using this valuable approach to quantify the interfaces between layer and substrate in a coating design allows a faster optimization of the coating design thus providing significant cost reduction.

To illustrate the features of this optimization method, various examples of characterization on coated samples will be presented, showing the flexibility of the technique for different situations.

8:40am **TS2-2-3 Deformation and Cracking of Hard Coatings**, *S. Liu*, University of Cambridge, UK, *J.M. Wheeler*, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland, *F. Di-Gioacchino*, University of Cambridge, UK, *X. Zeng*, SIMTECH, Singapore, *J. Michler*, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland, ***W. Clegg*** *(wjc1000@cam.ac.uk)*, University of Cambridge, UK **INVITED**

Fine-grained CrAlN-based hard coatings are known to have superior wear behaviour to conventional CrN coatings.The flow behaviour of some CrAlN-based hard coatings is studied, but appears to be predicted by conventional ideas. The cracking behaviour has therefore been studied. Various methods of measuring toughness exist, for instance indentation, but all have shortcomings. In this paper a double cantilever beam method has been used to study the nature of crack growth in hard coatings. The test method is first described, including a way of correcting for frictional effects between the punch and the sample and the limitations imposed by plastic flow on the range of materials that might be tested. The method is then used to describe the effect of microstructure in a range of hard CrAlN-based coatings and how this influences the toughness and nature of cracking in the hard coatings.

9:20am **TS2-2-5 A Critical Comparison Between XRD and FIB Residual Stress Measurement Techniques in Thin Films**, *E. Bemporad*, University of Rome "Roma Tre", Italy, *M. Brisotto*, *L.E. Depero*, ***M. Gelfi*** *(marcello.gelfi@ing.unibs.it)*, University of Brescia, Italy, *A.M. Korsunsky*, *A. Lunt*, University of Oxford, UK, *M. Sebastiani*, University of Rome "Roma Tre", Italy

Residual stress strongly affects the performance of thin films, in terms of adhesion, hardness, wear and fatigue resistance. Thus, when assessing innovative coatings or new deposition technologies, it is compulsory to evaluate the distribution of the stress by means of a reliable technique.

X-ray diffraction (XRD) is one of the commonly used techniques, because it is non destructive, surface sensitive and phase selective. Unfortunately, XRD can determine the stress only in case of crystalline materials and it may be not reliable in the presence of texture or stress gradients, often occurring in thin films.

Recently, a new class of methods for residual stress evaluation has been proposed, based on incremental focused ion beam (FIB) milling, combined with high-resolution in situ Scanning Electron Microscopy (SEM) imaging and full field strain analysis by digital image correlation (DIC).

The aim of the paper is to understand the different meanings of the stress values obtained either by XRD or FIB and to discuss the weaknesses and strengths of the two techniques. On this purpose, a Chromium Nitride (CrN) highly textured thin film samples have been deposited by cathodic arc evaporation PVD and the residual stress has been evaluated by using the two methods.

Considering the differences of XRD and FIB methods, a good agreement between the obtained stress values was obtained, provided that the issues related to (a) probe-to-sample interaction volume, (b) film's texture and (c) elastic anisotropy are carefully taken into account.

9:40am **TS2-2-6 From Interatomic Interaction Potentials via Einstein Field Equation Techniques to Time Dependent Contact Mechanics of Thin Films**, ***N. Schwarzer*** *(n.schwarzer@siomec.de)*, Saxonian Institute of Surface Mechanics, Germany

In order to understand the principle differences between rheological or simple stress tests like the uniaxial tensile test to contact mechanical tests and quasistatic contact experiments with oscillatory ones this study resorts to first principles respectively effective first principles. It will be shown how relatively simple models simulating bond interactions in solids using effective potentials like Lennard-Jones and Morse can be used to investigate the effect of time dependent stress-induced stiffening or enhancement in these solids.

The usefulness of the current study is the possibility of deriving relatively simple dependencies of the bulk-modulus B on time, shear and pressure P. In cases where it is possible to describe, or at least partially describe a material by Lennard-Jones potential approaches the above mentioned dependencies are even completely free of microscopic material parameters. Instead of bond energies and length, only specific integral parameters like Young's modulus and Poisson's ratio are required. However, in the case of time dependent (viscose) material behavior the parameters are no constants anymore. They themselves depend on time and the actual stress field, especially the shear field.

The influence of the time dependent pressure-induced Young's modulus change is discussed especially with respect to mechanical contact experiments and their analysis in the case of viscose thin films and substrates.

10:00am **TS2-2-7 Role of Activators on The Thermochemical Stability of Aluminide Coatings of Low Carbon Steel**, *B. Al-Anzi*, Kuwait University, Kuwait, *M. Al-Nabhan*, Petrochemicals Industries Corporation, Kuwait, *A.R. Khan*, ***A. Alhazza*** *(ahazza@kisr.edu.kw)*, Kuwait Institute for Scientific Research, Kuwait

Many metallic components used in chemical industries are exposed to aggressive corrosion. One of the methods used widely for corrosion control is the pack cementation process. This study aimed to improve the stability of aluminide coatings on low carbon steel. Powdered pack consists of Al and Al_2O_3, in addition two types of activators (NH_4F and NH_4Cl) were separately used. The diffusion coating was carried out at two different temperatures, 900°C and 1100°C. Appropriate microstructure examinations and surface morphologies analysis were conducted by SEM (Scanning Electron Microscope) and EDS to study the stability of aluminized coatings. The obtained results show that the pack aluminized steel substrates at 900°C using NH_4F activator exhibit good compact and more adherent coating layer, and that pack aluminized at 1100°C using NH_4Cl give embrittle Al_5Fe_2 and Al_3Fe phases tend to spalling.

10:20am **TS2-2-8 Surface Topography Corrected Analysis of Indentation Tests**, ***M. Fuchs*** *(m.fuchs@siomec.de)*, *N. Schwarzer*, Saxonian Institute of Surface Mechanics, Germany

One of the major effects, when it comes to indentation testing, is surface roughness. It can lead to a split-up of the assumed single contact area into a number of contact spots caused by many asperities underneath the indenter. However, even in cases where such a split-up does not matter roughness can still severely influence the indentation test results. The smaller the load the more important it is to take the actual surface curvature around the indented area into account. The supposedly normal load subjected to a supposedly flat surface could in fact become a complex mixture of the external normal load plus lateral, tilting and twisting moments caused by the surface curvature and inclination. Also the influence of the curvature on the resulting contact area can have a tremendous influence on the results. Especially hardness and elastic modulus can be dramatically overestimated if being measured on rough surfaces.

This work will cover how to account for such surface when analyzing contact problems like nanoindentation measurements by the means of the effective indenter concept being generalized to non-axial-symmetric loading and a curved surface solution applying paraboloid coordinates. It will also be shown how to evaluate the complete elastic fields and how to extend the approach to layered materials. In addition, it will be elaborated why the usual arithmetic averaging of many indentation measurements done on a rough surface does not give the correct hardness or Young's modulus, but still rather overestimated values leading to false ultra-hardness results.

10:40am **TS2-2-9 Electron Backscatter Diffraction Characterization of Blind Hole Fillings by Electrolytic Cu Deposition**, ***L.H. Hsu***, *C.E. Ho (ceho1975@hotmail.com)*, *C.W. Fan*, *C.C. Cnen*, *M.K. Lyu*, Yuan-Ze University, Taiwan

Blind hole (BH) filling by metallic deposition is widely usedin the high density interconnection (HDI) technology of three-dimensional (3D) packaging due to its high thermal and electrical conductivity and increased the efficiency of space utilization. The circuits in build-up layers of a HDI component are generally interconnected by electrolytic Cu fillings/platings. The morphology and crystallographic orientation/texture of the Cu fillings have been reported to pose significant influences on the electrical, thermal, and mechanical properties of interconnects, affecting the overall reliability of the HDI packages. Therefore, it is of great important to investigate the microstructural and crystallographic characteristics of the electrolytic Cu deposition in the BH structure.

In this study, the BHs were made by CO_2 laser drilling with a configuration of 60 μm (diameter) × 40 μm (depth) in a bismaleimide triazine (BT)-based substrate. The BH walls were deposited with a 1-μm-thick Cu film by electroless plating prior to the Cu electrodeposition. Subsequently, the substrate was subjected to a Cu electroplating process, where different current densities (j = 1, 2, 4, 6 A /dm^2) in direct current (DC) mode at room temperature were utilized. After electroplating to the "super-filling" stage, the BHs were cross sectioned and then were subjected to a metallurgical grinding-polishing process, to reveal the interior microstructure of the Cu platings in the BH structure. Additionally, a vibratory polisher (vibroMet™ 2) was employed to eliminate the artifacts resulting from the metallurgical treatment, to gain exact crystallographic information, e.g., grain size and boundary.

The microstructural and crystallographic characteristics of the electrolytic Cu BH filling in different current densities were examined by using optical microscopy (OM) and field-emission scanning electron microscope (FE-SEM) equipped with an electron backscatter diffraction (EBSD) analysis system. Correlations of grain size, grain boundaries (e.g., twin structure), crystallographic orientation, texture with j will be established in the present

study. These findings offer better understanding of the microstructural/crystallographic characteristics in the electrolytic Cu BH filling process.

11:00am **TS2-2-10 Raman, Structural, Electronic and Optical Characteristics of Mo:ZnO and Mo:ZnO/Graphene Composite Films**, ***M.C. Hsieh***, *H.S. Koo (frankkoo@must.edu.tw)*, Minghsin University of Science and Technology, Taiwan

2.0 wt% Mo-doped ZnO (Mo:ZnO) films, graphene monolayer films and graphene transferred onto 2.0 wt% Mo-doped ZnO (Mo:ZnO/graphene) bilayer composite films on copper and soda lime glass (SLG) substrates have been prepared by pulsed laser deposition, thermal chemical vapor deposition (TCVD) and transferred printing. Raman, structural, electronic and optical properties of Mo:ZnO films, graphene mono-layer films and Mo:ZnO/graphene bilayer composite films were investigated and demonstrated. Surface morphological images of Mo:ZnO and Mo:ZnO/graphene bi-layer composite films were observed to be homogenous, smooth and without defects. The optical transmittance of Mo:ZnO/graphene bi-layer composite film grown at 300^{o}C is observed to be 87% above in the wavelength range of 300-1000nm. The electrical resistivity, carrier concentration and mobility of Mo:ZnO/graphene bi-layer composite film grown at 300^{o}C is measured to be 2.22 x10^{-3} Ω-cm, 5.24 x 10^{20}/cm^{3} and 5.34 cm^{2}/V.s, respectively. Comparing with both Mo:ZnO and Mo:ZnO/graphene bi-layer composite films, the electrical and optical characteristics of Mo:ZnO/graphene bi-layer composite film is more excellent than those of 2.0wt% Mo:ZnO films, which were grown at 300^{o}C of substrate temperature.

11:20am **TS2-2-11 Effect of Annealing Environment on the Optical, Electrical and Thermoelectric Properties of MBE Grown ZnO Thin Films**, ***K. Mahmood*** *(khalid_mahmood856@yahoo.com)*, *M. Asghar*, The Islamia University of Bahawalpur, Pakistan, *I. Ferguson*, *M.A. Hasan*, *Y. Raja*, University of North Carolina, US, *Y.A. Xie*, University of California, Los Angeles, US

In this paper, we have demonstrated the effect of annealing environment on the optical, electrical and thermoelectric properties of MBE grown Zinc Oxide on Si (001) substrate. The grown films were annealed in oxygen, zinc, vacuum and zinc in vacuum rich environments at 600 ^{0}C for one hour. The grown films were characterized by X-ray diffraction (XRD), Photoluminescence spectroscopy (PL), Raman spectroscopy, Hall measurements and Seebeck effect. The PL results showed that intensity of band edge emission (3.28 eV) was improved by annealing in oxygen environment and degrades by annealing in Zn, vacuum and Zn in vacuum environments while FWHM showed vice versa behavior. Sebeck measurements also showed similar trend that Seebeck coefficient and power factor improved with annealing in oxygen. The Hall measurements demonstrated that sample annealed oxygen environment has lowest carrier concentration (3.97×10^{17} cm^{-3}) while sample annealed in Zn in vacuum has highest carrier concentration (5.11×10^{19} cm^{-3}). The improvement of optical and electrical properties while annealing in oxygen can be related with the fact that incoming oxygen spices fills the oxygen vacancies related donor defects and improves the structure. These results were discussed in detail with the help of available literature.

11:40am **TS2-2-12 Theoretical and Experimental Determination of the Cu Diffusivity in Molten Eutectic Sn–Ag System at 235 ° C– 280 ° C**, *C.E. Ho (ceho1975@hotmail.com)*, *W.Z. Hsieh*, *C.S. Liu*, ***C.H. Yang***, Yuan-Ze University, Taiwan

Copper-tin (Cu-Sn) is one of the most fundamental metallurgical systems and is now widely utilized in the microelectronic packages to join two metal parts of electronic devices. During soldering, the Cu would quickly diffuse/dissolve into the molten solder first and then a pronounced Cu/Sn chemical reaction at the interface follows. These two tightly connected processes not only cause a significant depletion in the Cu pads but produce a certain amount of brittle Cu-Sn intermetallic compound(s) (IMC) in the joining part, affecting the overall reliability of solder joints. Thus, understanding of the Cu diffusion/dissolution behavior in the liquid solder alloy is very important for advancing the quality of microelectronic packaging.

In this study, a mathematical model combined with experimental data was proposed to estimate the diffusion coefficient of Cu (D_{Cu}) in eutectic Sn-Ag (Sn-3.5Ag) alloy. The diffusion was conducted at temperatures ranging from 235 °C to 280 °C by using Cu/Sn3.5Ag solder bump joints, where the Cu is a solid but the Sn-3.5Ag is a liquid at the temperatures examined. To capture the overall scenario of the Cu diffusion in liquid Sn-Ag, the Cu concentration distribution across the entire Cu/Sn-3.5Ag joint was carefully analyzed using electron probe microanalysis (EPMA) line scans and elemental mappings. The mathematical model predicted that the average Cu concentration (C_{avg}) as a function of reaction time would approach saturation after 70 s at temperatures above 235 °C, which agrees well with that obtained through experiments. The saturation caused the slow down of the dissolution rate of existence Cu-Sn compound and consequently induced an evidently growth of Cu-Sn layer at the Cu/Sn-Ag interface. The combined results of calculation and EPMA data further showed that the average D_{Cu} are 1.2(±0.4) × 10^{-5} cm^{2}/s (235 °C), 2.4(±0.6) × 10^{-5} cm^{2}/s (250 °C), 2.6(±0.7) × 10^{-5} cm^{2}/s (265 °C), and 3.9(±1.6) × 10^{-5} cm^{2}/s (280 °C), respectively, which are of the same order with that obtained in pure Sn system. The insensitivity of D_{Cu} to the temperature reflects that the activation energy (Q) of the Cu diffusion in a liquid Sn-based alloy is not very large by contrasting with that of the solid diffusion. The Q was estimated to be approximately 13.3 kJ/mol at 235 °C– 280 °C on the basis of Arrhenius relation, which is slightly less than that acquired from the capillary-reservoir technique (17.6 kJ/mol) reported by Ma and Swalin in the literature.

Coatings for Use at High Temperatures
Room: Sunrise - Session A2-1

Thermal and Environmental Barrier Coatings
Moderator: K.A. Unocic, Oak Ridge National Laboratory, V. Maurel, Mines-ParisTech, France, K. Lee, Rolls Royce, US

1:30pm **A2-1-1 Lifetime and Interaction of New Single and Double Layer EB-PVD Thermal Barrier Coatings with Volcanic Ash**, ***U. Schulz*** *(Uwe.Schulz@dlr.de)*, German Aerospace Center (DLR), Germany, *A.U. Munawar*, University of Roma-Tre, Italy, *P. Mechnich, W. Braue, R. Naraparaju*, German Aerospace Center (DLR), Germany **INVITED**

Thermal barrier coatings (TBCs) are applied to increase lifetime and efficiency of highly loaded turbine components. New topcoat chemistries have been developed for TBCs that offer low thermal conductivity, improved sinter resistance, and higher phase stability. Degradation of those coatings by volcanic ash and calcium-magnesium alumino-silicate (CMAS) deposits is now recognized as an increasingly important fundamental degradation mechanism.

The presentation provides results on several TBCs deposited on top of NiCoCrAlY coated superalloys. Gadolinium zirconate (GdZ), lanthanum zirconate (LaZ), and dyprosia stabilized zirconia (DySZ) were investigated as single and double layers in comparison to standard 7YSZ coatings. In the double-layered TBC systems, a thin layer (~25µm) of 7YSZ was used between the new topcoat material and the bond coat. All coatings were deposited by electron-beam physical vapor deposition. The interaction of the coatings with artificial volcanic ash (AVA) and with CMAS was investigated at various temperatures. While the zirconia-based TBCs provide no mitigation potential due to complete infiltration by AVA and CMAS, the pyrochlore TBCs form crystalline phases rapidly which provides a potential for damage mitigation. A detailed microstructural analysis with special emphasis on the phases formed revealed that besides chemistry the TBC microstructure, in particular the width of the inter-columnar gaps, seems to play a decisive role for the interaction between TBC and deposits.

Selected TBCs were subjected to cyclic oxidation testing at 1100°C. Both single and double-layered GdZ and DySZ have shown longer lifetimes than the standard YSZ samples. Changes in microstructure, growth of the TGO layer, and diffusion of elements with testing time are discussed.

2:10pm **A2-1-3 Thermo-mechanical properties of calcium–magnesium alumino-silicate (CMAS) and CMAS infiltrated Electron Beam – Physical Vapor Deposited 7 wt. YSZ Thermal Barrier Coatings**, ***S. Ahmadian*** *(sha06001@engr.uconn.edu)*, *E. Jordan*, University of Connecticut, US

With the advancement of modern state-of-the-art thermal barrier coatings (TBC), gas turbines can operate at temperatures much higher than the melting point of the substrate. Now, the engine firing temperature is limited to the melting point of external particles with high concentration of calcium–magnesium alumino-silicate (CMAS) entering the gas turbine, which melt at about 1200-1400°C. The molten CMAS forms a glassy phase that reacts with the TBC's topcoat at high temperatures and causes spallation of the topcoat upon cool down, making it impossible to study the properties of CMAS infiltrated TBCs. In the present work, an easy method for CMAS infiltration involving CMAS delivery to the topcoat pores by epoxy capillary effects and flash melting made it possible to prepare TBC samples with CMAS infiltration up to 20-30% of topcoat thickness uniformly without delamination. For the CMAS infiltrated portion of the topcoat layer, the modulus of elasticity and thermal conductivity were measured respectively by four point bend rig and Laser Flash Analyzer (LFA), while the coefficient of thermal expansion (CTE) was obtained with a recently developed method utilizing the hot stage in Scanning Electron Microscopy (SEM) and quantified with image processing. In addition, the CMAS powder was formed into different sample geometries with a highly dense structure by hot pressing to measure its CTE, thermal conductivity and modulus by Thermo-Mechanical Analyzer (TMA), LFA and Nano-indentation. It was found that the CTE of infiltrated layer decreased by half and the conductivity and modulus increased by factors of 2.8 and 1.6 respectively.

2:30pm **A2-1-4 Mitigation of Deleterious Effects of Environmental Deposits on Thermal Barrier Coatings**, ***B. Nagaraj*** *(ben.nagaraj@ge.com)*, General Electric Aviation **INVITED**

With the current and projected growth in economic activity and passenger air travel in the hot and harsh regions of Middle East, Asia and Africa, the need for thermal barrier coated aircraft engine components to tolerate environmental deposits is becoming increasingly important. Typical chemistries of ingested sands and deposits on thermal barrier coated hot section components will be discussed. Examples of hot section thermal barrier coating and deposit interaction will be presented. Possible mechanisms of degradation of thermal barrier coatings due to deposits will be discussed. Approaches for mitigation of deleterious effects of deposits on thermal barrier coatings will be discussed.

3:10pm **A2-1-6 Degradation Study of 7 YSZ TBCs on Aero-engine Combustion Chamber Parts Due to Infiltration by Different CMAS Variants**, ***R. Naraparaju*** *(ravisankar.naraparaju@dlr.de)*, *U. Shulz, P. Mechnich*, DLR - Deutsches Zentrum für Luft- und Raumfahrt, Germany, *P. Doebber, F. Seidel*, MTU Maintance, Germany

At temperatures above 1200°C, ingested sand and debris particles melt on the TBC surfaces of aero- engine combustion chamber parts and form calcium-magnesium-alumino silicate (CMAS) deposits. The composition and melting point of CMAS vary according to the source and location of the sand and debris. The molten CMAS penetrates the 7 YSZ TBCs, changes the microstructure and reduces their strain tolerance which ultimately leads to failure. A damage assessment of TBC coated combustion chamber parts of aero-engines after service in heavily CMAS loaded areas was performed in this study. Parts from different engines were investigated by SEM and the extent of damage of the 7 YSZ plasma-sprayed TBC due to CMAS deposition and infiltration is estimated. With the help of XRD and EDX, CMAS chemical composition was analyzed and two different typical chemical compositions of CMAS were derived. These model CMAS compositions were synthesized in laboratory and their melting behaviour was determined by means of DSC. Both CMAS variants were subsequently deposited on air plasma sprayed yttria stabilized zirconia (APS-7YSZ) TBC specimens. Samples were subjected to isothermal heat treatments in air at temperatures ranging from 1200°C to 1250°C for times between 10h and 100h. The phase formations and microstructural changes were examined by SEM and XRD. Results from the CMAS/TBC interaction experiments are compared with the damage patterns on the real combustion chamber parts.

Furnace cycle tests (FCT) were conducted at 1135°C on TBC coated buttons with and without CMAS. The extent of TBC damage strongly correlates to the CMAS composition. The presence of Ca-sulphates in the CMAS plays a large role in damaging the 7YSZ and infiltration depth of CMAS. With raising temperature, the depth of infiltration increases rapidly and the CMAS has penetrated completely throughout the TBC thickness at 1250°C. In addition, the time to failure of the TBCs strongly depended on the type of CMAS deposited. The life time of the samples with Ca-sulphate containing CMAS was found to be the least compared to the samples without CMAS and with the sulphate-free CMAS variant.

3:30pm **A2-1-7 Lifetime Influence on Different TBC Systems in Laboratory and in Practise**, ***W. Stamm*** *(werner.stamm@siemens.com)*, Siemens Power Generation, Germany **INVITED**

Thermal Barrier coatings (TBC) are an important tool to increase life time and effiency of gas turbine components. All parts of the TBC systems like base material, bondcoat and ceramic on top must be an optimized unit. This lecture will provide basic informations about physical effects which can happen if the bondcoat itself and the base material/bondcoat composition are not well adopted. Examples will be shown and discussed from material point of view. Furthermore failure modes of EB-PVD coatings (PSZ) based on lab and own service experience will be discussed.. On the way to service introduction of the new developed GZO coating the behaviour of APS TBC-systems will be discussed shortly on the basis of service loaded blades. Finally test results on the new available GZO coating will be provided and explained on the bases of lab results only. Starting from powder investigations the mechanical and thermal properties of sprayed GZO coatings will be discussed. Finally the TBC degradation driven by the influence of detrimental elements will be provided by showing service loaded blades.

4:10pm **A2-1-9 Effect of Process Parameters on MCrAlY Bondcoat Roughness and Lifetime of APS-TBC Systems**, ***W. Nowak***, *D. Naumenko (d.naumenko@fz-juelich.de)*, Forschungszentrum Jülich GmbH, Germany, *G. Mor*, *F. Mor*, Flame Spray North America Inc., US, *D.E. Mack*, *R. Vassen*, *L. Singheiser*, *W.J. Quadakkers*, Forschungszentrum Jülich GmbH, Germany

The lifetime of air plasma sprayed (APS) thermal barrier coating (TBC) systems is well known to depend on the properties of MCrAlY (M = Ni, Co) bondcoat and in particular on the bondcoat roughness. The latter parameter is in turn strongly dependent on the bondcoat manufacturing process. Low pressure plasma spraying (LPPS) conventionally used for bondcoat production is competed nowadays by high velocity oxy-fuel (HVOF). The oxidation resistance of the optimized HVOF bondcoats is similar to that of the LPPS ones. However, the roughness of HVOF bondcoats is generally lower than that of LPPS coatings due to the intrinsic process limitations.

In the present work it is shown that the lifetime of the APS TBC systems with HVOF bondcoats can be substantially extended by application of a thin APS "flashcoat" layer onto the base HVOF bondcoat. The latter approach allows improvement of the bondcoat roughness profile to the extent typically obtained by LPPS. It is important to mention that the oxidation resistance of the flashcoat strongly depends on the used spray parameters. Deviation from the set of the optimized spray parameters was found to result in the catastrophic oxidation of the flashcoat and corresponding very rapid TBC-failure.

In order to explain the TBC lifetime variations between the various bondcoat morphologies, the roughness profiles of HVOF, LPPS and APS-flashcoat bondcoats were evaluated using fractal analysis. It is suggested that such an approach provides better correlation between the bondcoat morphology and TBC-lifetime than the calculation of the arithmetic mean roughness (Ra) of the bondcoat frequently used in practical application.

4:30pm **A2-1-10 Protective Coatings for Gas Turbines**, ***NJ. Simms*** *(n.j.simms@cranfield.ac.uk)*, *J. Sumner*, *J.R. Nicholls*, *A. Encinas-Oropesa*, Cranfield University, UK **INVITED**

Gas turbines are playing an increasingly important role in modern life via, for example, power generation from industrial gas turbines and air transport using jet engines. During their development there has been a steady increase in combusted gas temperatures, with components in this hot, combusted gas stream moving from being uncooled to cooled (using a range of technologies) and to now needing thermal barrier coatings (TBCs) on top of this air cooling. For some gas turbines, the combusted gas temperatures are above the melting points of the component materials. Surface degradation of gas turbine components can occur through simple oxidation, especially at the higher operating temperatures. However, contaminants (such as sulphur, chlorine and alkali species) can enter the gas turbine through the fuel and/or combustion air and cause the hot corrosion of metallic component surfaces (e.g., via type I or type II hot corrosion reactions). Other species (such as calcium, magnesium, aluminium and silicon compounds (i.e., CMAS), possibly mixed with iron and other compounds) can also enter through the combustion air and cause surface damage, especially to thermal barrier coatings. A wide range of coatings for environmental protection has been developed to combat specific forms of surface degradation.

Despite the existence of protective coatings for many current conditions, with the continuing need to increase the efficiencies and reliabilities of gas turbines used in different applications, and to enable fuel and operational flexibility whenever possible, their requirements are changing. Thus coatings for thermal and/or environmental protection form critical parts of the materials systems that are now used in gas turbines. This paper will review state of the art coating systems, and highlight the development of advanced multi-functional coating systems. Examples of these coating systems include: (a) the incorporation of sensing layers into thermal barrier coatings; (b) multi-layered TBCs to resist CMAS/Fe attack; and, (c) multi-layered metallic coatings for oxidation and hot corrosion resistance.

5:10pm **A2-1-12 Study on Hot Corrosion Behavior of ZrO_2-Y_2O_3-Ta_2O_5 Thermal Barrier Coating in Turbine Simulated Environment**, ***M.H. Habibi***, *S. Guo (sguo2@lsu.edu)*, Louisiana State University, US

Thermal barrier coatings (TBCs) are frequently used on the blades and vanes of gas turbines to provide thermal insulation. Although YSZ based TBC systems have been used widely in gas turbine industry, YSZ is prone to hot corrosion caused by molten salts, such as Na, S and V, contained in low-quality fuels at high working temperatures. The search for investigating new stabilizers of zirconia has been going on. One alternate approach to YSZ TBC improvement is using Ta_2O_5 as a stabilizer. This study compares the hot corrosion performance of yttria stabilized zirconia (YSZ), and YSZ-Ta_2O_5 (TaYSZ) composite samples in the presence of molten mixture of Na_2SO_4 + V_2O_5 at 1100˚C. Characterizations using X-ray diffraction (XRD) and scanning electron microscope (SEM) indicate that in the case of YSZ, the reaction between $NaVO_3$ and Y_2O_3 produces YVO_4 and leads to the transformation of tetragonal ZrO_2 to monoclinic ZrO_2. In ZrO_2-Y_2O_3-Ta_2O_5system, the compositions were selected to form tetragonal and orthorhombic phases of zirconium-tantalum oxides. For TaYSZ and TaSZ, minor amount of $NaTaO_3$, $TaVO_5$ and Ta_9VO_{25} are formed as the hot corrosion products with only traceable amount of YVO_4. Due to the synergic effect of co-doing of zirconia with Y_2O_3 and Ta_2O_5, TaYSZ sample has much better hot corrosion resistance than YSZ.

Hard Coatings and Vapor Deposition Technology
Room: Royal Palm 1-3 - Session B4-4

Properties and Characterization of Hard Coatings and Surfaces

Moderator: C. Mulligan, US Army ARDEC, Benet Laboratories, J. Lin, Southwest Research Institute, U. Beck, BAM Berlin

1:30pm **B4-4-1 Nanostructural Analysis of Magnetron Sputtered HfAlN Thin Films Grown on MgO(001) by Atom Probe Tomography**, ***D. Engberg*** *(daven@ifm.liu.se)*, Linköping University, IFM, Thin Film Physics Division, Sweden, *L. Johnson*, Sandvik Coromant, Sweden, *M. Thuvander*, Chalmers University of Technology, Department of Applied Physics, Sweden, *L. Hultman*, Linköping University, IFM, Thin Film Physics Division, Sweden

Thin films of transition metal nitrides are a field of great interest for academia and industry alike. TiAlN films exhibit high hardness, thermal stability and wear resistance, making them suitable for metal cutting applications. One major mechanism for maximizing hardness of such films is based on self-organized compositional modulations on the nanometer scale through spinodal decomposition and phase separation of immiscible components. All group IV transition metal nitrides are expected to phase separate when combined with AlN, owing to their immiscibility due to volumetric, electronic, and/or magnetic mismatch. Calculations have predicted that the mixing enthalpy of HfAlN is approximately twice that of TiAlN [1], yielding a stronger driving force for phase separation in HfAlN than in TiAlN. Previously, laser assisted atom probe tomography (ATP) methods were developed for TiAlN thin films [2,3]. In this study, $Hf_{1-x}Al_xN$ (x = 0.17, 0.29, and 0.48) thin films deposited by magnetron sputtering on MgO(001) substrates have been analyzed using ATP. We observe the very onset of compositional modulations in samples with x > 0.2, but with less discrimination than initially seen by scanning transmission electron microscopy (STEM) [4]. Differences in the results from tomography and microscopy evaluation are discussed with respect to the choice of field evaporation and reconstruction parameters, and the contrast-forming mechanisms (atomic number contrast vs. strain-field contrast), respectively.

[1] B. Alling, A. Karimi, I. A. Abrikosov, Surf. Coat. Technol. 203 (2008) 883.

[2] R. Rachbauer, E. Stergar, S. Massl, M. Moser, P.H. Mayrhofer, Scr. Mater. 61 (2009) 725.

[3] L.J.S. Johnson, M. Thuvander, K. Stiller, M. Odén, L. Hultman, Thin Solid Films 520 (2012) 4362.

[4] B. Howe, J. Bareño, M. Sardela, J.G. Wen, J.E. Greene, L. Hultman, A.A. Voevodin, I. Petrov, Surf. Coat. Technol. 202 (2007) 809.

1:50pm **B4-4-2 Investigations on the Diffusion Behaviour of Fe, Cr, and C in Arc Evaporated TiN- and CrN-based Coatings and Their Influence on the Thermal and Mechanical Properties**, ***C. Sabitzer*** *(corinna.sabitzer@tuwien.ac.at)*, *C. Steinkellner*, *B. Larrieu*, Vienna University of Technology, Austria, *P. Polcik*, Plansee Composite Materials GmbH, Germany, *M. Arndt*, *R. Rachbauer*, Oerlikon Balzers Coating AG, Liechtenstein, *J. Paulitsch*, *P.H. Mayrhofer*, Vienna University of Technology, Austria

Hard materials like CrN, TiN, CrAlN, and TiAlN are well established as protective coatings for tools used in various machining and forming applications. Even though the thermal stability and thermo-mechanical properties of such coatings have already been investigated in numerous studies only little information is available concerning the influence of transfer-material-diffusion during e.g. machining applications. Therefore, thin layers of Fe, Cr, and C ─ which are common transfer-elements during machining ─ were deposited on arc evaporated CrN, TiN, $Al_{0.7}Cr_{0.3}N$ as well as on $Ti_{0.5}Al_{0.5}N$ coatings. The concentration-depth profiles after vacuum annealed for 30 min at 600, 800, and 1000 °C were evaluated by cross-sectional EDX line-scans as well as by secondary ion mass spectroscopy. Additional to the determination of the diffusion coefficients

at high temperatures, low temperature annealing treatments at 600 °C for 10, 100, and 1000 min were carried out to investigate in more detail the in-depth diffusion behaviour of Fe, Cr, and C. These results serve as a basis for a better understanding of the complex interaction between coated tool and work-piece as well as the influence of impurities on the thermal and mechanical behaviour of ceramic-like protective coatings.

2:10pm **B4-4-3 Mechanical and Tribological Behavior of Nanocrystalline Ni-W Coatings: Importance of Grain Size and Grain Boundary State**, ***T. Rupert*** *(trupert@uci.edu)*, University of California Irvine, US **INVITED**

The high strength of nanocrystalline metals suggests that these materials are promising for wear-resistant coatings, where protective films must be able to survive the repetitive application of high contact stresses. However, nanocrystalline metals also demonstrate novel grain boundary-dominated deformation mechanisms and a tendency for mechanically-driven structural evolution. This talk first addresses the tribological response of nanocrystalline Ni-W alloys across a range of grain sizes from 3 to 100 nm, with a focus on understanding how the extreme conditions produced during wear can lead to dynamic nanostructures and properties. Both experiments and simulations reveal evidence of grain growth and relaxation of grain boundary structure during tribological contact, which are actually beneficial to wear resistance. We next isolate the importance of atomic grain boundary structure on mechanical properties using small-scale uniaxial testing and molecular dynamics simulations. An ordered boundary structure is found to increase strength at the expense of ductility. Finally, we synthesize these results and identify strategies for metallurgical design of optimal nanocrystalline coatings.

2:50pm **B4-4-5 Microstructure-Related Depth-Gradients of Mechanical Properties in Thin Nanocrystalline Films**, ***R. Daniel*** *(Rostislav.Daniel@unileoben.ac.at)*, Montanuniversität Leoben, Austria, *A. Riedl*, Materials Center Leoben Forschung GmbH, Austria, *T. Schöberl*, Montanuniversität Leoben, Austria, *B. Sartory*, Materials Center Leoben Forschung GmbH, Austria, *C. Mitterer*, *J. Keckes*, Montanuniversität Leoben, Austria

Physical and functional properties of nanocrystalline thin films are strongly dependent on their microstructure. Thermal (thermal expansion and conductivity), electrical and magnetic properties depend on the amount of structural defects, which affect the electron and phonon transport and magnetocrystalline anisotropy, thus controlling the macroscopic properties of nanostructured materials. The microstructure, however, also determines the mechanical properties of nanocrystalline films as the generation and motion of dislocations under mechanical loading may be effectively constrained by the presence of structural defects. This effect may be further promoted by compressive stress typically developed in PVD films. Due to inherent heterogeneous nature of nanocrystalline films related with non-equilibrium growth conditions, depth-gradients of microstructure, stresses, physical and functional properties are developed. In this paper, microstructure-related depth-gradients of mechanical properties will be discussed for nanocrystalline CrN films prepared under various growth conditions as single- and multilayers. Nanoindentation experiments performed on single layered films and at the small-angle cross-section of a multi-layered CrN film coupled with spatially resolved synchrotron nanodiffraction experiments will be shown to reveal changes of hardness and elastic modulus associated with a variation of the grain size and stress state across the film thickness.

3:10pm **B4-4-6 Corrosion Resistance of Zirconium Oxynitride/Zirconia Thin Film Growth by Spray Pyrolysis-nitruration and DC Sputtering Magnetron Unbalance**, *G. Cubillos (gcubillos@unal.edu.co)*, ***D. Posso***, *J.J. Olaya*, Universidad Nacional de Colombia Bogotá, Colombia

Were deposited ZrO_xNy/ZrO_2 thin films on stainless steel by two different methods ultrasonic spray pyrolysis-nitruration and DC sputtering magnetron unbalance technique. Using the first technique is initially deposited ZrO_2 and subsequently nitrided in anhydrous ammonia atmosphere at 750 ºC atmospheric pressure [1]. By DC sputtering the film is deposited in atmosphere of air/argon, with a flow ratio Φair/ΦAr of 3.0. The ZrO_xN_y/ZrO_2 films were obtained from a 4 in. ×1/4 in. Zr (99.9%) target (CERAC, Inc.). The parameter set used during the deposition process was: base pressure at 1.0×10^{-3} Pa, deposition time 30 min, target–substrate distance at 5 cm and argon (99.999%) flow at 9.0 sccm at room temperature (287 K) [2]. Structural analysis was carried out through X-ray diffraction (XRD); morphological analysis was done through scanning electron microscopy (SEM) and chemical analysis was determined using X-ray photoelectron spectroscopy (XPS). From spray pyrolysis-nitriding grows ZrO_xNy rhombohedral polycrystalline film, whereas DC sputtering the oxynitride films were grown with cubic crystalline structures Zr_2ON_2 and preferentially oriented along the (222) plane. Chemical analysis determined that in the last 5.0 nm, the Zr coatings present the following spectral lines: $Zr3d_{3/2}$ (184.6 eV) and $3d_{5/2}$ (181.7 eV), O1s (531.3 eV), and N1s (398.5 eV). SEM analysis presented the homogeneity of the films. Zirconium oxynitride films enhance the stainless steel's resistance to corrosion by the two techniques. The protective efficacy has been evaluated using electrochemical techniques based on linear polarizations (LP). The results indicate that the layer provides good resistance to corrosion in chloride-containing media [3,4].

3:30pm **B4-4-7 Structural Characterization of NbAlN Coating Deposited on AISI D2 Steel by TRD Method**, ***E. Abakay***, *S. Sen*, *U. Sen (ugursen@sakarya.edu.tr)*, Sakarya University, Turkey

In this study, Nb-Al-N coating was applied on pre-nitrided AISI D2 steel by the thermo-reactive deposition technique in a powder mixture consisting of ferro-niobium, ammonium chloride and alumina at 1000°C for 1–4 h. The coated samples were characterized by X-ray diffraction, scanning electron microscope and micro-hardness tests. Nb-Al-N layer formed on the pre-nitrided AISI D2 steel was compact and homogeneous. X-ray diffraction analysis showed that the phases formed on the steel surfaces are $NbN_{0.95}$, Nb_2CN, Nb_3Al_2N and AlN. The depth of the Nb-Al-N layer ranged from 3.63 µm to 10.05 µm, depending on treatment time. The higher the treatment time the thicker the Nb-Al-N layer observed. The hardness of the Nb-Al-N layer was changing between 1708 $HK_{0.01}$ and 2577$HK_{0.01}$.

3:50pm **B4-4-8 Surface Hardening of IF Steel by Plasma Nitriding and Pre-shot Peening**, *A.P.A. Manfridini*, Universidade Federal de Minas Gerais, UFMG, Brazil, *A.C. Bozzi*, Universidade Federal do Espírito Santo, UFES, Brazil, *J.C. Avelar-Batista Wilson*, Tecvac, Ltd., UK, ***M.V. Auad***, Auad Godoy Consultants, Brazil, *C. Godoy (cristinagodoyufmg@gmail.com)*, Universidade Federal de Minas Gerais, UFMG, Brazil

Shot peening and plasma processes are widely used to improve the surface properties of metals and alloys. This work aims at broadening the applicability of interstitial free (IF) steels by combining both processes. In addition, we evaluate the influence of prior shot peening on the plasma nitriding process, as shot peening introduces non-equilibrium defects on the surface, which enhance the diffusions rates of nitrogen [1, 2]. The plasma nitriding was carried out for 4h at temperatures of 450°C, 475°C and 500°C on a Ti-stabilized IF steel, with and without pre-shot peening. The microstructure and structural phases were characterized by means of backscattered scanning electron microscopy (SEM) and x-ray diffraction (XRD); while mechanical properties were investigated using micro- and nanoindentation as well as dry sliding wear tests.

SEM showed that the morphology and distribution of the precipitates formed in the surface layers strongly depend on the pre-shot peening and plasma process temperature. Long nitride needles were only observed in the samples without pre-shot peening. For all samples the XRD patterns showed the presence of ε-$Fe_{2-3}N$, γ'-Fe_4N and the Fe-α matrix ferrite peak. Ultramicrohardness exhibits a two fold increase in hardness values near the surface relative to the substrate, and a hardened region, which extends up to a depth of 500µm in the IF steel treated at 500°C. For all test temperatures, a slight increase in hardness was observed for the shot peened samples compared to the ones without prior shot peening. Further investigation of the sample cross-sections by nanoindentation showed that shot peening caused a hardening effect up to a depth of 20 µm on the untreated substrate. It was also shown that for the plasma processed samples at 500°C, up to a depth of 70 µm, the shot peened samples had a higher average nanohardness than the samples which were not pre-treated. This suggests that an enhanced nitrogen diffusion due to the pre-mechanical treatment might have increased the nitrogen concentration in this region. The dry sliding wear tests showed an improvement of wear resistance of the IF steel after the different treatments, which was compared by the worn volume and measured using 3D profilometry. Characteristic undulation on the coefficient of friction versus sliding distance curves indicated a tribochemical wear process [3], which is confirmed by EDS compositional maps of the wear tracks.

[1] Hashemi et al., Material and Design. 3287-3292 (2011) 32.

[2] Shen et al., Surf. Coat. Technol . 3222-3227 (2010) 204.

[3] Zhang et al. Tribology International. 214-223 (2013) 61.

4:10pm **B4-4-9 Influence of Cu Additions on the Mechanical and Wear Properties of NbN Coatings**, ***K.V. Ezirmik*** *(ezirmik@atauni.edu.tr)*, *S. Rouhi*, Atatürk University, Turkey

The influences of increasing copper content in the NbN-Cu coatings on mechanical and tribological properties were studied. The coatings were deposited on M2 tool steel by using reactive magnetron sputtering method. Copper content of the coatings was varied from 1 to 24at.%. The microstructure, microhardness and wear properties of the coatings were examined. The addition of Cu into NbN coatings has modified the grain size

and morphology. Mechanically, the microhardness values of the coatings other than NbN-1at% Cu were significantly reduced by Cu doping. The hardness of the films reached maximum level, 38GPa, at 1%at copper content and decreased with a further increase of the Cu content. Introduction of 1at % Cu into niobium nitride showed a beneficial effect on abrasive character of the coating. Wear of counter material increased at these coatings while others showed exact opposite behavior.

Advanced Materials for Modern Device Applications
Room: Golden West - Session C3

Advances in Electrode Materials for Modern Device Applications

Moderator: T. Terasako, Ehime University, J.A. Zapien, City University of Hong Kong

1:30pm **C3-1 A Novel Hierarchical Aluminum-doped Zinc Oxide Thin Film for Flexible Thin-film Solar Cells**, ***X. Huang***, *F.Y. Zhang (fengyanzhang1@gmail.com)*, Xiamen University, China

A novel hierarchical aluminum-doped zinc oxide thin films were deposited on low-cost flexible polymer substrates at room temperature using chemical bath deposition. The effects of reaction temperatures, precursor and time on film properties were investigated. And the morphological structure of ZnO:Al thin films, was studied using modern methods such as: X-ray photoelectron spectroscopy, X-ray diffraction (XRD) and atomic force microscopy. A simple growth mechanism had been proposed to interpret the formation of the hierarchical ZnO:Al films. Consequently, a low resistivity of ~ 8.7×10^{-4} Ω cm with a high normalized transparency index of > 0.9 for a 150 ± 10 nm thick room-temperature deposited film was obtained, representing one of the best results obtained to date. Moreover, the efficiency of the thin-film solar cell with this ZnO:Al top electrode reached 8%.

1:50pm **C3-2 Evaluation of TiN-Coated Aluminum Electrodes for DC High Voltage Electron Guns**, ***M.A. Mamun***, Old Dominion University, US, *E. Forman*, Thomas Jefferson National Accelerator Facility, US, *R. Taus*, Loyola Marymount University, US, *M. Poelker*, Thomas Jefferson National Accelerator Facility, US, *A.A. Elmustafa (aelmusta@odu.edu)*, Old Dominion University, US

DC high voltage thermionic and photoemission electron guns require cathode electrodes that do not exhibit field emission. Field emission is the unregulated release of electrons from the cathode electrode surface when the cathode is biased at high voltage. Field emission is problematic for a number of reasons: it degrades the vacuum level via electron stimulated desorption and leads to shortened operating lifetime of the gun, it creates unwanted x-rays that are harmful to nearby personnel, and high levels of field emission can damage electron gun components.

Cathode electrodes for electron guns are typically manufactured from hard metals like stainless steel, titanium-alloy, or molybdenum. Once fabricated at the machine shop, the relatively rough surface of the electrode must be mechanically polished by hand using silicon carbide paper and diamond grit, to obtain a smooth surface free of microscopic protrusions which cause field emission. However, the polishing process for electrodes manufactured from hard metals is time consuming and labor intensive.

In this research, the field emission characteristic of electrodes manufactured from soft aluminum metal were studied using a high voltage field emission test stand, before and after coating the surface of the electrodes with titanium-nitride (TiN). Electrodes manufactured from aluminum are relatively easy to polish, requiring only hours to obtain a mirror-like finish, rather than days. The electrodes coated with TiN performed markedly better than the uncoated electrodes and the best electrode exhibited no measurable field emission (<10 pA) at a field strength of > 22.5 MV/m. In sharp contrast, the uncoated electrodes exhibited significant field emission at field strength of just ~ 5 MV/m. The electrodes were evaluated using scanning electron microscopy with x-ray microanalysis (SEM/EDS) to investigate morphological and structural variations associated with the polishing and coating processes, and due to the high voltage processing which included gas conditioning with helium and krypton. Small test coupons were studied using an atomic force microscope and nanoindenter, to evaluate surface morphology, hardness and modulus of the TiN thin films.

2:10pm **C3-3 Effects of N_2O Addition During the Growth of ZnO Films using High-temperature H_2O Generated by a Catalytic Reaction**, *T. Nakamura, Y. Ohashi, N. Yamaguchi, E. Nagatomi, T. Kato, Y. Tamayama,* ***K. Yasui*** *(kyasui@vos.nagaokaut.ac.jp)*, Nagaoka University of Technology, Japan

ZnO is highly useful for various applications such as short-wavelength optoelectronics and transparent conductive electrodes. In a previous paper, we reported a new growth method for preparing ZnO films by reacting alkyl-zinc and high-temperature H_2O generated by a catalytic reaction [1]. The resulting ZnO films grown on a-plane sapphire (a-Al_2O_3) substrates exhibited excellent optical and electronic properties [2]. In this study, we investigated the influence of the N_2O gas supply during the growth on the properties of the ZnO films. The structure of the CVD apparatus and the growth procedure used in this study are the same as those shown in a previous paper [1], except for the addition of N_2O gas to the reaction zone. The ZnO films were directly grown on a-Al_2O_3 substrates at 773K for 60 min without any buffer layer. The thickness of the ZnO films characterized was 6–8 μm. Although the N_2O gas supply pressure varied from 3.2×10^{-3} Pa to 9.7×10^{-2} Pa, all films showed an n-type character. The electron mobility of N_2O doped (3.2×10^{-3} Pa) film at RT (290 K) was 234 cm^2/Vs, while that of non-doped ZnO film was 207 cm^2/Vs. The mobility increases significantly with decreasing temperature to 100 K for all films. The mobility of the N_2O doped film (234 cm^2/Vs at RT) increases to 1100 cm^2/Vs at 100 K. Electron concentrations at RT of all films were 4.3-5.9×10^{16} cm^{-3} and those of the N_2O doped ZnO films were smaller than that of the non-doped film from RT to 80 K. The FWHM value of the ZnO (0002) ω-rocking curve of the N_2O doped (3.2×10^{-3} Pa) film was 142 arcsec, while that of the non-doped ZnO film was larger than 194 arcsec. The FWHM value of PL peak (3.36 eV) at 10K for the N_2O doped film was 0.7 meV, while that of the PL peak (3.36 eV) for the non-doped film was 0.9 meV. A significant correlation between the electron mobility and the FWHM value of the ZnO (0002) ω-rocking has been observed [2]. The reduction in the fluctuation of the crystal orientation along the c-axis appears to have yielded the excellent electrical and optical properties in the N_2O doped ZnO films. Although a part of the donor impurities are compensated by the nitrogen acceptor, the intrinsic donor impurities caused by the defects are considered to be reduced by the doping of nitrogen in view of the large electron mobility for N_2O doped ZnO films.

Acknowledgements**:** This work was supported in part by Tokyo Electron Ltd. and a Grant-in-Aid for Scientific Research (No. 24360014) from the Japan Society for the Promotion of Science.

[1] K. Yasui et al., MRS Symp. Proc., **1315** (2011) 21.

[2] N. Yamaguchi et al., Thin Solid Films, (2013) in press.

2:30pm **C3-4 Conductivity and Morphology of Highly Textured In_2O_3(111) Films with Ultrathin In Seeding Layers**, ***C.C. Yu*** *(yucc@nuk.edu.tw)*, ***K.S. Yang***, National University of Kaohsiung, Taiwan

Transparent conductive oxides (TCO) are the most important materials in the modern optoelectronic devices such as light emitting diodes, solar cells due to its specific characteristics in optics and electricity. The most common TCO material used today is indium tin oxide (ITO) with a composition of In_2O_3: SnO_2 equal to 90:10. Such an ITO film has a transparency higher than 95% in the range of visible light and a resistivity with a magnitude in the order of 10^{-4} Ω-cm. It also presents excellent thermal and erosive resistance and, therefore, wildly uses in the consumer products. In this study, we utilized a thermal deposition to fabricate In_2O_3 films on glass substrates in three ways. In the first approach, In_2O_3 films were produced by the evaporation of In source under oxygen ambient (~ $2x10^{-3}$Torr). We also fabricated In_2O_3 films by the oxidation of In films as the second attempt. Finally, we combined previous two approaches to utilize an ultrathin oxidized In film as a seeding layer to obtain the highly textured In_2O_3(111) films.

In the first approach, polycrystalline In_2O_3 films with low resistivity, ranged from $3.8x10^{-4}$ to $9.6\ x10^{-4}$ Ω-cm as varying the deposition temperature (Tg), can be achieved without post annealing. For the Tg around 100°C, surface defects with pyramidal shape, due to the aggregation of In atoms, can be observed. For the Tg> 200°C, the In atoms evaporated out of the In_2O_3 film surface and a smooth In_2O_3 surface was achieved. For the second attempt, In_2O_3(111) films with rough surface and high resistivity were obtained through oxidation of In(101) films. For a 50nm-thick In_2O_3(111) films, the resistivity was around $3x10^{-2}$ Ω-cm and it was larger than the one of the polycrystal In_2O_3 film by two orders of magnitude. Such poor conductivity was a serious drawback in the electrical conduction application.The sheet concentration and AFM images suggested that In_2O_3(111) was isolated nanodots for thickness lower than 7nm. The behavior of resistance versus thickness can be well fitted by Namba's model and was resulted by the scattering of rough surface. In the third approach, an ultrathin oxidized In(101) seeding layer was deposited prior to the deposition of In_2O_3 film. In this approach, highly textured In_2O_3(111) films with good conductivity,

high transparency and smooth surface were obtained. With the help of low surface scattering, the observed resistance was around $8x10^{-4}$ Ω-cm. The value of resistivity is in the same order of magnitude with the resistivity of the In_2O_3 polycrystal film. Such an In_2O_3(111) film with smooth surface can serve as a seeding layer of crystal growth and provide functions of transparency and conductivity.

2:50pm **C3-5 Enhancement of Open-circuit Voltage on Organic Photovoltaic Devices by Al-doped TiO_2 Modifying Layer Produced by Sol-gel Method**, *R. Valaski, C. Arantes, C.A. Achete,* Inmetro, Brazil, ***M. Cremona*** *(cremona@fis.puc-rio.br)*, PUC-RIO, Brazil

Sol-gel method has shown several advantages for oxide synthesis, such as lower cost production, coating large areas, lower processing temperatures and ease insertion of doping materials, thus, it has also been an attractive method in solar cells manufacturing. In this work, aluminum-doped titanium dioxide ($AlTiO_2$) modifying layers were synthesized by sol-gel method onto fluorine doped tin oxide (FTO) electrodes, in order to improve the efficiency of organic photovoltaic devices (OPVs). Before device fabrication, the structural, compositional, optical and electrical properties of the transparent oxide films were determined and compared with those obtained from undoped TiO_2 layers produced under the same conditions. The optimum Al-dopant concentration was determined by DC conductivity measurements on FTO/$AlTiO_2$ /Al devices. The performance of OPVs was investigated based on the FTO/$AlTiO_2$ (30nm)/CuPc (20nm)/C_{60} (40nm)/Alq_3 (20nm)/Al device under dark and standard illumination conditions (1Sun, M1.5G). $AlTiO_2$ modifying layer improves the direct current under illumination and increases significantly the open-circuit voltage, V_{oc}, resulting in a value of 750 mV, while the devices based on FTO and TiO_2 presented a V_{oc} of about 250 mV. These results indicate the Al-doping of TiO_2 thin films induces a strong built-in potential modification. It is known that Al induces strong dipole interaction on interfaces poly(thiophene)/Al, increasing, considerably, the Voc. In the $AlTiO_2$/CuPc interface, the enhancement of built-in potential can result from dipole phenomena induced by Al-dopant. All the results will be presented and discussed in the work.

3:10pm **C3-6 Thermochromics and Electrochromics for Energy Efficient Fenestration**, ***C. Granqvist*** *(Claes-Goran.Granqvist@Angstrom.uu.se)*, Uppsala University, Angstrom Laboratory, Sweden **INVITED**

Thermochromic and electrochromic materials, and devices based on these, can be used in energy efficient fenestration and lead to significant drops of the energy that is used for heating and cooling of buildings. Thermochromics allows temperature-dependent control of the inflow of visible light and solar energy, and electrochromics can give a similar functionality that is electrically controlled. This paper summarizes recent work, mainly from the author's laboratory, on thermochromic thin films and nanoparticles as well as on electrochromic devices embodying thin films of tungsten oxide and nickel oxide. The presentation covers materials, devices, operating principles, and prospects for the mentioned technologies.

3:50pm **C3-8 Degradation Mechanism of ZnO thin Film for TCO of Flexible a-Si:H PV Module due to Moisture**, ***J.-S. Jeong*** *(jjseicp@keti.re.kr)*, Korea Electronics Technology Institute, Republic of Korea

The TCO thin film is an important layer which influence on Rs (series resistance) of a-Si:H PV(photovoltaic) modules. So the stability test of physical/chemical properties of TCO (transparent conducting oxide) under weather environment stress is required. Flexible tandem a-Si:H PV modules were produced. ZnO thin film was used for TCO. To verify the stability of environment stress, reliability test based on MIL-STD-883G was conducted. Efficiency was decreased after damp heat (85℃, 85%RH) stress. This study is about degradation mechanism by analyzing reaction mechanism due to the moisture of ZnO thin film which TCO material was used in flexible a-Si:H PV modules. For fault isolation, cell defect by using electrical parameters of PV and EL(electroluminescence) from I-V characteristic was analyzed. Among electrical parameters, Rs showed dramatic increase but Isc and Voc showed a little change. There was no hot spot or dead cell in cell. This result can tell that the resistance of ZnO was increased by moisture so it increased Rs of a-Si:H PV. The changing mechanism of physical/chemical properties of ZnO by Moisture was analyzed. ZnO properties were analyzed with efficiency degradation rate of a-Si:H PV. Efficiency degradation sample was made by virgin, -5%, -10%, -20% and -50% level. Resistivity, surface profile and change of physical/chemical structure are analyzed by XRD, XPS, Raman, AFM, TEM etc. ZnO degradation mechanism was analyzed through the analyzing result

4:10pm **C3-9 Growth Mechanism of Silver Chloride Nano Wires by Electrodeposition Route**, ***A.D. Derardja***, *S.S.M. Seghir Mechouar (seghirs@hotmail.fr)*, LaMSM, University of Batna, Algeria

The progress of nanotechnology requires a fundamental research on the growth modes which may include different interaction parameters. Indeed, the experimental observations would be more robust by theoretical understanding of the growth process and hence to predict and control the microstructures to be obtained. This work is an attempt to understand the growth mechanism of AgCl obtained through an electrochemical process at room temperature. In effect, nanowires of Agcl are obtained under low potentials in AC mode and the microscopic investigation by SEM reveals clearly a new morphology of the surface which may be described as a random nanosheets. We think that the most suitable theory in this case is based on the STRANSKI KRASTANOV method. Consequently, the way is open to determine new mechanical and physical properties.

Tribology & Mechanical Behavior of Coatings and Engineered Surfaces
Room: California - Session E3-2

Tribology of Coatings for Automotive and Aerospace Applications

Moderator: S. Dixit, Plasma Technology Inc., A. Gies, Oerlikon Balzers Coating AG, Liechtenstein, G. Doll, University of Akron

1:30pm **E3-2-1 Effect of Powder Manufacturing Methods on Aircraft Wear Coatings**, ***M. Froning*** *(marc.j.froning@boeing.com)*, Boeing Research and Technology, US **INVITED**

Thermal spray wear coatings are used extensively in jet engines and on aircraft structures. Traditionally Cr_3C_2-NiCr coatings have been used for high temperature wear applications, however their lower density and ability to produced quality coatings via air plasma spray has renewed interest for lower temperature internal diameter wear application. In this paper, five Cr_3C_2-NiCr powders with similar chemical composition but produced by different manufacturing methods (mechanically blended, agglomerated and sintered, plasma-densified, chemically clad, and gas atomized) were compared. The five powders were sprayed using a rotating air plasma system on a simulated internal diameter. The resulting coatings were evaluated for microstructure, microhardness, and phase composition. A comparison of results by manufacturing method is reported.

2:10pm **E3-2-3 Solid Particle Erosion Resistant Nanolayered CrAlTiN and Multilayered CrAlTiN-AlTiN Coatings**, ***Q. Yang*** *(qi.yang@nrc-cnrc.gc.ca)*, *R. McKellar*, National Research Council, Canada

Airborne particles ingested by gas turbine engines may cause severe erosion damage to compressor gas-path components, leading to structural and aerodynamic engine performance deterioration and, in extreme cases, causing engine failure. Applying hard coatings on airfoil surfaces is proven to be an effective approach to mitigating erosion damage to engine components. Nanolayered or multilayered coatings, because of their capability of tailoring the properties through modifications in the chemistry and architecture of layer constituents, have been explored as potential candidates for this specific application. In this study, nanolayered CrAlTiN coatings with different modulation periods, along with multilayered CrAlTiN-AlTiN coatings having different number of layers and different thickness of individual layers, were fabricated, characterized and evaluated. All the coatings significantly outperformed the CrN baseline coating in erosion resistance, and their performance was strongly affected by the modulation period of the nanolayered coatings or the layer architectural characteristics of multilayered coatings.

2:30pm **E3-2-4 Microstructure and Properties of WC-Co(-Cr) HVOF Coatings Obtained from Standard, Superfine and Modified by Sub-microcrystalline Carbide Powders**, *K. Szymański,* Silsian University of Technology, Poland, *G. Moskal (grzegorz.moskal@polsl.pl),* ***H. Myalska***, Silesian University of Technology, Poland

In this paper microstructure and basic mechanical properties of WC-Co coatings obtained by HVOF technique were shown. Two different feedstock powders of WC-Co 83-17 type were used for coatings deposition on a steel substrate. First of them was a standard powder of Amperit 625.074, second one was Inframat from category Infralloy™ S7400 superfine powder. Four different powders were used to modify coating deposited from Amperit 625.074. Sub-microcrystalline powders applied in order to modify standard WC-Co coating were as follow: WC, Cr_3C_2, B_4C, TiC. The aim of

investigations was to compare microstructure and some mechanical properties of coatings deposited from different types of carbides. An influence of sub-microcrystalline additions on basic mechanical properties of coatings was analyzed. the range of investigations included short characterization of feedstock powders by SEM, EDS, EBSD and XRD methods and theirs technological properties as well. Then deposited coatings were characterized. Overall quality, porosity, adhesion of coatings to substrate and theirs tendency to making cracks were analyzed.

Financial support of Structural Funds in the Operational Program - Innovative Economy (IE OP) financed from the European Regional Development Fund - Project No POIG.0101.02-00-015/09 is gratefully acknowledge.

2:50pm **E3-2-5 Corrosion and Tribological Properties of Thick Diamond-like Carbon (DLC) Coatings Deposited using a Meshed-PIID Process**, ***R. Wei*** *(rwei@swri.org), J. Lin, L. Caseres, V.Z. Poenitzsch*, Southwest Research Institute, US

In this paper, preliminary results of thick (up to 20 micrometer) diamond-like carbon (DLC) coatings are presented. These coatings were prepared using a meshed plasma immersion ion deposition (PIID) process. Carbon steel and 304 stainless steel, as well as Si wafer coupons, were used as the substrates. They were installed in a meshed metal cage and then processed using the PIID process. The meshed-PIID process is similar to that of a hollow cathode process in which a much higher current density can be achieved, and hence, a higher deposition rate and thickness can be achieved than the conventional PIID process. Four different DLC coatings were prepared, including: (1) a thin single-layered DLC (10 micrometer), (2) a thick single-layered DLC (20 micrometer), both derived from C_2H_2, (3) a multilayered DLC (SiC/DLC, 7.5 micrometer) derived from TMS/C_2H_2, and (4) a single-layered DLC variant (7.5 micrometer) derived from hexamethylsiloxane (HMDSO). The microstructure and morphology of the applied DLC coatings were analyzed using Raman spectroscopy, atomic force microscopy, and scanning electron microscopy. The hardness and modulus of elasticity were measured using nanoindentation technique. The coefficient of friction and sliding wear rate were evaluated using a pin-on-disc tester. The corrosion resistance of the coatings was studied using electrochemical impedance spectroscopy (EIS) and anodic-cathodic polarization tests. It has been observed that the thick DLC coating exhibited highest wear resistance, while the multi-layered coating exhibited the highest corrosion resistance. The principles for the increased wear and corrosion resistance and the potential applications of these DLC coatings will be discussed.

3:10pm **E3-2-6 MoSx/WC PVD Coatings for Harmonic Drive Gears in Space Applications Characterized by Vacuum Pin on Disc Tests and XPS**, ***C. Gabler*** *(gabler@ac2t.at)*, AC²T research GmbH, Austria, *A. Merstallinger*, Aerospace & Advanced Composites GmbH, Austria, *M. Jansson*, Harmonic Drive AG, Germany, *J.L. Viviente*, Tecnalia, Spain

One of the major issues for the use of devices in spacecrafts is the reduction of their mass and lowering power consumption. Harmonic drive gears provide these requirements since the high gear ratio possible, enables the use of small actuator motors (low mass and power). State of the art in harmonic drive technology is the grease lubricated gear. The drawback of these gears in space application is that the used lubricant tends to outgas which causes a reduction of the lubrication ability plus the resulting vapours can contaminate sensible surfaces e.g mirrors, which is even more defacing for the functionality of the respective devices.

The aim of the presented research work here was to apply solid lubrication in the field of harmonic drive gears for vacuum application. The main problem of coatings providing this lubrication is their durability under the high contact stress occurring in theses gears.

After discussing the specifications needed, a multilayer coating of nanoperiod of MoS_x/WC PVD coating with a WC interlayer between substrate and coating was selected. This coating was already tested in space on the ISS in the TriboLAB tribometer and is known for its good tribological properties under space conditions.

The coating was characterized in vacuum pin on disc tests with varying substrate material for pin and discs. This was important since also the condition of the substrate material is important for a successful coating and the components engaged in a harmonic gear, are manufactured out of materials with different properties (e.g. stiffness).

The main focus of this paper will be the surface analysis of the resulting wear tracks of the pin on disc tests and the characterization of reference samples of the MoSx/WC coating by XPS and the deduction of wear mechanisms of the MoSx/WC under space conditions.

3:30pm **E3-2-7 Tribological Behaviour of the Non-Hydrogenated Diamond-like Carbon (DLC) Coatings Against Ti-6Al-4V: Effect of Surface Passivation by Alcohol**, *S. Bhowmick,* ***A. Banerji****, A. Alpas (aalpas@uwindsor.ca)*, University of Windsor, Canada

The role of alcohol in the tribological behaviour of non-hydrogenated DLC (NH-DLC) coated M2 steel disks sliding against Ti-6Al-4V have been investigated. Pin-on-disk tests were performed in argon (0% RH) and ambient (40% RH) atmosphere and while the samples were submerged in water and ethanol. The running-in friction behaviour of the NH-DLC coatings under each condition was studied. The highest coefficient of friction (COF) of 0.55 was observed for tests conducted under an argon atmosphere. A slightly lower running-in COF of 0.43 was observed for ambient air while the running-in COF reduced by 50% (0.21) in water due to OH passivation. Alcohol was more effective in providing OH passivation, as evident from the lowest running-in COF of 0.14. Based on the COF results, the NH-DLC coated drills were used in machining tests for Ti-6Al-4V; a 45% reduction in drilling torque and 75% reduction in thrust force were obtained when 10% alcohol was added to metal removal fluid (MRF) compared to an alcohol free MRF consisting of oil-water mixture.

3:50pm **E3-2-8 Diamond-like Carbon Nanocomposite Coatings to Mitigate Friction and Wear in Harsh Environments**, ***S.V. Prasad*** *(svprasa@sandia.gov), J.E. Mogonye*, Sandia National Laboratories, US **INVITED**

Diamond-like carbon (DLC) coatings exhibit an unusual combination of tribological and mechanical properties: low coefficients of friction and high hardness/high elastic modulus. However, synthesizing a single DLC material to achieve low friction and low wear in all environments (e.g., from ultra-high vacuum to humid air and from ambient to elevated temperatures) is a challenging task. Most commercial DLCs are either doped with metals, hydrogen or synthesized as nanocomposites. This talk will first provide a brief overview of the roles of chemistry and composition of multi-phase DLCs and nanolaminates in imparting environmental robustness. The role of substrate-coating interface reliability, specifically the onset of plastic deformation in the underlying substrate, on the tribological performance of DLCs will be discussed. In this context, finite element modeling was used to predict the contact stresses at which the transition from elastic to plastic deformation in a metallic substrate underneath a hard DLC coating occurs. Experimental data confirmed that accumulated plastic strains at the coating-substrate interface can lead to fracture and subsequent removal of the coating, highlighting the need for incorporating a load bearing nanolaminate underneath the DLC.

The second part of the talk will address the high temperature tribology of DLCs. A tetragonally bonded amorphous DLC and a silica doped diamond like nancomposite (DLN) coating were selected for this study. Friction and wear measurements were made at 300°C in lab air with a RH of 40-50% against a 440C steel ball in reciprocating sliding motion. Results indicate that the silica doped nanocomposite showed low friction (0.05-0.1) and low wear (2E-9 mm3/Nm) both at ambient temperature and at 300°C. Time of flight SIMS and Raman spectroscopy analyses of the interfaces, i.e., wear tracks and transfer films, were used to gain a fundamental understanding of the role of interfacial chemistry on friction and wear mechanisms, and to elucidate the "chameleon" nature of the nanocomposite.

* Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

4:30pm **E3-2-10 Micro-scale Abrasion Behaviour of Electroless Ni-P-SiC Coating on Aluminium Alloy**, *M. Franco,* ***W. Sha*** *(w.sha@qub.ac.uk), S. Malinov*, Queen's University Belfast, UK

Electroless nickel (EN) and electroless nickel composite (ENC) coatings were deposited on aluminium alloy substrate, LM24. The micro abrasion test was conducted to study the wear behaviour of the coatings with the effect of SiC concentration. Microhardness of the coatings was tested also. The wear scars were analysed using optical microscope and scanning electron microscope (SEM). The wear resistance was found to be improved in composite coating that has higher microhardness as compared to particles free and the bare aluminium substrate. In as-deposited condition for the composite coating, the wear volume increases on increase in SiC percentage in the coating but is found to be minimum for lower SiC percentage. The increase in hardness on heat treatment at 400°C is due to the hardening or grain coarsening with the formation Ni_3P.

Thin Films and Coatings for Fuel Cells & Batteries

Moderator: C. Ramana, University of Texas at El Paso, L. Lei, Shanghai Jiaotong University

1:30pm **F6-1 Surface Modification of Electrode Materials for Lithium-ion Batteries**, ***M. Julien*** *(christian.julien@upmc.fr)*, Université Paris-6, France, *A. Mauger*, UPMC, Paris, France, *K. Zaghib*, IREQ, Canada **INVITED**

While little success has been obtained over the past few years in attempts to increase the capacity of Li-ion batteries, significant improvement in the power density has been achieved, opening the route to new applications, from hybrid electric vehicles to high-power electronics and regulation of the intermittency problem of electric energy supply on smart grids. This success has been achieved not only by decreasing the size of the active particles of the electrodes to few tens of nanometers, but also by surface modification and the synthesis of new multi-composite particles. It is the aim of this talk to review the different approaches that have been successful to obtain Li-ion batteries with improved high-rate performance and to discuss how these results prefigure further improvement in the near future.

Currently, it is recognized that the main limiting elements of a Li-ion battery are the positive electrode materials which can be divided into three different families. One is the family of lamellar compounds obtained by the multi-ion substitution of transition-metal ions. The archetype of this family is $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ (NMC). The second family is the olivine group, the archetype of which is $LiFePO_4$ (LFP) for which coating the particles with conductive carbon has been a remarkably successful surface modification. The third family consists of compounds with spinel structure such as $LiMn_{1.5}Ni_{0.5}O_4$ (LMN), which is of great interest because it provides access to the Ni(IV)–Ni(II) formal valences at about 4.7 V *vs.* Li^+/Li. However, cathode/electrolyte surface reactions lead to degradation in the electrochemical performance.

Recent progress in the reduction in size of the active particles of the electrodes below 100 nm has increased the surface contact with the electrolytes, thus improving the power density of the Li-ion batteries. At the same time, however, the surface-over-volume ratio increases, so that the surface layer, as well as SEI effects, becomes increasingly important. Recent improvements for the positive electrodes have been obtained by well-crystallized surface layer of both lamellar compounds and olivine compounds. The increase of energy density with remarkable thermal stability has been achieved by $LiFePO_4$-coated particles working at higher operating voltage. The coating is protecting the inner core of the particles from contact and reaction with the electrolyte, which not only prevents the formation of a resistive SEI layer, but also increases the safety of the Li-ion batteries. In particular, the multi-composite particles open the route towards the 5 V operating Li-ion batteries will be presented.

2:10pm **F6-3 Experimental and Ab Initio Investigations on Textured Li-Mn-O Spinel Thin Film Cathodes**, ***J. Fischer*** *(Julian.Fischer@kit.edu)*, Karlsruhe Institute of Technology (KIT), Germany, *D. Music*, RWTH Aachen University, Germany, *T. Bergfeldt, C. Ziebert, S. Ulrich, H.J. Seifert*, Karlsruhe Institute of Technology (KIT), Germany

This paper describes the tailored preparation of nearly identical Lithium-Manganese-Oxide thin film cathodes with different global grain orientations. The thin films were produced by r.f. magnetron sputtering from a $LiMn_2O_4$-target in a pure argon plasma. Under appropriate processing conditions, thin films with a cubic spinel structure and a nearly similar density and surface topography but different grain orientation, i.e. (111)- and (440)-textured films, can be achieved. The chemical composition was determined by inductively coupled plasma optical emission spectroscopy and carrier gas hot extraction. The constitution- and microstructure were evaluated by X-ray diffraction and Raman spectroscopy. The surface morphology and roughness were investigated by scanning electron and atomic force microscopy. The differently textured films represent an ideal model system for studying potential effects of grain orientation on the lithium ion diffusion and electrochemical behavior in $LiMn_2O_4$-based thin films. They are nearly identical in their chemical composition, atomic bonding behavior, surface-roughness, morphology and thickness. Our initial ab initio molecular dynamics data indicate that Li ion transport is faster in (111)-textured structure than in (440)-textured one.

2:30pm **F6-4 Production of Core–shell Copper/Tin/MWCNT Composite Electrodes for Li-ion Batteries**, *M. Uysal*, Sakarya University, Engineering Faculty, Turkey, *T. Cetinkaya*, Sakarya University, Turkey, ***M. Kartal*** *(kartal@sakarya.edu.tr)*, Sakarya University, Engineering Faculty, Turkey, *M. Guler, A. Alp, H. Akbulut*, Sakarya University, Turkey

In this work, firstly core Sn/Cu composite powders were produced using an electroless process. Then, Sn/Cu/MWCNTs composite electrodes were prepared with dispersing different amount of MWCNT (10 wt. %, 20 wt.%, 40 wt.%) by high energy mechanical milling method. The surface morphology of the produced Sn/Cu/MWCNTs composite powders was characterized using scanning electron microscopy (SEM), and energy dispersive spectroscopy (EDS) was used to determine the elemental surface composition of the composites. X-ray diffraction (XRD) analysis was performed to investigate the structure of the Sn/Cu/MWCNTs composite powders. The electrochemical performance of Sn/Cu/MWCNTs nanocomposites studied by charge/discharge tests and cyclic voltammetry experiments. Cyclic voltammetry (CV) tests were performed for revealing the reversible reactions of tin with lithium. Galvanostatic charge/discharge (GC) measurements were carried out in the assembled CR2016 cells by using anode Sn/Cu/MWCNTs produced by electroless method

2:50pm **F6-5 Influences of Feedstocks on the Processes and Microstructures of the Flame-sprayed SOFC Anode**, ***H.C. Tseng***, *Y.C. Yang (ycyang@ntut.edu.tw)*, National Taipei University of Technology, Taiwan

This study is to fabricate a porous anode coating of solid oxide fuel cell by flame spraying technique. Flame spraying method, with a reduced thermal stresses and the advantages of easy process, is relatively low temperature in the manufacturing process. Since the low-temperature flame spray coating process, the initial selection of the feedstocks will affect the coating preparation. The anode of SOFC is a porous cermet material, therefore, choose Ni-based materials with yttria stabilized zirconia (8YSZ) as the raw materials. In this study, two groups of feedstocks were employed. One is prepared using spraying dried powder, NiO/8YSZ, Ni/8YSZ, NiO/8YSZ/Na2CO3 were included. Second is the commercial thermal spray powder, nickel coated graphite powder (Ni-coated graphite, NiGr) and 8YSZ powder. With different powder mix and spraying parameters used for anode coating preparation were studied. The results showed that NiO/YSZ powder can be obtained uniform, flat, small pores and good adhesion coating. Using Ni/YSZ powder can be obtained non-flat and multi-pores coating, which has bad adhesion with substrate. Using NiO/YSZ/Na2CO3 powders can be obtained uniform, non-flat, good adhesion coating, which can be increased porosity by removing pore former. Using commercial thermal powder of Ni-coated graphite can be obtained non-uniform, multi-pores and good adhesion coating, which can be created continues pore by oxidation treatment. Using ceramic YSZ powder can be obtained non-flat and bad adhesion coating. The above results show that use of NiO / YSZ / NiGr (1 : 1: 1 wt. %)powder, experimental parameters for the working distance 150mm, neutral flame parameters of preparation, can be obtained relatively smooth, uniform, and porous structure coating(30 - 40%)

3:10pm **F6-6 Li Ion Technology for Vehicle Electrification**, ***G. Dadheech*** *(gayatri.dadheech@gm.com)*, *M. Verbrugge*, General Motors Research and Development Center, US, *S. Sriramulu*, TIAX, Inc., US **INVITED**

Electric vehicles with high energy density Li ion batteries show great promise that can revolutionize the automotive industry in coming years. The success of lithium ion batteries would largely depend on its component material properties in order to achieve high energy, power, cycle life, abuse tolerance and cost. In this talk, we would discuss the developments and challenges of high capacity electrodes materials and the potential surface engineering approaches to overcome them.

3:50pm **F6-8 Improvement on the Corrosion Behaviour and Surface Conductivity of Coblast Coatings by Pack Cementation**, ***A. Oladoye*** *(atinuke.oladoye2@mail.dcu.ie)*, *J. Carton*, Dublin City University, Ireland, *A. Olabi*, University of the West of Scotland, UK

Stainless steel alloys offer many advantages over traditional graphite bipolar plates in proton exchange membrane fuel cells (PEMFC). However, low corrosion resistance and the resultant loss of surface conductivity of these alloys in the warm and humid environment of the PEMFC are major concerns. In this work, pack cementation was employed to enhance the functionality of graphite/alumina coatings deposited on AISI316 stainless steel alloy via a microblasting process named CoBlast™. The coatings were characterised and electrochemically polarised in 0.5M H_2SO_4 +2ppm HF at 70^0C while contact resistance was measured at room temperature. The results showed that the hybrid coatings formed at 900^oC showed about three order of magnitude reductions in the corrosion current and about fourfold decease in the contact resistance of the initial coatings at typical PEMFC

compaction pressure. The chromized coatings also exhibited better stability under PEMFC working conditions. These results are discussed in relation to the targets for bipolar plates.

Applications, Manufacturing, and Equipment
Room: Tiki - Session G5

Coatings, Pre-treatment, Post Treatment and Duplex Technology
Moderator: T. Takahashi, KCS Europe GmbH, Y. Chang, National Formosa University

1:30pm **G5-1 Selective Wear Protection of Forging Dies through Localized Plasma Duplex Treatments**, ***H. Paschke*** *(hanno.paschke@ist.fraunhofer.de), M. Weber,* Fraunhofer IST, Germany, *T. Yilkiran*, Institute of Forming Technology and Machines, Germany

During production processes hot forging tools are subject to complex load regimes (spectra), which are additionally acting localized depending on the geometry of the die. The resulting extensive wear is caused by simultaneously acting high mechanical, tribological, chemical and thermal cyclic loads.

The rapid failure of the form giving tool components is limiting the cost effectiveness of the processes. Hence there is a big interest in reducing the occurring wear.

Recent research results suggest the promising use of locally applied duplex processes consisting of plasma nitriding and plasma deposition techniques.

There were found process-related and geometrically depended wear mechanisms acting in selected zones of the dies. This can be the loss of the strength of the base material caused by annealing processes, abrasive and adhesive wear caused by the material flux and cracking in the surface near zone caused by mechanical and thermal cyclic loads. In order to increase the operating life of the forging tools there is a demand to adapt duplex treatments.

The nitriding as state-of-the-art treatment of forging tools shows an additional demand for further optimization. With respect to the appropriate load situation there are existing different possibilities in applying localized treatments by covering the tools mechanically. Thus, it is possible to obtain different intensities of the nitriding considering a two-step treatment. As a result, intense thermally loaded zones can be stabilized with intense nitriding while ductile material properties are maintaining crack sensitive zones.

The combination with newly developed vanadium doped chromium nitride or boron containing titanium nitride coating systems enables the reduction of abrasive and adhesive wear components. Both are thermally stable and reveal high hardness combined with friction reduction properties.

The presented duplex treatments are improving the properties of the surface and surface near zones of forging tools. Thus, this technology allows an economic and sustainable manufacturing process.

1:50pm **G5-2 The Boriding Process in CoCrMo Alloy: the Presence of Indentation Size Effect and Fracture Toughness on Cobalt Boride Coatings**, *I. Campos-Silva (icampos@ipn.mx), D. Bravo-Bárcenas*, Instituto Politecnico Nacional, Mexico, *H. Cimenoglu*, Istanbul Technical University, Turkey, *U. Figueroa-López*, ITESM-CEM, Mexico, ***M. Flores-Jiménez***, Instituto Politecnico Nacional, Mexico

New data about the fracture toughness (K_C) of cobalt boride coatings (CoB and Co_2B) were estimated from depth-sensing Vickers microindentation technique. The formation of the CoB and Co_2B coatings on the surface of the CoCrMo alloy was performed by the powder-pack boriding process at temperatures of 1223-1273 K with different exposure times for each temperature. The mechanical characterization of the boride coatings was divided in two procedures: first, Vickers indentations were conducted at constant distances from the surface using loads ranging from 15 to 450 mN. For all sets of experimental conditions, five acceptable indentations were carried out for each applied load to establish the behavior of the hardness (H) as a function of the diagonal length (d) and to verify the presence of the indentation size effect (ISE) in the boride coatings. Based on these results, the apparent or real hardness (H_o) of the CoB and Co_2B coatings was determined using the deformation band (DB) model. Second, the crack lengths developed on the corners of the indentations marks (with applied loads above 250 mN) were measured on both coatings using a scanning electron microscope (SEM).

Considering the indentation results in the set of experimental conditions of the boriding process, the K_C of the cobalt boride coatings were estimated using a universal crack equation applicable independently of the cracking mode. The results indicated that the CoB and Co_2B coatings exhibited two types of cracking modes (intermediate and radial-median, respectively), in which the fracture toughness of the Co_2B coating was ten-fold greater than the CoB coating.

2:10pm **G5-3 Pre-treatment of Polymer Based Substrates and High Rate Deposition of Silicon Dioxide Films Using a New Dual Magnetron Plasma Source**, ***P. Morse*** *(pmorse@sputteringcomponents.com), J. German, W. Meredith, D. Crowley, S. Williams*, Sputtering Components Inc., US

Large area surface modification and silicon dioxide deposition process parameters are explored for a new multi-function plasma source. The Dual Magnetron Plasma Source has demonstrated the ability to pre- treat several common polymer based substrates prior to vacuum deposition and deposit SiO2 films from HMDSO with high rates . The pre- treatment process results are reported and the process variables for the deposition process are statistically analyzed to determine the critical interactions.

2:30pm **G5-4 Influence of Nitriding Parameters on the Tribological Properties and the Adhesion of Ti- and Cr-based Multilayer Designs**, *W. Tillmann,* ***M. Dildrop*** *(markus.dildrop@tu-dortmund.de), T. Sprute*, TU Dortmund University, Germany

The growing competitive pressure in the industry makes the reduction of process costs increasingly important. One possibility to decrease the costs is to increase the life time of the tools by applying of wear resistant and friction reduced PVD coatings. Especially in the field of hot forming, tools are exposed to high mechanical and thermal loads. The special requirements of these tools can be met by multilayer systems such as Ti/TiAlN or Cr/CrAlN, which provide properties such as a high hardness, sufficient heat resistance, and smooth surfaces. However, varying hardnesses and different thermoelastic properties between the multilayer systems and the substrate can lead to the delamination and spallation of the layers. Using an upstream plasma nitriding process, it is possible to produce a hardness gradient between the basis material and the coatings, thus ensuring a sufficient supporting effect for the coating. In this work, the nitriding parameters were successively varied and the influence of the parameters on the material performance in the nitriding zone was examined. Afterwards, the adhesion of the applied PVD layers was investigated in dependency on the nitriding parameters. The PVD layers were deposited on tool steel substrates AISI H11 (1.2343) by means of magnetron sputtering. The mechanical and tribological properties as well as the adhesion of these coating systems were studied using a scratch tester, a nanoindenter, and a ball-on-disc test.

2:50pm **G5-5 The Powder-Pack Nitriding Process: Growth Kinetics of Nitride layers on pure iron**, *I. Campos-Silva (icampos@ipn.mx),* Instituto Politecnico Nacional, Mexico, *M. Ortiz-Dominguez*, Universidad Politecnica de Pachuca, Mexico, *M. Elias-Espinosa*, Itesm, Csf, Mexico, *M. Flores-Jiménez, L.F. Jiménez-Tinoco,* ***D. Bravo-Bárcenas***, Instituto Politecnico Nacional, Mexico

Nitriding is the process of surface nitrogen saturation in metallic materials, which is performed to improve the fatigue, corrosion and/or tribological properties. The nitriding on the surface of ferrous alloys results in the formation of a compound layer of γ′ and ε types nitrides or a mixture of γ′ and ε with a nitrogen diffusion zone beneath the nitride layer. The nitride (compound) layer can be beneficial for the resistance against wear and corrosion. The diffusion zone brings about a strong increase of the fatigue resistance and also increases the wear resistance. The broad range of properties of the nitride layer required by different applications needs the control of the nitriding process. In order to get an optimal result all the process variables have to be under control.

The powder-pack nitriding is a process analogous to pack carburizing. It employs certain nitrogen-bearing organic compounds as a source of nitrogen, in which the compounds used in the process form reaction products that are relatively stable at temperatures up to 843 K.

In this study, new data about the growth kinetics of (γ′ and ε) layers developed during the powder-pack nitriding process on the surface of ARMCO pure iron were estimated. The powder-pack nitriding of the pure iron was performed according to the Pulnieren© (H.E.F. Durferrit) method by using a "Pulnier"-powder and an activator, and was conducted at 773 – 848 K for different exposure times (2 – 12 h) for each temperature. In addition, according to the set of experimental variables of the nitriding process, three different "Pulnier" powder - activator mixtures (0.20, 0.25 and 0.30) were used to evaluate the activation level during the growth of the nitride layers.

The kinetics of the nitride layers over the surface of the ARMCO pure iron were estimated by two mathematical approaches, which consider the mass balance equations at the growth interfaces, the nitride incubation times, the parabolic growth constants, and the limits of the nitrogen concentration in

each nitride layers. The resulting expressions of the nitrogen diffusion coefficients in the nitride layers were evaluated as a function of the nitriding temperatures and the different powder-activator mixtures. Finally, the diffusion models were extended to estimate the γ′ and ε layer thicknesses at 798 and 823 K with 9 h of exposure for each temperature, based on the experimental parameters ascribed to the powder-pack nitriding process.

3:10pm **G5-6 Influence of Substrate Pre-treatments on Residual Stresses and Tribomechanical Properties of PVD Coatings**, *W. Tillmann, **T. Sprute** (tobias.sprute@tu-dortmund.de), D. Grisales*, Technische Universität Dortmund, Germany

The residual stresses before and after the deposition process of PVD coatings have a strong influence on the coating adhesion and lifespan of machining and forming tools. Therefore, the understanding and control of the system's residual stresses will lead to a better performance of the coated parts. Moreover, investigations have been conducted in the field of stress analysis of PVD coatings, yet they were not specifically focused on the interdependency of residual stress states in the coating and the substrate.

In this investigation, three different metallographically prepared substrate pre-treatments were used. SiC grinding, Diamond grinding, and SiC grinding and plasmanitriding preparations were selected, due to the substantial difference in their final residual stress state. Additionally, Ti/TiAlN multilayer coatings and a reference TiAlN monolayer were deposited on each pre-treated substrate.

Their initial and final residual stress states were measured by X-ray diffraction. In addition to the residual stress analyses, tribo-mechanical tests were conducted in order to correlate the results with the identified residual stress states. In order to complement the tribo-mechanical measurements, nano-indentation, ball-on-disc, as well as scratch tests were performed.

3:30pm **G5-7 Improvement of Coating Performance by Combining Different PVD/PACVD Technologies and Surface Treatments**, ***M. Eerden** (meerden@hauzer.nl), J. Landsbergen, D. Doerwald, M. Horstink, T. Krug*, IHI Hauzer Techno Coating BV, Netherlands **INVITED**

PVD and PACVD coatings offer surface engineering solutions in many applications, like in the tool, tribological and decorative fields. The combination of the PVD/PACVD coating with other surface treatments can improve the performance of the coated component. An overview of examples for different applications will be given.

A plasma nitriding pre-treatment of forming tools (duplex treatments) will improve the load bearing capacity for the PVD coating. Edge honing of cutting tools allows thicker PVD coatings and can clearly improve the lifetime of the cutting tool.

A polishing intermediate treatment has been found to be advantageous to improve corrosion resistance. The effect of the treatment on the corrosion resistance of Cr/CrN coated steel will be shown.

Polishing post-treatments are a well-known finishing for arc evaporated coated cutting and forming tools to reduce the roughness, improve friction and chip removal. Examples of polishing of sputter/PACVD coated components to reduce running-in effects will be presented as well.

4:10pm **G5-9 Effect of Mechanical Post-treatment Techniques on the Characteristics and Performance of Arc-evaporated AlTiN Coating in Dry Machining of Stainless Steel**, *A. Singh, **S. Gangopadhyay** (soumya.mech@gmail.com)*, National Institute of Technology Rourkela, India

The current study investigates the effect of mechanical post treatment techniques like micro blasting and polishing on the microstructure, mechanical properties and cutting performance of AlTiN coating deposited using cathodic arc evaporation on cemented carbide turning inserts. Post deposition micro-blasting is carried out on using Al_2O_3 granulates, where as polishing is done using fine grain polishing papers and diamond paste. Scanning electron microscopy (SEM) and X-ray diffraction (XRD) reveal grain refinement of micro blasted specimens. Hardness values of 31 and 34 GPa are obtained for as deposited and micro blasted specimens respectively. Rockwell indentation shows better adhesion (HF1) for micro-blasted carbide insert than its untreated counterpart. The polished tool does not reveal significant change in hardness and adhesion properties. Due to lower thermal conductivity and strain hardening tendency, machining of austenitic stainless steel (AISI 316 grade) has been a major concern. Therefore, the effect of mechanical post-treatment on tool wear characteristics of cemented carbide inserts is studied during dry turning of AISI 316 grade stainless steel. The results clearly demonstrate that the resistance to coating failure is enhanced for micro blasted insert. It is also observed that mechanical polishing results in improvement in adhesive wear where as the micro blasted tool significantly decreases abrasive and notch wear compared to as deposited AlTiN coating particularly during machining stainless steel at high cutting speed (180 m/min.).

Topical Symposia
Room: Sunset - Session TS5

Plasma Diagnostics and Modeling
Moderator: Y. Gonzalvo, Consultant, A. Hecimovic, Ruhr Universität Bochum

1:30pm **TS5-1 Erosion Characteristics of AlCr Composite Cathodes in Cathodic Arc Plasma with Inert and Reactive Gas Atmospheres**, ***R. Franz** (robert.franz@unileoben.ac.at)*, Montanuniversität Leoben, Austria, *P. Polcik*, PLANSEE Composite Materials GmbH, Germany, *A. Anders*, Lawrence Berkeley National Laboratory, US

In the field of hard and wear-resistant coatings, thin compound films based on the system aluminium and chromium represent the state of the art. With the addition of nitrogen and/or oxygen ceramic coatings covering a wide compositional range can be synthesised. In commercial applications, the deposition of these coatings is frequently done by means of cathodic arc deposition since high ionisation and deposition rates can be achieved that enable the optimisation of the film growth conditions and, in particular, the reduction of the process time. The employed cathodes are commonly composite cathodes containing both elements as such an arrangement facilitates easier process control and reproducibility. However, the plasma conditions in the cathodic arc plasma of composite cathodes and their erosion behaviour in the used gaseous atmospheres are scarcely investigated.

In the present study, AlCr cathodes with compositions of 100/0, 75/25, 50/50, 25/75 and 0/100 at.% were exposed to a cathodic arc plasma in Ar, N_2 and O_2 atmosphere. The cathode erosion was evaluated by analysing the cathode surface by means of light optical and electron microscopy. Due to periodic heating and cooling of the cathode's near-surface region in the cathode spots, an intermixing of the elements Al and Cr occurred. In addition, reactions of metal atoms on the cathode with gas molecules or atoms in N_2 and O_2 atmosphere resulted in the formation of nitride and oxide phases on the cathode surface, which is commonly referred to as cathode poisoning. Such phase formations were analysed by X-ray diffraction while the spatial distribution of the elements was characterised by scanning electron microscopy. The results regarding the cathode erosion are put in context with recently reported ion charge state distributions and ion energy distribution functions obtained with the same AlCr cathodes and gas atmospheres [1].

References:

[1] R. Franz, P. Polcik, A. Anders; *IEEE Transactions on Plasma Science* 41(8) (2013) 1929–1937

1:50pm **TS5-2 Plasma Characteristics of High Power Impulse Plasma Source (HiPIPS) For Low Temperature Diamond Growth**, ***V.Z. Poenitzsch** (vpoenitzsch@swri.org), R. Wei, J. Lin, K. Coulter*, Southwest Research Institute, US

Southwest Research Institute is currently developing a High Power Impulse Plasma Source (HiPIPS) that supplies a high flux of energetic reactants to a surface while maintaining a low processing temperature. Specifically, we have investigated the HiPIPS processing space using methane and hydrogen plasmas towards low temperature diamond thin film growth. Several complementary techniques, including threshold ionization mass spectroscopy (TIMS), secondary ionization mass spectroscopy, optical emission spectroscopy (OES) and electrical and thermal probes were employed, for measuring and calculating the plasma characteristics in a wide range of the HiPIPS process parameters and conditions. The preliminary HiPIPS experiments have revealed that high peak power (~40 kW) in the pulses can be achieved resulting in a high peak current (~200 A) and increased plasma density (i.e. n = •CH3:10^{16} $cm^{-2}s^{-1}$; H:10^{18} $cm^{-2}s^{-1}$) while maintaining a low average power (200W) and a low substrate processing temperature (50-150 °C). In this presentation, an overview of HiPIPS will be given with a specific focus on plasma characteristics and areas for further development.

2:10pm **TS5-3 Characterization of Transport of Sputtered Particles from Target to Substrate in Multiple Frequency Driven Discharges**, ***S. Bienholz** (bienholz@aept.rub.de)*, Ruhr-University Bochum, Germany, *S. Ries, N. Bibinov, P. Awakowicz*, Ruhr University Bochum, Germany

PVD processes have been of industrial importance over many decades. Various different concepts of capacitively coupled plasmas mainly magnetically enhanced are available. However, industrial chambers most often do not allow detailed process characterization using plasma diagnostics. Therefore, a large area capacitively coupled plasma was designed with several flanges for diagnostic purposes. As excitation concept, multiple frequency excitation is chosen to allow separate control of

ion flux and ion energy distribution at the target. Whereas, a very high frequency excitation, namely 60 MHz, only affects the plasma density and therefore the ion flux toward the target, the lower frequencies, namely 13.56 MHz and 27.12 MHz, set the bias voltage and therefore the ion energy distribution at the target. In addition, discharge geometry by means of electrode distance can be varied fairly simple.

In this contribution a complete plasma characterization including specially resolved electron density, electron temperature and gas temperature of an Al PVD process using Ar as a sputtering gas is performed by evaluating the optical emission detected with an absolute calibrated spectrometer. Also, the emission provides further information on Al density in the plasma. This data is compared to a model of the PVD process which includes TRIDYN simulations as well as drift models for sputtered particles. A comparison of the theoretical model and measured data is performed for various sputter conditions, to get a better understanding of the material transport of PVD processes. It can be shown that resputtering of deposited film at high substrate sheath voltages can significantly influence the metal density profiles in the plasma. By means of film analytic, deposition rates, predicted by the applied model, can be verified. In some cases, effective sticking of particles can be fairly low depending on the chosen conditions.

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2:30pm **TS5-4 Status and Challenges in Electrical Diagnostics of Processing Plasmas**, ***E. Stamate*** *(eust@dtu.dk)*, Technical University of Denmark, Denmark **INVITED**

Reactive plasmas produced in oxygen, nitrogen, hydrogen and other complex gas mixture are used for various applications including thin films, etching, ion implantation, ashing, particles growth, oxidation and other surface functionalization processes. Most of the reactive gases are also electronegative so that, the role of negative ions cannot be neglected. The continuous decrease of the features size in micro- and nanoelectronic industry requires a precise control of plasma parameters including the negative ions. Despite of a good progress in plasma diagnostics, yet more is to be done for developing techniques compatible with the strict requirements for device-making setups. Moreover the properties and possibilities to control the electronegative discharges are not completely understood. The aim of this work is to review the main electrical diagnostics techniques available to investigate reactive plasmas. Electrostatic probes have been used to diagnose electronegative plasma since 70's. While this technique can give good results for density ratios of negative ion to electron higher than 10 its applicability for lower density ratios is questionable. In this context is was demonstrated that double hump structures observed in the electron energy probability function close to plasma potential cannot be associated with negative ion parameters because those structures are produced by a particular change in the work function over the probe surface as a result of discrete ion focusing. Another way to detect the plasma parameters in the presence of negative ions is to use the sensibility of the test function in the mid and high energy tail of the distribution function. The presence of negative ions is also associated with a lower heat flux to the probe, a fact that led to the development of a thermal probe that allows one to record at the same time not only the current bias, but also a temperature bias characteristic. The recent discovery of the discrete and modal focusing effects, associated with three-dimensional plasma-sheath-lenses has created the possibility to detect even low densities of negative ions using the sheath-lens probe. The positive ion extraction from reactive plasmas is rather easy. However, this is not the case for negative ions. The influence of biased electrodes, of small or large dimensions on plasma parameters in electronegative discharges can give more information about the possibility to control and use these plasmas for processing. Development of reactive plasma sources for both applications and basic science is rather challenging and some of these efforts will be presented in direct correlation with diagnostic approaches.

3:10pm **TS5-6 Study of Substrate Heating during Reactive Magnetron Sputtering**, *J. Restrepo (johansrestrepo@hotmail.com)*, Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México,, Mexico, ***J. Cruz***, *S. Muhl, S.E. Rodil*, Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Mexico

Substrate heating by the plasma during magnetron sputtering is known to occur, however, there have been very few detailed studies of this process which involves a combination of bombardment by ions, excited and neutral species and UV radiation incident on the substrate. We have studied the heating of the substrate during DC magnetron sputtering of a 4" titanium target as a function of a variety of experimental conditions; plasma power, Ar gas pressure, floating, grounded and biased substrates. We have also studied the plasma heating during two reactive sputtering processes of the titanium target using a gas mixture of argon with either nitrogen or oxygen. It is known that the crystalline orientation of titanium nitride depends on the sputtering conditions, whilst titanium oxide prepared at low temperatures is normally amorphous. In this work we report the effect of the plasma substrate heating on the morphology and the crystalline structure of titanium oxide and nitride. The properties of the films were analyzed using EDX, SEM and X-ray Diffraction and the film thickness was measured using a stylus perfilometer. The measurements of the non-reactive sputtering showed that the substrate temperature could reach temperatures higher than 200ºC with a plasma power of 200W and showed a non uniform temperature distribution over the substrate, with the highest temperature in front at the race track and the lowest temperatures in front of the target edge.

3:30pm **TS5-7 Simulation of Magnetron Discharges and Modeling Approaches Towards HiPIMS**, ***A. Pflug*** *(andreas.pflug@ist.fraunhofer.de)*, *M. Siemers, T. Melzig, L. Schäfer*, Fraunhofer Institute for Surface Engineering and Thin Films IST, Germany, *A. Hecimovic, T. de los Arcos, J. Winter*, Ruhr Universität Bochum, Germany **INVITED**

In spite of its long term history and broad technical applicability, the dynamics of magnetron sputter discharges are not yet fully understood in all details. Recent high speed image processing experiments on High Power Impulse (HiPIMS) magnetron discharges reveal that the ring plasma of a PVD sputter source is not homogeneous but consists of several propagating plasma waves, which are also referred to as »spokes«.

In order to improve the knowledge of the inherent mechanisms, particle based simulation methods, namely »Direct Simulation Monte Carlo« (DSMC) for rarefied gas dynamics and »Particle-in-Cell Monte Carlo« (PIC-MC) for non-equilibrium plasma discharges are developed. In recent years, due to the increasing availability of high performance computing hardware and their exploitation by massive parallel algorithms, the feasibility of both methods even for large and complicated reactor geometries is significantly improved.

We present three-dimensional PIC-MC simulations of a circular magnetron source operating at DC power in Ar gas under different process conditions regarding power and total pressure. Even for moderate DC power levels we find similar propagating features in the simulated plasma which can qualitatively explain the experimentally observed spokes. By analyzing the electron and ion flux distributions, a more detailed picture about the role of the plasma fluctuations in the overall discharge dynamics is obtained.

Besides of the 3D PIC-MC discharge simulations, further approaches towards modeling different aspects of magnetron sputtering e. g. the gas heating effect in front of the target, transport of ionized sputter particles and the use of global models are discussed.

4:10pm **TS5-9 Time-resolved Plasma Diagnostics in Reactive High-power Impulse Magnetron Sputtering Discharges**, *N. Britun, M. Palmucci, R. Snyders,* ***S. Konstantinidis*** *(stephanos.konstantinidis@umons.ac.be)*, University of Mons, Belgium

It is now commonly accepted that the ionization rate of metal atoms is dramatically increased during High-Power Impulse Magnetron Sputtering discharges as compared to conventional DC magnetron plasmas. It is therefore assumed that the dissociation rate of molecular gases might also be significantly increased during reactive HiPIMS processes, hence leading to formation of a very reactive environment. In this study, titanium was sputtered in an $Ar+O_2$ gas mixture in a HiPIMS discharge. Several discharge parameters such as the pulse duration, discharge frequency, Ar pressure, etc. were examined.

In this contribution, we first show how it is possible to determine the absolute densities of metastable atomic oxygen atoms during the pulse ON and OFF times by utilizing resonant optical absorption spectroscopy (ROAS) technique. The photons corresponding to $2s^22p^3(^4S)3s - (^4S)3p$ transition ($\lambda \sim 777$ nm, the lower energy state is metastable) necessary for performing the ROAS measurements were produced in a microwave Ar/O_2 discharge and guided to the HiPIMS chamber by a fiber optics. ROAS measurements were carried out 5 cm above the sputter target.

It is demonstrated that the absolute densities vary in time and present a maximum after the end of the plasma pulse. Our results are consistent with relative density data reported by Vitelaru *et al.* (Appl. Phys. Lett. 103, 104105 (2013)) who used a laser spectroscopy method. The maximum of the density value measured in this work is $\sim 5 \times 10^9$ cm^{-3} for the 20 µs long pulse. Increasing the pulse energy allows for and increased dissociation rate of the oxygen molecules. The obtained results are compared to the time-resolved mass-spectrometry data obtained in the same system, as well as to the ROAS results corresponding to non-reactive HIPIMS.

4:30pm **TS5-10 Measuring and Controlling the Plasma in Pulsed Laser Deposition of Thin Films**, *S. Rajendiran, A. West, T. Gans,* ***E. Wagenaars*** *(erik.wagenaars@york.ac.uk),* York Plasma Institute, University of York, UK

Metal oxide thin films like ZnO, Al_2O_3 and TiO_2 are widely used in industry in microelectronics, catalysts and display devices. Plasma-based deposition techniques for the production of these films such as pulsed laser deposition (PLD), suffer from a lack of fundamental understanding of the underlying physical plasma processes and hence a lack of control of the deposited film properties.

This research focuses on establishing a detailed understanding of the plasma that is used for thin film deposition in PLD. This includes the interaction of the laser with the solid target, the creation of the ablation plasma, the expansion in the vacuum chamber or surrounding atmosphere and the plasma-surface interaction for film growth at the substrate. By employing a combination of plasma modelling and experimental diagnostic techniques such as laser-induced fluorescence and optical emission spectroscopy, we are able to accurately measure and subsequently predict the plasma properties such as species densities and temperatures, as well as the formation of the thin film in the plasma-surface interaction. This understanding will be used to tailor and control the Zn and ZnO plasma to obtain the desired film properties.

Additionally, a new form of PLD is introduced, plasma-enhanced PLD (PE-PLD). In PE-PLD we combine the laser-produced metal ablation plasma with an electrically produced oxygen plasma. With this method a Zn target is ablated which subsequently expands in an oxygen plasma rather than neutral oxygen gas. This oxygen plasma contains well-characterised and controllable, reactive oxygen species such as atomic oxygen, ozone and singlet delta oxygen. This method offers additional control of the Zn and O interactions and concentrations in the depositing ZnO plasma.

Coatings for Use at High Temperatures
Room: Town & Country and San Diego - Session AP

Symposium A Poster Session

AP1 The Corrosion Resistance of Fe-W-Cr-Nb Alloy, AISI 1020, 420 Coatings Produced by Thermal Spray, ***E.A. Lopez Covaleda*** *(ealopezco@unal.edu.co)*, *J.J. Olaya*, Universidad Nacional de Colombia, Colombia

Three materials were deposited over AISI-SAE 4340 steel using the wire arc thermal spray technique. The deposited materials are the alloy Fe, Nb, Cr, W and the traditional steels AISI-SAE 1020 and 420. With the aim of evaluating the best strategy for increasing the corrosion resistance in the coating-substrate system, the coatings were deposited in three different ways: (1) homogeneous monolayers of each material, (2) bilayers composed of a monolayer of the alloy over a monolayer of either 1020 or 420, and (3) simultaneous monolayer-type coatings achieved by depositing the alloy + 1020 in the first case and the alloy + 420 in the second case. The coatings were characterized by optical microscopy and X-ray diffraction. The corrosion resistance was evaluated using electrochemical impedance spectroscopy and potentiodynamic polarization.

It was found that the corrosion resistance in the fabricated coatings depends on the defect concentration in the microstructure and on the deposition strategy. For example, the resistance to polarization of the material deposited in bilayers was increased through the congestion of defects with corrosion products, while the simultaneous monolayers achieved increased corrosion resistance by the reduction of defects with respect to the alloy. The details and mechanisms of corrosion in the fabricated coatings are described in this study.

AP2 Influence of Deposition Process Parameters on the Durability and Stresses in Films AlCrN, AlCrN Based and AlCrN/TiSiN, used in the Milling Machining of Super-duplex, ***W. Mattes***, Centro Universitário Católica de Santa Catarina, Brasil, *S. Martins (saletealves@ect.ufrn.br)*, UFRN, Brasil, *J. Paiva Junior*, SENAI, Brasil

In this paper, we seek to know the performance of coated tools in milling machining in alloys with high content of chromium. When machining materials with these characteristics, the tool is exposed to high temperatures. In this type of situation, the coated tool should support the emergence of thermal cracks due to the continuous cycle of heating and cooling, as well as acting as a diffusion barrier and prevent wear mechanisms such as loss of coatings and chipping. Super duplex stainless steels are used in components for oil exploration in deep waters, the pre-salt layer, and demand for materials with high resistance to hydrogen embrittlement (H_2), carbon dioxide (CO_2) and hydrogen sulfide (H_2S). Thus, the use of super-duplex stainless steel is suitable for this application due to the high content of chromium and nickel, which gives the material high resistance to corrosion, suitable property requests imposed by the pre salt. Due to the high content of chromium and nickel present in these alloys, and it is a two-phase materials, the machinability of the material is made worse, especially for the low thermal conductivity of the material. Aiming at improving the machining process, this research studies the use of three coatings AlCrN, AlCrN based and AlCrN / TiSiN. Therefore, it was necessary to characterize the tribological behavior of the coatings proposed in this research, determining the values of adhesion of coatings on cemented carbide substrates, analyze the surface topography of carbide tools, before and after the deposition of coatings, determine the coefficient friction between super-duplex steel and cutting tools with and without coatings, analyze the cutting influence, fluid tribological behavior, super duplex steel and cutting tools. The results were, difficulties in Super-duplex machining, due to the large amount of austenite, low thermal conductivity and high rates of hardening strain, thus hindering the chip formation, resulting in high temperatures. The coating showed better AlCrN, based Accession, the pair AlCrN coating and stainless steel super-duplex showed the lowest friction coefficient. With the use of cutting fluid lower levels of coefficient of friction for the tribological pair. The burr formation during machining mechanical shocks generated in tool wear caused by plastic deformation. It is recommended that the cutting speed is increased in order to obtain a higher temperature in the shear zone chip, thus improving the chip flow in the secondary tool also recommend the use of tools with a cutting edge Positive thus should reduce contact between chip and tool.

AP3 Galvanic Corrosion Resistance of a Magnesium Alloy AJ62 and Carbon Fibre Coupling Improved by Plasma Electrolytic Oxidation Process, ***T. Cheng***, University of Windsor, Canada, *S. Cui*, University of Toronto, Canada, *X. Nie (xnie@uwindsor.ca)*, University of Windsor, Canada

Reducing fuel consumption and further protecting our living environment without compromising driving performance and customer comfort can be definitely achieved by the reduction of vehicle weight. Magnesium alloys and carbon fibre are two promising lightweight materials being researched and applied in the automotive industries for years. However, magnesium alloys exhibit very poor corrosion resistance, especially galvanic corrosion, caused by their chemically active nature. Carbon fibre is a very efficient cathode and very noble in the galvanic series. Therefore, contact between carbon fibre composites and metals (such as magnesium alloys) will be extremely undesirable. In this study, a plasma electrolytic oxidation (PEO) process in an environmentally friendly aluminates electrolyte was used to produce oxide coatings with thickness of 8~40 micron on AJ62 magnesium alloy. Galvanic corrosion behaviour between coupled carbon fibre and PEO-coated AJ62 magnesium alloys were investigated using potentiodynamic polarization and zero resistance ammetry (ZRA) methods in a 3.5 wt% NaCl solution. The morphology and composition of the coatings before and after corrosion tests were analyzed by Scanning Electron Microscope (SEM) and Energy Disperasive X-ray Spectroscopy (EDS). It was found that the PEO coatings may provide a promising solution for corrosion protection of the magnesium alloy when it contacts carbon fibre composite materials and thus explores more applications for the automotive industry.

AP6 Corrosion Inhibition of Mild Steel in Hydrochloric Acid Solution using Potassium Gluconate as Inhibitor, ***O.L. Akanji*** *(lukmanao@tut.ac.za)*, Tshwane University of Technology, South Africa

The inhibition effect of potassium gluconate on the Corrosion of mild steel in 0.5M HCl at ambient temperature has been studied by weight loss, polarization and electrochemical impedance spectroscopy(EIS) Measurement. morphology of the mild steel specimens were examined using scanning electron microscopy in presence and absence of inhibitors. the inhibition efficiency increased with increasing concentration of inhibitors. polarization curves reveal that the used inhibitor is a mixed type inhibitor, the adsorption of the inhibitor on the mild steel surface is in agreement with Temkin adsorption isotherm.

AP7 nc-TiN/a-SiN_x Thin Films Prepared by Means of High-Power Impulse and Pulsed–DC Magnetron Co-Sputtering, ***M. Arab Pour Yazdi*** *(mohammad.arab-pour-yazdi@utbm.fr)*, IRTES-LERMPS-UTBM, France, *F. Lomello*, LRC CEA-IRTES-LERMPS-UTBM, France, *F. Sanchette*, LRC CEA-ICD LASMIS, Nogent International Center for CVD Innovation (Nicci), UTT Antenne de Nogent, France, *F. Schuster*, CEA, France, *A. Billard*, IRTES-LERMPS-UTBM, France

nc-TiN/a-SiN_x coatings were synthesized by means a hybrid deposition technique of high power impulse (HIPIMS) and pulsed-DC magnetron co-sputtering. The coatings were processed employing two targets of Ti- and Si-connected to HiPIMS and pulsed-DC generators, respectively.

The discharge current on the Si-target was increased from 0 to 0.9 A whereas the deposition parameters of titanium were fixed at 2 A. As a result, the Si-content increased progressively from 0 to 19.72 at. %. The increase in silicon content allows to favour the amorphous SiN_x phase which is responsible for embedding the metal nitride.

Since matrix grain sizes evolved from 41 to ≈ 5 nm with increasing Si content, the hardness values followed the trend up to a threshold of about 40 GPa when grain size decreased around 7 nm corresponding to ≈ 10 at. % Si content. As a consequence, this phenomenon allows obtaining different wear behaviours in the tribological tests.

Similarly, the oxidation resistance was studied by submitting the samples to thermal annealing at 700°C in air atmosphere. After annealing, the mechanical properties strongly decrease but this softening is less pronounced as Si content in the films increases. Indeed, the sample containing the maximum content ≈ 20 at.% kept the hardness at ≈ 18.5 GPa whereas TiN hardnes was about only 12 GPa. This particular sample containing 20 at.% Si presented low rutile-TiO_2 content among the others, meaning an improved resistance to oxidation.

Finally, the samples were analyzed by SEM and TEM with the aim of studying the morphology and their microstructure evolution.

AP8 Isothermal Oxidation Behavior And Kinetics Of Thermal Barrier Coatings Produced By Cold Gas Dynamic Spray Technique, ***K.M. Doleker****, A.C. Karaoğlanlı (cahitkaraoglanli@gmail.com),* Bartın University, Turkey, *A. Turk*, Sakarya University, Turkey, *I. Ozdemir*, Katip Celebi University, Turkey

The cold gas dynamic spray (CGDS) and atmospheric plasma spray (APS) technologies were employed to deposit the CoNiCrAlY bond and *yttria-stabilized zirconia* (*YSZ*) top coats of a thermal barrier coating (TBC) system, respectively. The oxidation behavior of the coatings were investigated under isothermal oxidation at 1000 °C, 1100 °C and 1200 °C for 8, 24, 50 and 100 hours. Recent studies on TBCs have concentrated on CGDS process and its properties under working conditions. The motivation of this study is composed of the investigation of oxidation properties of TBCs produced using CGDS technique under service conditions and of determination of oxidation kinetic behavior on which there is only a few studies. Emphasis was placed upon the growth kinetic behavior of *thermally grown oxide* (*TGO*) and also its isothermal oxidation behavior. The results show that the isothermal degradation of coatings was considerably influenced by oxidation temperature, oxidation time, microstructure of coating and interfacial oxide growth rate.

Keywords: Plasma spraying, Cold gas dynamic spraying, Thermal barrier coatings, Oxidation, Thermally grown oxide

AP9 Pulsed Laser Deposition and Properties of TiAlN Thin Films, *E. Camps (enrique.camps@inin.gob.mx)*, ***J. Quiñones-Galvan***, National Institute for Nuclear Research, Mexico, *S. Muhl*, Universidad Nacional Autonoma de Mexico, *E. Garcia*, Universidad Nacional Autónoma de Mexico, *M. Flores*, Universidad de Guadalajara, Mexico

The substitutional incorporation of Al into the TiN lattice to form the ternary alloy TiAlN, has been seen to improve some of the properties of the TiN thin films, such as hardness and thermal stability. In the present work TiAlN thin films have been prepared by the simultaneous laser ablation of a Ti and an Al target in an Ar/N2 atmosphere. The film properties could be controlled by adjusting the plasma parameters, which were monitored using a planar Langmuir probe at the substrate position. The amount of Al incorporated in the TiAlN films was found to be, for a fixed titanium target-plasma, directly proportional to the density of the plasma formed during the ablation of the aluminum target. This study was restricted to relatively small amounts of incorporated aluminum up to 15 at%. The structural characterization of the deposits was carried out using X-ray diffraction and it was found that the films were highly oriented in the (111) direction of TiN. Small shifts of the diffraction peaks towards higher values of 2θ were observed and were correlated to the distortion of the TiN lattice due to the incorporation of Al. The hardness reached a maximum value of 40 GPa at an aluminum concentration close to 11 at%. The thermal stability of the films was studied by micro-Raman spectroscopy, in order to detect their transformation to one of the TiO2 phases, in the temperature range from 500 to 700 °C. The results indicated that the inclusion of aluminum, in general, led to an improved thermal stability. We also report the variation of the improvement of the friction coefficients and wear rate of the films as a function of the aluminum content.

This work was partially supported by CONACYT under contract No. 128732.

AP10 Diffusion Behaviour of NiAlRu Coatings on X750 Substrates, ***L. Fu***, *M. Weaver (mweaver@eng.ua.edu)*, The University of Alabama, US

In this present work, coatings with nominal composition Ni Al Ru and Ni Al Ru (at. %) were deposited onto X750 substrates by magnetron sputtering. Both coatings were found consist of γ-Ni(Ru, Al) and β-(Ni, Ru)Al phases. Isothermal oxidation at 1000°C and 1100°C produced rapid diffusion of Ru into the substrates and the formation of oxide precipitates within the coating layer. A semi- continuous α-alumina scale formed on the coating surfaces during oxidation. However, when oxidation times exceeded 50 hrs, significant degradation of the substrate was observed. These results suggest that oxygen can be diffuse into coating and substrate with Ru along grain boundaries and other defects within the coatings.

AP11 High Temperature Oxidation of EB-PVD TBCs on Pt-diffused Single Crystal Ni Superalloy, ***R. Swadzba*** *(rswadzba@gmail.com), J. Wiedermann*, Institute for Ferrous Metallurgy, Poland, *T. Jung*, Fraunhofer IST, Germany, *U. Schulz*, DLR - Deutsches Zentrum für Luft- und Raumfahrt, Germany, *L. Swadzba*, *B. Witala*, Silesian University of Technology, Poland

The paper presents the results of high temperature oxidation of EB-PVD TBCs deposited on a Pt-diffused second generation single crystal Ni-based superalloy. The Pt-diffused bond coating was obtained using a novel PVD method applying a Closed Hollow Cathode (CHC) for deposition of 5μm of Pt layer and subsequent annealing at 1140 °C for 2h in vacuum. The TBC system was thermally cycled in 1h cycles at 1100 °C for 730h until delamination of 10% of YSZ (Yttria Stabilized Zirconia) top coating. A non-destructive 3D optical scanning method was applied for a macroscopic examination of the YSZ delamination which allowed predicting and revealing of the regions of YSZ buckling prior to its spallation. The microstructure of the TBC system in the as-deposited and thermally cycled conditions was studied using FEG-SEM. The growth and evolution of the TGO (Thermally Grown Oxide) scale was performed using high resolution FEG-S/TEM and FIB methods. The TGO in the as-deposited condition was found to consist of porous α-Al_2O_3 which grew to form distinctive dense and columnar grains with ionic diffusion of reactive elements (Hf and Y) through grain boundaries during high temperature exposure. Additionally the formation of high volume oxides containing Ni was found to accelerate the spallation of the YSZ top coat.

AP12 Electric Arc Spray Coatings For The Naval Industry, ***L. Dimate*** *(lauradimate@gmail.com), J.J. Olaya, J.E. Alfonso*, Universidad Nacional de Colombia Bogotá, Colombia

Carbon and stainless steel, as well as Fe-Nb-Cr-W nanocomposite coatings were deposited over steel substrates using electric arc spray, and the feasibility of applying such coatings in the naval industry was analyzed. To achieve this, the microstructure before and after the tests was characterized to evaluate resistance to corrosion and abrasive wear, as well as the properties of the thermal barrier on the coatings produced. Corrosion resistance was analyzed by Polarization and Electrochemical Impedance Spectroscopy (EIS) tests using a NaCl electrolyte at 3 %; abrasive wear resistance was measured using a three-component system following ASTM G-65 recommendations, while state and quality control of the thermal barriers were studied using EIS tests. The microstructure of the coatings was characterized by Scanning Electron Microscopy (SEM), optical microscopy and X-ray diffraction (XRD).

In this paper correlation results for corrosion, abrasive wear and thermal barrier against microstructure are presented. It was concluded that 140 MXC is the coating which presented better properties regarding hardness, resistance to corrosion and abrasive wear, and thermal barrier properties; followed by 560 AS and 530 AS respectively. The importance of the substrate in the corrosion tests was determined, observing that the substrate has more alloy content, such as Chromium, to increase resistance to corrosion.

AP13 Effect of High-temperature Stress on the Hot-dipped Aluminide Mild Steel with NaCl Deposit, ***C.Y. Tung***, *C.J. Wang (cjwang@mail.ntust.edu.tw)*, National Taiwan University of Science and Technology, Taiwan

In this study, mild steel was coated by hot-dipping into a molten aluminum bath and salt spray. The effect of stress on the microstructure of the aluminide layer was investigated by applying free stress、stress than applied stress on the aluminide layer during diffusion at 750 °C in static air.

The results showed that the number of the void in the aluminide layer suffered stress is larger than in the aluminide layer of free stress. It can also be found that the thickness of the aluminide layer under applied stress is less than that of the aluminide layer without stress. This phenomenon can be attributed to the deformation of the aluminide layer caused by the applied stress, which in turn accelerated the formation of the void. From the observation of the morphology of crack in the aluminide layer, it revealed that the crack in the aluminide layer suffered low stress initial began at the void, which formed by the diffusion. While the aluminide layer suffered high stress, the crack was easily to form at the initial crack in both the aluminide layer and the tongue-like Fe-Al intermetallic layer. Salt spray specimens than hot-dip aluminum specimens have better tensile strength.

AP14 Microstructure and Oxidation Resistance of Ti-B, Ti-B-N, and Ti-B-N-Si Films Deposited by High Power Impulse Magnetron Sputtering, ***J. Kim***, *J. Jang, E. An, I.-W. Park (ipark@kitech.re.kr), D.-G. Nam*, Korea Institute of Industrial Technology (KITECH), Busan, South Korea, *Y. Kim, N. Kang*, Pusan National University, South Korea, *Y.-D. Park*, Dong-Eui University, South Korea

Nanocomposite coatings have been extensively studied due to their potential for achieving very high hardness, oxidation resistance and lubrication characteristics, in an effort to improve wear behavior of tools and components in several applications. Coatings containing nanoscale features may be produced by alternatively depositing nanolayers of different materials in a laminated structure or by co-depositing immiscible phases. Nanocomposite films produced by co-deposition may comprise only nanocrystalline phases (nc-nc) or nanocrystalline and amorphous phases (nc-a). The successful production of hard isotropically nanostructured films containing crystalline and amorphous phases depends on the appropriate size and distribution of these nanoscale phases. On the other hand, the oxidation resistance is a very important property for multicomponent and multiphase thin films that are especially designed for a wide variety of

applications, such as high temperature protective coatings and high speed cutting tool protective coatings. The present work investigates the co-deposition of Ti-B-N-Si nanocomposite films from a composite target of TiB_2 and a pure boron doped Si target using high power impulse magnetron sputtering in an Ar/N_2 gas mixture. The microstructure for the films were investigated in various Si contents and were evaluated by X-ray diffractometer (XRD), scanning electron microscope (SEM), X-ray photoelectron spectroscope (XPS), and high-resolution transmission electron microscope (HRTEM). The oxidation resistance studied here was conducted in an effort to understand the temperature dependent structural and compositional evolution of Ti-B, Ti-B-N, and Ti-B-N-Si films in an oxidizing atmosphere. Dynamic oxidation was studied using a Netzsch model STA-409C thermal analyzer with differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) in flowing air atmosphere.

AP15 Laser Surface Aluminizing of SAE 4340 Steel, *G. Vasconcelos (getuliovas@gmail.com)*, ***V. Teleginski***, *D. Chagas, R. Becker*, Institute for Advanced Studies, Brazil

In this work the laser coating of steel with aluminum powder was evaluated. A pre coating of aluminum powder was applied on samples of SAE 4340 steel by a pneumatic pistol and irradiated with a defocused CO_2 laser beam of 125W and 0.3mm diameter. The laser beam parameters (intensity and scanning speed) were adjusted to promote the solid diffusion of the aluminum powder on the steel surface. All the tests were performed using a N_2 gas to prevent the steel oxidation in the heat zone. X-ray diffraction analyses indicates the formation of a layer of iron aluminides of FexAly on the steel surface and Vickers hardness indentation in this layer presented $1100Hv_{0,01}$ with substrate hardness near to $280Hv_{0,01}$. The solid state diffusion in the steel surface was confirmed by EDS analysis.

AP16 Cyclic Oxidation Tests of Aluminide Coatings Produced by VPA Method on Directionally Solidified Ni Superalloy, ***B. Witala*** *(bartosz.witala@polsl.pl), L. Swadzba, M. Hetmanczyk, B. Mendala, G. Moskal*, Silesian University of Technology, Poland, *R. Swadzba*, Institute for Ferrous Metallurgy, Poland, *L. Komendera*, Subcarpathian Aviation Cluster, Poland

The oxidation resistance and failure mechanisms of different diffusion aluminide coatings developed by VPA were investigated. The results of cyclic oxidation test confirmed that the composition of the coating as well as the processing method can affect the life of the system. The study effort to evaluate the relative protectiveness of diffusion aluminide coatings. Coatings of each type were furnace cycled to failure in 23 h cycles at 1100 °C to assess average coating lifetime. The mass change diagrams were made to compare lifetime of different aluminide coatings. The results presented in this paper concentrate on microstructure and chemical composition changes and surface instability of the coating. The microstructural characterization involved use of X-ray diffraction (XRD), electron microscopy (SEM), chemical analysis in microareas (EDS) and glow discharge optical emission spectroscopy (GDOS).

AP17 Oxidation Resistance of Titania-doped Yttria-stabilized Zirconia TBC Coatings, ***S. Liscano***, *L. Gil (lindaegil@gmail.com)*, UNEXPO, Venezuela (Bolivarian Republic of)

High temperature coatings are used to prevent surface degradations or as thermal barriers against hot atmosphere. In this line, the present work studies the oxidation behavior of plasma sprayed titania-doped yttria stabilized zirconia (YSZ) TBC coatings. ZrO2–10% Y2O3–18% TiO2 coating and NiCoCrAlY bond coat were deposited on AISI A36 steel coupons by atmospheric plasma spraying (APS). Cyclic oxidation process in 4 h intervals was performed in an air electrical furnace at two temperatures: 800 and 1100 °C. During each cycle the specimens were cooled in the furnace. The mechanical properties of the coating were evaluated using microindentation hardness and bonding strength tests in as sprayed and after oxidation conditions. The microstructure and phase composition of the coating were characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD). It was observed that system ZrO2–10% Y2O3–18% TiO2 obtained a good performance for the temperature evaluated.

Key Words: titania- doped, YSZ, Plasma-sprayed, bond strength, microhardness.

AP18 Film Cooled Recession of SiC/SiC Ceramic Matrix Composites: Test Development, CFD Modeling and Experimental Observations, ***D. Zhu*** *(Dongming.Zhu@nasa.gov), B. Sakowski, C. Fisher*, NASA Glenn Research Center, US

SiC/SiC ceramic matrix composites (CMCs) systems will play a crucial role in next generation turbine engines for hot-section component applications because of their ability to significantly increase engine operating temperatures, reduce engine weight and cooling requirements. However, the environmental stability of Si-based ceramics in high pressure, high velocity turbine engine combustion environment is of major concern. The water vapor containing combustion gas leads to accelerated oxidation and corrosion of the SiC based ceramics due to the water vapor reactions with silica (SiO_2) scales forming non-protective volatile hydroxide species, resulting in recession of the ceramic components. Although environmental barrier coatings are being developed to help protect the CMC components, there is a need to better understand the fundamental recession behavior of in more realistic cooled engine component environments.

In this paper, we describe a comprehensive film cooled high pressure burner rig based testing approach, by using standardized film cooled SiC/SiC disc test specimen configurations. The SiC/SiC specimens were designed for implementing the burner rig testing in turbine engine relevant combustion environments, obtaining generic film cooled recession rate data under the combustion water vapor conditions, and helping developing the Computational Fluid Dynamics (CFD) film cooled models and performing model validation. Factors affecting the film cooled recession such as temperature, water vapor concentration, combustion gas velocity, and pressure are particularly investigated and modeled, and compared with impingement cooling only recession data in similar combustion flow environments. The experimental and modeling work will help predict the SiC/SiC CMC recession behavior, and developing durable CMC systems in complex turbine engine operating conditions.

AP20 In-situ Polymerization for Anti-corrosion Polyimide/Boron Nitride Hybrid Films with Different Polymer Configurations, ***Y.C. Huang***, *W.T. Whang (wtwhang@cc.nctu.edu.tw)*, National Chiao Tung University, Taiwan

A in-situ polymerization process is presented to synthesize anti-corrosion polyimide/boron nitride (PI/BN) hybrid films through different polymer configurations. Different configurations of polymer show the different crystallinity of PI/BN hybrid films. Rigid polymer shows high crystallinity water vapor transmission rate (WVTR). However, the crystallinity of rigid polymer decreased with increased BN content. On the contrary, The crystallinity of flexible polymers are the same with different BN contents. It should be noted that BN mixed into the different PI matrix can effectively enhance the corrosion protection performance on steel.

AP21 Characterization of Microstructure and Oxidation Resistance of Silicide Coatings on Mo, W and Nb, *G. Moskal (grzegorz.moskal@polsl.pl)*, ***S. Polis***, Silesian University of Technology, Poland

Characterization of microstructure of silicide coatings obtained during diffusion process of out-of-pack type was showed in this article. The basic materials were pure Mo, W and Nb sheets. The coatings were deposited in out of pack process with four different times of exposure. The temperature of deposition process was constant. In first step of investigations the phases compositions of coatings was described by XRD analysis. In each cases the silicide's of Mo, W and Nb respectively was revealed on top surface of the coatings. The morphology of the top surface of coatings was very similar as well. In all cases the coatings were characterized by presents of network of cracks. Additionally there was no influence of depositions time on phases constituent and coatings topography. LM and SEM analysis revealed that internal coatings morphology was very similar in each of types of coatings (for Mo, W and Nb respectively) independently to time of exposure. Basic differences was related to the thickness of coatings. All coatings were good quality without deep cracks. EBSD analysis revealed that microstructure of coatings was single –layered and a columnar-like type without pores and voids. There was to transition zone between coatings and basic materials. Oxidation resistant of silicide coatings was characterized during isothermal oxidation test at temperature 1200°C.

This work was supported by National Centre for Research and Development, project no PBS1/B5/3/2012 realized as a part of Applied Research Programme

AP22 Experimental Study and Numerical Simulation of Thermal Barrier Coating Systems with Thermal Cycling, ***J.G. Zhu*** *(zjg0511@gmail.com), W. Chen, Liu*, Jiangsu University, China, *H.M. Xie*, Tsinghua University, China

Thermal barrier coating (TBC) systems are widely used in industrial gas-turbine engines. However the premature failure has impaired the use of TBCs and cut down their lifetime, which requires a better understanding of their failure mechanisms. In this paper, experimental studies of isothermal cycling were carried out to evaluate how cracks occur and propagate according to the observation and estimation of microstructures. The results show that cracks initialize at the peak of TBC near the interface and propagate along the interface. Furthermore, a finite element model, based on an elastic-plastic theory, was established for stress analysis. Detailed residual stress distribution in the TBC was obtained to reflect the influence

of mechanical properties, oxidation and interfacial roughness on stress. The calculated results show that the maximum tensile stress concentration appears at the peak of TBC and continues to increase with the thermal cycles, which is helpful to analyze the failure mode of TBC in the experiments. Finally, a failure mechanism of plasma sprayed TBC system was proposed based on the numerical results and experimental data, which can provide a basis to develop a more accurate life prediction model.

Keywords: thermal barrier coating (TBC); experimental study; residual stress; finite element method; failure mechanism.

AP23 Hot Corrosion Studies of Thermal Sprayed Nanostructured Coatings Deposited by Mechanically Milled NiCrAlY Powder, ***N. Rana*** *(nidhiranathakur@gmail.com), R. Jayaganthan, S. Prakash*, Indian Institute of Technology Roorkee, India

The present investigation deals with the production of nanopowders of NiCrAlY from the commercially available bulk NiCrAlY powder through mechanical milling and use it subsequently as feed stock for the deposition of nanostructured coatings by means of Low Velocity Oxy Fuel thermal spray process (LVOF). The literature is scarce on hot corrosion behaviour of LVOF coatings. Hence, the hot corrosion behaviour of nanostructured NiCrAlY coatings at 900°C in the presence of $Na_2SO_4 + V_2O_5$ salt has been investigated under cyclic conditions, in the present work. The kinetics of the hot corrosion and its rate constant were evaluated by continuous monitoring of weight change, which occurs during degradation of coatings. The morphological and compositional features of the corroded coatings were analysed by XRD, FESEM/EDS techniques. It has been observed that the degradation of nanostructured coatings occurs significantly due to the migration of Na and V inside the coating. The present study confirms that that the nanostructured coatings with high porosity exhibit poor hot corrosion resistance as compared to its corresponding conventional coatings. The degradation mechanisms of coatings were substantiated through XRD and SEM results.

Hard Coatings and Vapor Deposition Technology
Room: Town & Country and San Diego - Session BP

Symposium B Poster Session

BP2 Investigation of Adhesion and Corrosion Properties of CrAlYN/CrY Multilayer Coatings Deposited by Unbalanced Magnetron Sputtering, *M. Tahmasebian Myandoab (tahma@atauni.edu.tr), I. Efeoglu, K.V. Ezirmik, E. Arslan, Y. Totik,* ***E.E. Sukuroglu***, Atatürk University, Turkey, *Ö. Baran*, Erzincan University, Turkey

Transition metal nitride coatings such as CrN and CrAlN are known for their excellent Tribological and corrosion properties. Adding yttrium to these coatings improves their oxidation resistance. Furthermore, CrAlYN coatings due to their outstanding mechanical properties and thermal stability are highly valued for various industrial applications. In the present study, CrAlYN/CrY multilayer films were deposited by unbalanced magnetron sputtering (UBMS) from two CrY and one Al targets. The structural properties of the coatings were analyzed by electron microscopy, X-Ray diffraction and energy dispersive spectrometry. Additionally, the adhesion properties of the coatings were evaluated via scratch tests. Corrosion properties of the coatings were investigated by potentiostat test unit.

BP3 DLAg and DLSiO Films with Good Tribological and Corrosion Resistance Properties for Aerospace Applications, ***F.L.C. Lucas***, Universidade do Vale do Paraíba, Brazil, *P.A. Radi, S.F. Fissmer*, Technologic Institute of Aeronautics, Brazil, *P.M.S.C.M. Leite, R.S. Pessoa, H.S. Maciel, L.V. Santos (lvs.lucia@gmail.com)*, Universidade do Vale do Paraíba, Brazil

About solid lubricant development for aerospace application, three issues are crucial to obtain good tribological performance: wear resistance related with fretting during the satellite launch, high adhesion on the substrate, and high lubricant life associated with low friction coefficient environment (less than 0.3) and its resistance in atomic oxygen.

This paper presents comparative studies on amorphous diamond-like carbon (DLC) containing silver nanoparticles (DLAg) and Silicon oxide bonds (DLSiO) obtained via automated plasma enhanced chemical vapor deposition (PECVD) using methane, silver cage, and Hexamethyldisiloxane, as carbon, silver, and silicon precursors. The films were produced in order to obtain repeatability and traceability on tribological behavior for aerospace use associated with high corrosion resistance in atomic oxygen atmosphere.

The DLAg and DLSiO were deposited on titanium alloy surfaces and the growth parameters (work pressure, temperature, discharge power, and duty cycle) were controlled to guarantee repeatability and traceability of the films. Friction, wear and adhesion tests were run out in a Bruker Tribometer. The corrosion resistance was evaluated by atomic plasma oxygen etching and chemical structure degradation was analyzed with Raman spectra.

BP4 Production and Characterization of Niobium Carbide Coatings on Gray Cast Iron by Termorreactive Difussion/Deposition, ***A.A. Amaya A.*** *(aaamayaa@unal.edu.co), O.E. Piamba Tulcan, J.J. Olaya*, Universidad Nacional de Colombia Bogotá, Colombia

Production research for industrial coatings from thermochemical processes plays an important role in materials science. Thermoreactive Diffusion deposition technique (TRD), to obtain homogeneous, continuous and resilient coatings for a simple procedures at cost.

The coating was deposited in gray iron pearlitic matrix with randomly distributed lamellar graphite and 3.5% total carbon percentage. The process was carried out in a salt bath of molten borax at 940 °C for 2 to 5 hours. Ferro-niobium is used as the carbide-forming element and aluminum as the reducing agent.

The coatings obtained were characterized by scanning electron microscopy (SEM), Auger Electron Spectroscopy (AES), and X-ray diffraction (XRD). SEM showed compact, continuous, homogeneous coatings and smooth interface. From XRD was observed with a composition consisting of NbC, with preferential orientation in the (111) and (200). From AES was verified the presence of Niobium at 167.7 eV and carbon at 266.8 eV mainly. It also determined a significant increase in the Vickers hardness of 510 to 2198± 97 Vickers for casting at niobium carbide coating. Finally, it was found that the corrosion resistance and adhesion to the substrate increases, when evaluated by the technique of potenciodimnamic polarization and resistance for Scratch respectively.

BP5 Radiation Exposed Hydrogenated Amorphous Carbon Films: Microstructure and Wettability, *K.C. Hofelmann, M. Partichelli, R.A.S. Zanon*, Universidade do Estado de Santa Catarina, Brazil, *C.A. Achete*, InMetro - Instituto Nacional de Metrologia, Brazil, ***J.M. Pureza*** *(pureza58@gmail.com)*, Universidade do Estado de Santa Catarina, Brazil, *M.M. Lacerda*, Universidade Federal do Rio de Janeiro, Brazil

Microstructure and wetting character of radiation exposed hydrogenated amorphous carbon (a-C:H) films were evaluated by Raman spectroscopy, by measuring their contact angle with water droplets and by calculating their surface tension. a-C:H films were deposited by plasma enhanced chemical vapor deposition (PECVD) at room temperature from pure acetylene (C_2H_2) gas used as carbon and hydrogen atoms precursor. Samples were exposed to ultraviolet and gamma radiation and to alpha particles. They were analyzed as a function of the deposition pressure that ranged between 13 Pa and 400 Pa. Their microstructures were analyzed at two Raman excitation wavelengths, 514.5 nm and 1064 nm. Results show that the a-C:H structure is formed by a combination of sp and sp^2 carbon-carbon bonds and sp^3 carbon-hydrogen bonds. Typical D and G bands at both excitation frequencies are presented in all spectroscopy data and different features could be observed depending on the Raman excitation energy. At green excitation an intermediate band between D and G bands and close to 1500 cm^{-1} can be accessed. It is associated to sp^3 carbon-hydrogen bonds. At 1064 nm a band close to 1850 cm^{-1} is an evidence of the presence of sp carbon bonds. As-deposited a-C:H film wetting character results show a very dramatic change in the contact angle between the surface and deionized water droplets. Samples deposited at C_2H_2 pressure as low as 26 Pa are hydrophilic, while those deposited at 400 Pa are super hydrophobic with contact angle above 160°. Post deposition radiation changes the surface tension of all samples; although modifications are dependent on the radiation energy. It changes the surface structure of the samples, but the bulk microstructure remains the same.

BP6 Reactive and Non-reactive Deposition of Al-Cr-N Coatings using Metallic, Intermetallic, and Ceramic Target Material, ***C. Sabitzer*** *(corinna.sabitzer@tuwien.ac.at)*, Vienna University of Technology, Austria, *S. Kolozsvári*, Plansee Composite Materials GmbH, Germany, *M. Arndt, R. Rachbauer*, Oerlikon Balzers Coating AG, Liechtenstein, *J. Paulitsch, P.H. Mayrhofer*, Vienna University of Technology, Austria

Physical Vapour Deposition techniques, like magnetron sputtering or arc evaporation, are highly valued for industrial applications to synthesize hard protective coatings with superior performance. Generally, powder metallurgically prepared targets composed of e.g. metallic Al and Cr particles are used in a reactive nitrogen atmosphere to deposit $Al_xCr_{1-x}N$. For both deposition processes, the influence of various deposition parameters – like partial pressure, gas mixture, or temperature – on the coating performance is well investigated, but only little information is

available concerning the impact of the target material itself. Therefore specially developed powder metallurgical prepared targets, with a comparable Al/Cr ratio, consisting of metallic Al and Cr, intermetallic Al_8Cr_5, and ceramic AlN and CrN powder were used to deposit $Al_{0.7}Cr_{0.3}N$ films. Furthermore, due to the possibility to use a ceramic target material comparative investigations on the influence of a reactive (Ar/N_2 atmosphere) and non-reactive (Ar atmosphere) deposition were carried out. Detailed analysis of the resulting microstructure, mechanical properties as well as thermal stability and oxidation resistance indicate a strong influence of the different targets used. Changing from the metallic target materials to the ceramic-like target and from reactive to a non-reactive deposition process the preferred orientation of the $Al_xCr_{1-x}N$ film can be altered from preferred (111) to (200). Further on, fracture cross sections indicate a more nano-crystalline-like morphology as well as a significantly increase in deposition rate from values between 11 and 16 nm/min to 23 nm/min, respectively, when using non-reactive deposition to prepare $Al_xCr_{1-x}N$. Hardness evaluations demonstrate that values around 25 GPa can be obtained when using the nitride target material, which is twice as high as for reactively deposited coatings from standard metallic Al/Cr targets using similar process parameters. Also, investigations on the thermal stability, especially with respect to the onset of Cr-N dissociation, indicate a clear shift of decomposition to higher temperatures for coatings prepared from optimized target materials.

BP7 Impact of Point Defects on Stability of $(Al_{1-x}Cr_x)_2O_3$ Phases from First Principles, ***C.M. Koller*** *(christian.martin.koller@tuwien.ac.at)*, Vienna University of Technology, Austria, *J. Ramm*, Oerlikon Balzers Coating AG, Liechtenstein, *P. Polcik*, Plansee Composite Materials GmbH, Germany, *D. Holec*, Montanuniversität Leoben, Austria, *J. Paulitsch*, *P.H. Mayrhofer*, Vienna University of Technology, Austria

A central subject of current protective coating development is the phase formation in low temperature physical vapour deposited, PVD, $(Al_{1-x}Cr_x)_2O_3$ coatings. Experimental results have shown that magnetron sputtered or arc evaporated coatings synthesised at temperatures as low as 500 °C usually crystallise in an amorphous or metastable face centred cubic based phases, like the defect-spinel γ- or the B1-type. This is however in contradiction to *ab initio* phase stability predictions, which suggest the desired and industrially important corundum type solid solution α-$(Al_xCr_{1-x})_2O_3$ to have lower energy of formation, thus being the stable phase and preferentially formed.

Within our investigations of three phases (corundum α, defect-spinel γ, and B1-like fcc) across all Al compositions, x, of $(Al_xCr_{1-x})_2O_3$ we find that the α solid solution is more sensitive to randomly generated defects than the γ-type and B1-type. We propose that these findings in addition to exceptionally high surface energies for certain terminations of the corundum structure can explain the favoured formation of γ- and B1-$(Al_xCr_{1-x})_2O_3$ during low temperature PVD processes, which generally lead to high defect densities and small crystallite sizes.

BP8 Synthesis and Characterization of Thin Films Doped with Cobalt by MOCVD, ***N.E. Mendez Lozano***, *L.M. Apatiga Castro (apatiga@unam.mx)*, Universidad Nacional Autonoma de Mexico, Mexico

In this work thin films doped with cobalt were prepared by Metal – Organic Chemical Vapor deposition. Photocatalytic activity of TiO2 particles has been investigated extensively because of their strong oxidizing power, high chemical durability, and nontoxicity. It is well known that nanometer-sized anatase particles with high crystallinity have a high photocatalytic activity [1]. However, the absorption wavelength of anatase ($\lambda \leq 385$ nm) does not fit with the solar spectrum; the solar energy above 3.0 eV ($\lambda \leq 410$ nm) is less than 5%.

In this study, thin films of TiO2 doped with cobalt deposited on glass and silicon substrates were synthesized using the technique of vapor phase chemical deposition from metal-organic precursors such as titanium isopropoxide and cobalt acetylacetonate , the films were doped with different concentrations of cobalt 2 %, 4% 6 %, 8% and 10 %.

With the synthesis and characterization of our material is achieving a better understanding of the synthesis methodology also improved to some extent on the different physical and chemical properties of the material. The crystal structure of all prepared samples were characterized by X-ray diffraction to confirm the existence of anatase phase of TiO2; Raman spectroscopy results were complemented observing the characteristic vibrational modes of TiO2 in its anatase phase.

The morphology and growth of the films was characterized by electronic microscopy (SEM) observed a flower-like growth in all samples. Finally the optical characterization of the samples was performed by UV-Vis spectroscopy obtained with these results a value of bandwidth allowed for each sample obtained and the relationship between the amount of impurities in each sample and its improvement in their electronic properties.

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BP9 Microstructure, Mechanical and Electrochemical Properties of Vanadium-Niobium Rich Carbide Layers Grown by TRD, ***F. Castillejo***, Universidad Santo Tomás Bogotá, Colombia, *J.J. Olaya (jjolayaf@unal.edu.co)*, *J.E. Alfonso*, Universidad Nacional de Colombia Bogotá, Colombia

Nb-V complex carbide coatings were produced onto AISI D2 steel by the thermo-reactive diffusion (TRD) process to improve the surface hardness and corrosion resistance of this tool steel. The carbide coating treatment was performed using molten borax added with ferroniobium, ferrochrome and aluminum at temperatures of 1223, 1293 and 1363 K during 2, 3, 4 and 5 h. The coating layers were characterized by optical and Scanning Electron Microscopy Microscopy (SEM), X-ray diffraction (XRD), energy-dispersive X-ray spectroscopy (EDS) and X-ray fluorescence spectrometry (XRF). The coating growth rates were studied, and a kinetically model of the layer thickness as a function of the treatment time and temperature was established. The hardness of the coating was measured by nanoindentation and its resistance to corrosion was evaluated with electrochemical tests of potentiodynamic polarization. The carbide layers produced a homogeneous thickness as well as an improved hardness and corrosion resistance as compared to the uncoated steel.

BP10 Electrochemical and Tribological Properties of Cr-Nb Carbides produced by TRD Process., *F. Alfonso (fabiocastillejo@usantotomas.edu.co)*, Universidad Santo Tomas, Colombia, ***J.J. Olaya***, *O. Piamba*, Universidad Nacional de Colombia Bogotá, Colombia

Niobium-Chromium carbide coatings were deposited by thermo-reactive diffusion (TRD) deposition technique on three different tool steels (AISI D2, 1045 and H13). The carbides were obtained using salt baths composed of molten borax, aluminum, and ferro-niobium or ferro-chromium. All steels were treated through TRD process performed at 1020 °C for 4 hours. The thickness and morphology of the coatings were characterized by optical and Scanning Electron Microscopy (SEM) and the crystalline structure was studied through X-ray diffraction (XRD). Chemical composition was evaluated by energy-dispersive X-ray spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS). Hardness of the coatings was measured by nanoindentation, and its wear resistance was studied by bole on disk test. The rate of corrosion was assessed with potentiodynamic polarization and the corrosion resistance was evaluated via electrochemical impedance spectroscopy (EIS) tests. The XRD results confirmed the formation of NbC and Cr_xC_y phases in all carbides. SEM results shows good homogeneity in the coatings thickness, and nanoindentation results showed that the coatings have higher hardness in comparison to the uncoated steel. XPS results indicated that the coatings are formed by carbides of chromium and niobium and the corrosion resistance is higher compared to the uncoated steel.

BP12 Corrosion Protection Coatings with Atomic Layer Deposition, ***E.M. Härkönen*** *(emma.harkonen@helsinki.fi)*, University of Helsinki, Finland, *S. Tervakangas*, *J. Kolehmainen*, DIARC-Technology Inc., Finland, *I. Kolev*, Hauzer Techno Coating B.V., The Netherlands, *B. Díaz*, *J. Swiatowska*, *V. Maurice*, *A. Seyeux*, *P. Marcus*, Chimie ParisTech (ENSCP), France, *M. Fenker*, FEM Forschungsinstitut Edelmetalle & Metallchemie, Germany, *L. Tóth*, *G. Rádnoczi*, Research Centre for Natural Sciences HAS, Hungary, *M. Vehkamäki*, *M. Ritala*, University of Helsinki, Finland

Atomic layer deposition (ALD) is a chemical vapor deposition (CVD) based method for growing thin films with high precision.[1] The growth proceeds through alternating and saturating surface reactions of two or more gaseous precursors. Because the precursors are pulsed in the reaction chamber alternately and separated by inert gas purging, excellent conformality even on high aspect ratio structures can be achieved. The films grow one atomic layer per cycle and thus both the thickness and composition can be controlled down to nm level. ALD thin films are known to have low defect density already at <10 nm thicknesses.

In the present work three types of ALD corrosion protection coating systems were studied on low alloy steel. Firstly, single 50 nm ALD coatings combining the excellent barrier properties of Al_2O_3 and chemical stability of Ta_2O_5 were considered. The aim was to optimize the coating structure for best sealing properties and durability. Secondly, a 10 nm filtered cathodic arc deposited (FCAD) film was grown under the optimized 50 nm ALD coatings. The FCAD layer homogenized the steel surface for a more ideal ALD growth, which led to improved protective properties. Thirdly, the conformality of ALD was utilized in sealing pinhole defects in physical vapor deposited (PVD) CrN coatings. The corrosion protection properties of

the coatings were studied with electrochemical measurements (LSV and EIS) and neutral salt spray (NSS) testing. Additionally, the morphology and composition of the coatings were analyzed to gain insight into the protection mechanism. The ALD coatings had excellent barrier properties, reaching a decrease of three orders of magnitude in the corrosion current density of the steel. The long-term durability of the single ALD coatings was found to be insufficient but could be improved with the FCAD sublayers. Moreover, the NSS durability of CrN coated steel could be increased from 2 to 168 hours with ALD sealing.

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BP14 Investigation of Hysteresis Effect and Influence of Bias Voltage during Deposition of HPPMS Aluminum Oxide Coatings, *K. Bobzin, N. Bagcivan,* ***R.H. Brugnara****, S. Basturk (basturk@iot.rwth-aachen.de),* RWTH Aachen University, Germany

Crystalline PVD alumina coatings offer a high potential for application as protective coating material on cutting tools due to their high hot hardness, high chemical inertness, high thermal stability and good wear resistance. Especially over the last decade the High Power Pulsed Magnetron Sputtering (HPPMS) technology has gained a growing interest. This technology offers possibilities to improve the coating properties such as microstructure and mechanical properties.

In the first part of this work the hysteresis behavior of Al target sputtered in a HPPMS discharge and a $Kr/Ar/O_2$ mixture was investigated for various HPPMS pulse lengths (30, 50, 100, 200 µs) at constant pulse frequency and average power in an industrial scale unit. Cathode current and voltage were recorded for the different pulse lengths. In a second step, aluminum oxide coatings were deposited on cemented carbide substrates at a constant pulse length of 50 µs and various bias voltages (-100, -200 and -250 V). The coating thickness and morphology are determined using SEM (Scanning Electron Microscopy). Hardness and Young's modulus were measured using nanoindentation. Phase composition was investigated by using XRD (X-ray Diffraction). Decreasing of pulse length from 200 to 30 µs at constant average power leads to a considerable increase of cathode current from 76 A to 468 A, respectively. It could be observed that the peak current has a strong influence on the amount of maximum allowable oxygen flow in the reactive process. Longer pulse lengths and so lower peak current allow a higher oxygen flow in the coating process compared to short pulses. The characterization of deposited coatings shows that at higher bias values a dense fine grained crystalline morphology is observed. However, a decrease of the deposition rate was observed with increasing bias from -100 V (1,26 µm/h) to -250 V (0,77 µm/h). Regarding the phase composition, peaks of crystalline γ-Al_2O_3 were detected for all deposited HPPMS aluminum oxide coatings.

Keywords: PVD, HPPMS, HiPIMS, Al_2O_3, aluminum oxide

BP15 Effect of Composition on Fracture Toughness of TiZrN Hard Coatings, ***Y.F. Chen****, J.-H. Huang (jhhuang@mx.nthu.edu.tw),* National Tsing Hua University, Taiwan

Fracture toughness is one of the most important mechanical properties for both bulk and thin film materials. For bulk materials, fracture toughness can be easily measured through ASTM standard procedures. In contrast, fracture toughness measurement of thin films is still problematic. Many kinds of testing methods have been developed and used to evaluate the fracture toughness of thin films. Recently, our group proposed an energy-based method without using the external stress, but employed the residual stress as the stress source to induce cracking. The proposed method has been applied on both TiN and ZrN hard coatings, and the results showed that the fracture toughness of random-textured TiN hard coating was 16.5 that was a reasonable value compared with previous literatures. On the other hand, the results of ZrN hard coatings showed an anisotropic variation with crystal orientation. In this research, TiZrN ternary nitride film was chosen for a model material because TiZrN is a single phase material when deposited at temperatures lower than 500°C. According to Griffith criterion, fracture toughness is the release of elastic energy that can create two new surfaces of a crack for brittle materials, which is associated with atomic bonding energy of the fracture surface. In TiZrN thin film, the bonding energy may change with Ti/Zr ratio, and thus composition may strongly affect the fracture toughness. The objective of this study was to investigate the effect of composition on the fracture toughness of TiZrN hard coatings. TiZrN coatings with different Ti/Zr ratio were prepared by unbalanced magnetron sputtering. Following our previous testing method, residual stress was used as the stress source for the toughness measurement, which could be measured by the laser curvature method. For the proposed energy-based method, the average storage energy (Gs) was evaluated from the residual stress before crack initiation, and then the fracture toughness (G_c) of the TiZrN coatings can be obtained from Gs.

Keyword: Fracture toughness, TiZrN, residual stress

BP16 Comparison of Corrosion Resistance of N-doped ZrO_2 Thin Films Deposited by HCD-IP and Grown by Heat Treating ZrN Thin Films in Vacuum, ***S.A. Chou****, J.-H. Huang (jhhuang@mx.nthu.edu.tw),* National Tsing Hua University, Taiwan

ZrO_2 is commonly used as a protective coating for metal substrates owing to its excellent corrosion resistance, while ZrO_2 coating is difficult to be deposited on the stainless steel because of the wettability problem. The purpose of this research was to overcome the wetting issue by producing ZrO_2 coatings on the stainless steel using ion plating or by heat treating ZrN coatings in vacuum. In this study, we used two approaches to deposit ZrO_2 films on stainless steel. One approach is to directly deposit ZrO_2 on stainless steel substrate using hollow cathode discharge ion-plating (HCD-IP) method, where the HCD-IP provided high ionization rate and solved the wetting issue. The other one was to deposit ZrN films on the stainless steel substrate, and then oxidize the ZrN films by heat treated the specimens in vacuum at 1000°C converting part of the ZrN to ZrO_2. The growth mechanisms of ZrO_2 are different in these two methods. In the former method, the ZrO_2 film grows in the way of the columnar grain growth from bottom-up direction. However, in the latter method, the ZrO_2 film grows inside the ZrN film from top-down direction and the ZrO_2 layer becomes nano-granular structure in the vacuum heat treatment. The 500-hr salt spray tests indicated that the ZrO_2 coatings produced by both methods shows excellent corrosion resistance. The corrosion resistance of the ZrO_2 films was further evaluated by AC impedance and potentiodynamic polarization scan. The AC impedance wa s undergone in the 1N H_2SO_4 and potentiodynamic polarization scan was carried out in 5% NaCl and in 1N H_2SO_4.

BP17 Effect of Processing Parameters on Wear Resistance and Mechanical Properties of Thick TiN Film on D2 Steel Deposited by Unbalanced Magnetron Sputtering, ***C.I. Chiu****, J.-H. Huang (jhhuang@mx.nthu.edu.tw),* National Tsing Hua University, Taiwan

Due to their excellent mechanical properties, t itanium nitride (TiN) coatings have been widely utilized in tool industry as wear resistant and protective coatings. The usage of hard coatings can not only protect the substrate, but also significantly extend the service life of the products. The major requirements of wear resistant coatings are high hardness with substantial thickness, a least a few mm. However, with the increment of film thickness, the internal residual stress may accumulate, and lead to film spallation. The objective of this study was to deposit thick TiN coatings (> 5mm) on AISI D2 tool steel substrates without using Ti interlayer, and to investigate the influence of different processing parameters on wear resistance and mechanical properties of the coatings. TiN coatings were deposited on AISI D2 steel substrates using unbalanced magnetron sputtering at different deposition parameter s. The main controlling deposition parameter s to produce thick TiN coatings were the opening of gate valve between turbomolecular pump (TP) and deposition chamber and the pumping speed of TP. The flux of argon and nitrogen was at a fixed ratio. X-ray diffraction (XRD) was used to determine the preferred orientation of the TiN films. The hardness of the TiN coatings was measured using nanoindentation. The residual stresses of the TiN coatings were determined by $\cos^2\alpha \sin^2\psi$ XRD and laser curvature method. The adhesion between the coating and substrate was evaluate d by scratch test. The influence of deposition parameter on wear resistance of the coatings was evaluated using pin-on-disk wear test. By adjusting deposition parameters, we could successfully produce thick TiN films on D2 steel with low residual stress and superior wear resistance. In addition, the deposition process consumed much less energy than traditional processes, and therefore the results will be useful for industrial appl ications.

Keyword: titanium nitride, AISI D2 tool steel, wear resistance, micrometer size

BP18 Effect of Substrate Bias on Structure and Mechanical Properties of Synthesis of (Ti, Zr)N Hard Coatings by DC Unbalanced Magnetron Sputtering, ***H.A. Chen****, G.P. Yu (gpyu@mx.nthu.edu.tw),* National Tsing Hua University, Taiwan

Ternary TiZrN thin films were deposited by DC unbalanced magnetron sputtering from dual guns(Ti,Zr) targets onto Si (100) substrates. In this work, we investigate the effect of substrate bias on the structure and properties of ternary TiZrN thin films (exchanging bias from -20V to -100V). The substrate bias primarily affected the properties and structure containing hardness, preferred orientation, packing factor, etc. Consequently, substrate bias is a sensitive factor for process parameters of TiZrN coating. The crystal structure and preferred orientation of TiZrN films were characterized using X-ray diffraction (XRD). Experimental results indicate that the preferred orientation of TiZrN films is changed from (200) to (111) with increasing substrate bias. Zr adatoms are re-sputtered more easily than Ti adatoms during film growth. However, the experimental results show that Ti / Zr ratio did not vary obviously with different substrate bias. The crystallinity and packing factor, which

associated with hardness, were enhanced by increasing substrate bias. TiZrN films had maximum hardness 32GPa as the bias voltage reached the critical value. Due to strengthening mechanism of the TiZrN are solid solution strengthening and grain boundary strengthening, the optimal solid solution strengthening effect(greatest inhomogeneous stain) can be obtained by controlling the ratio of Ti/Zr close to 1 for all the specimens. Both hardness and packing factor decreased as the bias voltage exceeded the critical value. Resistivity increased with increasing bias and with decreasing packing factor.

Keyword: Sputtering, Substrate bias, TiZrN

BP19 Effect of Temperature on Exchange Bias of $BiFeO_3$/FePt Bi-layer Films Epitaxial System Deposited by Radio-frequency Sputtering, ***L.C. Huang***, *G.P. Yu (gpyu@mx.nthu.edu.tw)*, National Tsing Hua University, Taiwan

The objective of the study is to investigate effects of temperature on $BiFeO_3$(BFO)/FePt epitaxial bi-layers system structure. In this paper, we prepared the BFO (10 nm) / FePt (10 nm) thin films epitaxially grown on (111) $SrTiO_3$ (STO) single crystal substrates and systemically study effect of deposition temperature of FePt. The formation of epitaxial films structure was confirmed from the x-ray diffraction and (00L) Bragg reflection of x-ray. A slight partial relaxation of out-of-plane strain in epitaxial systems was observed. Synchrotron radiation XRD results display c lear six fold symm etries and (111) FePt/BFO films by using (111) azimuthally sc an, unambiguously indicating that the present samples are epitaxially thin films. Large exchange bias of 150 – 360 Oe at room temperature were obtained for the epitaxial (111) FePt (10 nm)/BFO (10 nm) films at different growth temperatures (400 – 700 ºC). The exchange bias for the samples grown on (111) STO subs trate is high er than those of samples deposited on (100) STO substrate. An intuitive and reasonable explanation for this discrepancy is the surface spin configuration of BFO layer, because BFO (111) has an uncompensated surface and (001) has a compensated surface. With regard to temperature of FePt, there have exchange bias for the samples with FePt temperature below 600 ºC. As FePt temperature excesses the blocking temperature, the exchange bias decreases dramatically. The effect of surface roughness of BFO layers on exchange bias in the present samples was also investigated. In conclusion there has a large exchange bias on BFO/FePt bi-layers due to well epitaxial structure.

Keywords: epitaxial, BFO/FePt, excha nge bias

BP20 Closed Drift Type Circular Ion Source, ***J.-K. Kim*** *(kjongk@kims.re.kr), K.-T. Kim, Y.-J. Kang, D.-G. Kim, S. Lee*, Korea Institute of Materials Science, Korea

In the past, closed drift type linear ion sources have been developed for many vacuum treatments. We investigated closed drift type circular (4 inch) ion source because the circular ion source is useful to treat small samples briefly. The circular ion source also uses ExB drifting electrons and accelerates ions near anode surface. In this work, the effect of electrode gaps on ion extraction was investigated. The B-field distributions at the various gaps were analyzed by using 3D magnetic field calculations. 2D particle-in-cell calculation was used to predict ionization and ion acceleration. And the discharge current and ion current were measured when the two gaps of cathode-cathode and anode-cathode is varied. Typical discharge voltage was 1~3 keV and the average ion energy was almost 40% of the discharge voltage. The ion energy distribution was measured by using a retarding field energy analyzer.

BP21 Mechanical Properties of CrSiN Coatings by Cathodic Arc Deposition with Different Arc Currents, ***W.Y. Ho*** *(weiyuho@mdu.edu.tw), Y.S. Chang, B.Y. Chou, C.L. Lin,* MingDao University, Taiwan, *C.S. Hsu*, Tatung University, Taiwan

Several researches have been developed in order to evaluate the effect of Si addition on the properties of CrN thin films. Results showed that hardening is better explained by a solid solution mechanism with silicon concentrations varying from 2 to 10 at.%. In this study, CrSiN coatings were successfully deposited onto tungsten carbide substrates prepared by using cathodic arc deposition (CAD) technique with different arc currents at a low temperature. CrSi alloy target with the Cr/Si atomic ratio of 80/ 20 was used. Their structure and mechanical properties were investigated with various arc currents. CrSiN peak was clearly observed with the similar orientation of (111) and (200) peaks. The arc current can greatly influence the adhesion strength, surface roughness and hardness of the CrSiN coatings as the arc current increased from 90 A to 150 A. The difference of Si content between the coatings with different arc current is not clear. It was also found that a brief improvement of corrosion resistance was observable when increasing the arc current.

BP22 Optical Properties Of Tetrahedral Amorphous Carbon Films And Their Potential For Lab-On-A- Chip, ***K. Guenther*** *(guenthe2@hs-mittweida.de),* University of Applied Sciences Mittweida, Germany, *F. Sonntag,* Fraunhofer IWS, Germany, *S. Weißmantel*, University of Applied Sciences Mittweida, Germany

Several micrometer thick super-hard tetrahedral amorphous carbon (ta-C) films have been deposited by pulsed laser deposition (PLD) using an excimer laser (248 nm wavelength) onto polished tungsten carbide and silicon substrates.

The aim was to investigate the optical properties (e.g. the optical band-gap as well as the refractive and absorption index in the visible and near-infrared wavelength range) of these layers in dependence of the laser fluence on the target. It will be shown that the refractive index of 2 µm thick ta-C films varies between 2.3 and 2.8 at 632 nm wavelength in dependence of the sp^3-content. Besides the absorption index is as low as 0.03 at the highest sp^3 content of some 80 %.

The partial transparency of these ta-C layers in the visible range results in interference even at a film thickness up to 2 µm.

Furthermore, it will be shown that the ta-C films have low background fluorescence in the wavelength range of 380 - 750 nm, which may be used, as we are going to show, for optical and biotechnological applications.

One possible application is Lab-on-Chip (LOC). Thereby, the ultrasensitive detection of fluorescence markers and of dyes is one challenge in LOC applications. In order to increase the signal-to-noise-ratio, we developed a setup, which uses the specific optical properties of ta-C films produced by PLD. An integrated ta-C film based reflector combines the low background fluorescence, the low reflectivity at the excitation wavelength and the high reflectivity at the emission wavelength.

In this paper, we will show how we can improve the detection of fluorescence photons and with it the resolution of the fluorescence images by using ta-C films.

We will show that ta-C films, which are produced by PLD, have a high potential for optical applications.

BP23 Raman Study on Structural Changes of DLC Films Deposited on Curved Surfaces, ***J. Choi*** *(choi@mech.t.u-tokyo.ac.jp), T. Hatta, T. Kato*, The University of Tokyo, Japan

Bipolar-type plasma based ion implantation and deposition (bipolar PBII&D) is a promising surface coating technique for complex-shaped target surfaces. In this study, diamond-like carbon (DLC) films were deposited on steel rods with various radii of curvatures using bipolar PBII&D and the plasma behavior in surrounding of the steel rods (i.e., flux and energy of incident ions and electrons) was calculated using Particle-In-Cell Monte Carlo Collision (PIC-MCC) Method. The positive and negative pulse voltages varied from +1.0 to +1.5 and from -1.0 to -5.0, respectively. The structure of DLC films was evaluated by Raman spectroscopy and the hardness of DLC films was measured using nanoindentation. It was found from Raman and nanoindentation measurements that the structures of DLC films coated on the rod-shaped surfaces are different from those of DLC films coated on the flat-shaped surfaces, which are affected by the flux and energy of incident ions and electrons.

BP24 Effect of Amino Acid Additives on the Microstructure of Electrodeposited Nickel Films, ***T. Nagai***, *K. Hodouchi, H. Matsubara (maruma@analysis.nagaokaut.ac.jp),* Nagaoka University of Technology, Japan

20 kinds of amino acids were added to Ni electroplating bath in order to the effect on the characteristics of electroplated nickel films, i.e., surface morphology, film composition, crystal structure, and hardness.

Nickel films with higher hardness due to smaller crystalline size were obtained by the addition of basic amino acids, S-containing amino acids and certain aromatic amino acid.

BP25 Effect of Nb Content on Superelastic, Mechanical and Damping Properties of NiTi Shape Memory Thin Films, ***N. Kaur***, *D. Kaur (dkaurfph@iitr.ernet.in)*, Indian Institute of Technology Roorkee, India

In the present study NiTiNb shape memory thin films were fabricated at various Nb concentrations by Co-Sputtering of NiTi and Nb targets. The thin films were characterized in terms of structural, morphological, phase transformation, mechanical and damping properties by X-ray diffraction (XRD), atomic force microscopy, field emission scanning electron microscopy, four probe resistivity measurements and nanoindentation. The enhancement in mechanical properties is observed due to precipitate strengthening of Nb rich particles (β-Nb) in NiTi (Nb) matrix. The presence of large number of interfaces between NiTi(Nb) and β-Nb phase serve as important source of damping to dissipate the internal friction. NiTiNb thin films possess very low martensite start (Ms) temperature relative to

austenite start (As) resulting in wide thermal hysteresis and therefore has a large service temperature range. It exhibit excellent superelasticity at room temperature due to presence of complete austenite phase and can be used as new damping material for many room temperature applications.

Keywords: Co- sputtering, NiTi, Nanoindentation ,Superelasticity

BP26 Mechanical Properties of TiAlSiN Coatings by Hybrid Process, ***J.-H. Yang*** *(jhyang72@rist.re.kr), J.-I. Jeong, M.-A. Song, J.-H. Jung,* Research Institute of Industrial Science and Technology, Republic of Korea

Titanium aluminum silicon nitride (TiAlSiN) has unique properties such as high hardness, wear resistance, and oxidation resistance at relatively high temperature. Synthesis methods for TiAlSiN coatings are cathodic arc deposition and reactive magnetron sputtering etc. In this report, cathodic arc and magnetron sputtering (hybrid process) have been used for deposition of TiAlSiN films. TiAlSiN films have been deposited on stainless steel, high speed steel, and tungsten carbide substrate. Ti-50at%Al arc target of 120 mm diameter and Si sputtering target of 6 inch diameter have been used. The mixture of Ar and N_2 gas has been used for the deposition. Prior to the deposition, the substrate was cleaned by arc, which was created by only Ar gas, with -1000 V dc substrate bias. TiAlSiN coatings were carried out at R.T. and with -100 V dc substrate bias. TiAlSiN films have been investigated their morphology and mechanical properties. The hardness of the TiAlSiN film was ~34 GPa.

BP27 Electrochemical Characteristics of Heterostructural Nanolayer Tantalum Nitride Coatings, ***F.B. Wu*** *(fbwu@nuu.edu.tw), K.Y. Liu,* National United University, Taiwan

Tantalum nitrides, TaN, were deposited by magnetron sputtering technique with sequential crystalline and amorphous layer stacking to form heterostructurally nanolayer films. The single component TaN layers with amorphous and crystalline phases could be controlled by $N_2/(Ar+N_2)$ inlet gas ratio during fabrication. The amorphous TaN layer was formed under a $N_2/(Ar+N_2)$ ratio over 0.25, while the TaN layer crystalized at a ratio lower than 0.10. Sharp and intact interfaces between amorphous and crystalline layers could be observed through detailed microstructure analysis. Electrochemical tests, including potentiodynamic scanning and A.C.(alternating current) Impedance, were utilized to evaluate the chemical stability of the TaN nanolayer films. The single layer crystalline and amorphous TaN coatings were also investigated for comparison. The amorphous TaN layer exhibited a highest non-negative corrosion potential, E_{corr}, around 0.3 V, while the nanolayer coating with amorphous/crystalline stacking possessed a lowest corrosion current, I_{corr}, of $2.0*10^{-6}$ A/cm$_2$. Furthermore, the impedance of the crystalline TaN single nitride coating was enhanced by the heterostructural nanolayer feature.

BP28 Ab Initio Studies on the Adsoprtion and Adhesive Transfer of Al and Fe to Nitride Coating Materials, ***H. Riedl*** *(helmut.riedl@tuwien.ac.at),* Christian Doppler Laboratory for Application Oriented Coating Development at Vienna University of Technology, Austria, *J. Zálešák,* Montanuniversität Leoben, Austria, *M. Sobiech,* Oerlikon Balzers Coating AG, Liechtenstein, *P. Polcik,* Plansee Composite Materials GmbH, Germany, *D. Holec,* Montanuniversität Leoben, Austria, *P.H. Mayrhofer,* Vienna University of Technology, Austria

Computational studies such as finite element methods (FEM), molecular dynamics or *ab initio* calculations are integral parts of state of the art materials design. While FEM is commonly used to investigate flow behavior, strain and temperature profiles in various machining processes, this work focuses on utilization of *ab initio* calculations for an atomistic insight into material transfer phenomena during metal machining.

Material transfer from the workpiece onto the coated tool surface is generally considered as troublesome in machining operations, as the tool and/or work piece surface can severely lack quality over operational time. However, the material adhesion results from a complex interaction of machining conditions, workpiece and coating material. As one crucial parameter we focussed on the tribological contact between nitride coating and work piece material and employed *ab initio* calculations to estimate the chemical driving force for the formation of transfer material build-up at the coated tool surface.

We thereby investigated the adsorption energies of iron and aluminum with respect to different coating systems (TiN, AlN, TiAlN, TiSiN, CrN, and CrSiN) and were thus able to describe the energetic interplay between workpiece and coating material. The obtained results propose that especially Si containing coatings clearly decrease the adsorption energy for Al, but have less effect on Fe.

The present study introduces a methodology to thoroughly understand tribosystems at the atomic level, which further enables for an efficient coating material screening and selection as an alternative to cost and time consuming experiments.

BP29 Structure and Elastic Properties of Ternary Metal Nitride $Zr_{1-x}Ta_xN$ Alloys Thin films: Experimental Study and First-principles Calculations, ***P. Djemia*** *(djemia@univ-paris13.fr),* LSPM-CNRS, Université Paris 13, Sorbonne Paris-Cité, France, *Q.-M. Hu,* Shenyang National Laboratory for Materials Science, China, *M. Benhamida, K. Bouamama,* Laboratoire Optoélectronique et Composants, Ferhat Abbas University, Algeria, *L. Belliard,* UPMC, Paris,France, *G. Abadias,* Pprime Institute - UPR CNRS 3346 - Université de Poitiers - ENSMA - France

We investigated the structure and mechanical properties of ternary alloys thin films $Zr_{1-x}Ta_xN$ with $0 \leq x \leq 1$ deposited at Ts=300°C by reactive dc magnetron co-sputter deposition from individual Zr and Ta targets in $Ar+N_2$ plasma discharge. The total working pressure was fixed at 0.30 Pa by setting the Ar flow to 16 sccm, while the N_2 flow was adjusted to obtain stoichiometric nitride compounds. The structural properties of the ternary $Zr_{1-x}Ta_xN$ compounds were characterized by X-ray Diffraction and X-ray reflectivity, whereas the picosecond ultrasonic and Brillouin light scattering techniques were employed to measure their acoustic and elastic properties as function of the chemical composition. Density functional theory (DFT) within the generalized gradient approximation with both the virtual crystal approximation and the coherent potential approximation was employed to calculate the electronic structure as well as predict the evolution of the lattice parameter and elastic properties, including single-crystal elastic constants and polycrystalline elastic moduli, of ternary $Zr_{1-x}Ta_xN$ compounds with cubic rocksalt structure.

BP30 Morphological Transition of Fe Films on Si Substrates with an Fe_5Si_3 Intermediate Layer, ***C.C. Yu*** *(yucc@nuk.edu.tw), H. Chang,* National University of Kaohsiung, Taiwan, *C.T. Liu, W.C. Cheng,* National Taiwan University of Science and Technology, Taiwan, *Y.D. Yao,* National Pingtung University of Education, Taiwan

The delamination problem is an important issue in the field of semiconductor industry, especially in a system composed of semiconductors and metals. The metal hillocks usually form on the surface of semiconductor substrates during a post annealing and cause a delamination in the semiconductor devices. Many mechanisms, including surface diffusion, grain boundary diffusion and interfacial diffusion, have been reported. This mass transport phenomenon is mainly driven by the relaxation of compressive stress. In this study, utilizing thermal evaporation, Fe films were fabricated on Si(100) substrates under Ar ambient (~ $6x10^{-1}$ Torr). The distance between the Si substrate and the Fe source was kept at 7mm. The temperature of the iron source was monitored by a thermo spot meter and maintained at 980°C during deposition. The substrate temperature, detected by a K-type thermal couple attached on the back side of the substrate, was around 850°C during deposition. The film thickness was calculated by a cross-sectional SEM image. The nominal thicknesses of Fe films were 110, 220 and 330nm for the deposition time equal to 20, 40 and 60 mins, respectively. The morphological transition, structures and magnetism of Fe films on the Si(100) substrates with the Fe_5Si_3 intermediate layer was investigated for the first time.

During deposition, as indicated by the θ-2θ X-ray diffraction, a thin Fe_5Si_3(100) layer formed on the interface between the Si(100) substrate and the Fe(110) layer due to the high deposition temperature (~850°C) and a strong diffusion ability of iron adatoms. For the Fe film with a thickness equal to 110nm, towering Fe hillocks with average diameter and height equal to 520nm and 1.3μm, respectively, were found. The magnetization of the Fe film displayed a canted magnetic anisotropy due to the shape effect of the hillocks. For the 220nm-thick Fe film, instead of hillocks, irregular islands were observed. A magnetic hard axis obtained along the film normal indicated the formation of a continuous Fe layer. The morphological transition of the Fe films can be well understood by the competition between the bcc Fe lattice and the compressive stress applied by the Fe_5Si_3 layer. For the thin Fe film, the compressive stress drives the surface diffusion of Fe atoms and results in the formation of Fe hillocks. unlike the previous reports, the hillocks formed during the cooling from 850°C to room temperature. In contrast, the thick Fe film can resist the driving force from the underlying Fe_5Si_3 layer, but it displays irregular islands. For the 330nm-thick Fe film, a relative smooth surface was observed. It indicates a less strain effect from the Fe_5Si_3 layer.

BP31 Electrical and Reliability Characteristics of HfO_2 Gate Dielectric Under Oxygen Treatment, *Y.L. Cheng,* ***T.C. Bo*** *(S101323524@mail1.ncnu.edu.tw),* National Chi-Nan University, Taiwan

The electrical characteristics and reliability performance of high-*k* HfO_2 dielectric films under various oxygen treatment s are investigated in this study. The films deposited by an atomic layer deposition (ALD) technique using TEMAHf precursor and O_3 as the oxidant. For oxygen treatment, thermal or plasma method was performed before and after HfO_2 dielectric deposition. The experimental results indicate that irrespective of both oxygen treatment methods, the bulk HfO_2 layer remains unchanged, but a thicker interfacial layer was observed for the thermal oxygen treatment.

This leads to a better electrical and reliability performance for high-k HfO_2 dielectric with thermal oxygen treatment. On the other hand, in case of high-k HfO_2 dielectric with plasma oxygen treatment, although improved adhesion ability was observed, a larger stress-induced carrier generation or trapping was detected irrespective of pre- and post-treatments. This results in a degrading reliability performance with a much shorter TDDB lifetime. Therefore, plasma treatment should not use in fabrication of high-k HfO_2 gate dielectric.

BP32 Effect of Ion Irradiation on NI Films Prepared on a Flexible Substrate Material Using Unbalanced Magnetron Sputtering Assisted by Inductively Coupled Plasma, ***T. Koda*** *(m111302@cc.it-hiroshima.ac.jp), H. Toyota*, Hiroshima Institute of Technology, Japan

We fabricated Ni films on a flexible substrate material using unbalanced magnetron sputtering assisted by inductively coupled plasma. A Ni target with a purity of 99.95%, thickness of 5 mm, and diameter of 200 mm was used. Ar gas with a purity of 99.9999% was used as the sputtering gas. The Ar gas pressure was 2.7×10^{-1} Pa. The RF and target DC power were 30 and 700 W. The magnetic flux densities B_C on the center axis of the external solenoid were 0, 3, and 5 mT. The substrate DC bias voltages V_S were 0, −40, and −80 V. The Ni film was deposited on a polyimide substrate with an area of 15×15 mm^2 at room temperature. The film thickness was about 750 nm for all samples. To examine the effects of ion irradiation on the fabricated Ni films, we measured the emission spectrum of plasma and substrate current I_S by a spectrometer and an ammeter. The properties of the fabricated Ni films were measured by atomic force microscopy (AFM), X-ray diffraction (XRD), and a standard four-point probe method. From the result of emission spectrum, we found that the ArII peak increased with B_C and V_S. Moreover, I_S increased with B_C and V_S. I_S saturated above $V_S = -40$ V for each B_C. The value of the saturated I_S for B_C = 0, 3, and 5 mT was about 52, 180, and 270 mA, respectively. These results suggest that the plasma generated by RF power is expanded toward the substrate surface by B_C and that the ions are accelerated toward the substrate by V_S. We observed that the value of I_S, varied by controlling B_C and V_S, regulated the extent of ion irradiation. From the result of AFM, we confirmed that the average surface grain size D_G increased with B_C and V_S. For $V_S = -40$ V, D_G for B_C = 0, 3, and 5 mT was 88.2, 95.4, and 104.4 nm, respectively. We found that D_G of the fabricated Ni films increased with I_S. From the result of XRD, the (111) and (200) peaks are clearly visible for the fabricated Ni films. The ratio of the integrated intensities $I(111)/I(200)$ increased with V_S. Moreover, we confirmed that crystallite size t increased with I_S. We found that increase in I_S promoted the crystallization of the Ni films. The resistivity ρ of the fabricated Ni films decreased for increasing I_S. At B_C = 3 mT and $V_S = -40$ V, the measured ρ value of 8.96×10^{-6} ohm*cm was minimum. We determined that the structure of the fabricated Ni films on the flexible substrate material was affected by the values of I_S, varied by B_C and V_S. We conclude that sputtering with ion irradiation is effective for high-quality film formation on flexible substrate material.

BP33 Effects of Deposition Conditions on ZNO Thin Film Prepared Using RF Magnetron Sputtering, ***Y. Takiguchi*** *(m111305@cc.it-hiroshima.ac.jp), H. Toyota*, Hiroshima Institute of Technology, Japan

We fabricated ZnO films on a glass substrate by changing target RF power and Ar gas pressure using RF magnetron sputtering. We investigated the effects of deposition conditions on the properties of the fabricated ZnO films from the viewpoint of controlling plasma. A ZnO target with a purity of 99.99%, thickness of 3 mm, and diameter of 101.6 mm was used. Ar gas with a purity of 99.9999% was used as the sputtering gas. As the deposition conditions, we changed target RF power P_T and Ar gas pressure P_{Ar} in the range of 30-100 W and 0.1-1.1 Pa, respectively. The ZnO film was deposited on an alkali free glass substrate at room temperature. The sputtering time was 10 min constant. To examine the properties of the ZnO films fabricated for each deposition condition, we used atomic force microscopy (AFM), X-ray diffraction (XRD), a standard four-point probe method, and a spectrometer. Moreover, we investigated the effects of controlling plasma by the measurements of emission spectrum using a spectrometer. From the result of the emission spectrum, it was found that the peak intensity of Ar Ⅱ increased with P_T and P_{Ar}. Increase in the peak intensity of Ar Ⅱ indicates that the number of ions in the vacuum chamber increases. The thickness of the ZnO films T was changed for P_T and P_{Ar}. T increased with P_T, while T decreased for increasing P_{Ar}. From this result, for P_T, it was found that the deposition rate increased with the number of ions. From the AFM measurements, the average surface grain size D_G increased with P_T. For P_{Ar} = 0.1 Pa, D_G for P_T = 30, 50, 70, 80, and 100 W was 29.0, 33.8, 48.1, 42.6, and 61.2 nm, respectively. While D_G for P_{Ar} was about 47.4 nm constant. From these results, it was found that D_G of ZnO films was controllable for P_T. From the XRD measurements, the (002) and (101) peaks are clearly visible for the fabricated ZnO films. The ratio of the integrated intensities $I(002)/I(101)$ of the ZnO films decreased for increasing P_T, while the ratio of $I(002)/I(101)$ increased with P_{Ar}. We found that crystal structure of the ZnO films was controllable for P_T and P_{Ar}. We confirmed that the resistivity ρ of the fabricated ZnO films decreased for increasing P_T. In the range of 0.1-0.7 Pa, ρ decreased for increasing P_{Ar}, thereafter, ρ drastically increased at P_{Ar} = 1.1 Pa. At P_T = 70 W and P_{Ar} = 0.7 Pa, the measured ρ value of 2.4×10^{-3} ohm*cm was minimum. From the transmittance measurements, we confirmed that the average transmittance was more than 80% in the visible region from 380 to 850 nm for all samples. We found that the controlling plasma by changing P_T and P_{Ar} affected on the structure of the fabricated ZnO films.

BP34 Microstructure and Properties of Vanadium Nitride Hard Coating Prepared by Arc Ion Plating, ***T. Eom*** *(etk@taegutec.co.kr), M. Yoon, B. Song, C. Yun, S. Song*, TaeguTec, Republic of Korea, *B. Min*, Yeungnam University, Republic of Korea

Recently, high speed dry machining without coolant in the milling application is an important issue in the cutting tool industry to reduce the machining cost and the environmental problems.

One candidate for achieving this goal is deposition of PVD coating layer on the cutting tool which has the rigid low friction property for easy lubrication and high wear resistance in the high speed dry machining conditions.

For that reason, Vanadium Nitride (VN) hard coating has been widely investigated for various cutting tools applications as end mills, drills and various inserts, because of its excellent sliding wear resistance with low friction coefficient (μ=0.4).

Several previous studies have reported that low friction of VN hard coating is come from formation of surface oxide phase, such as V_2O_5, where the suitable heat and pressure generating conditions are satisfied, and self-lubrication by easy sharing of oxide phase.

In this study, VN films were grown on the commercial cemented tungsten carbide substrate via Arc Ion Plating (AIP) method. And the influence of nitrogen partial pressure and negative substrate bias voltage effects for the microstructure and mechanical properties of VN films were investigated. Additionally, the oxidation behavior of the VN coated layer was also evaluated.

Microstructure, phase and chemical bonding analysis of each coating layer are done by Transmission Electron Microscopy (TEM), X-Ray Diffraction (XRD) and X-ray Photoelectron Spectroscopy (XPS), respectively.

And a ball-on-disc type tribometer was used to identify the fiction characteristics and behaviours of various VN films at the dry sliding condition.

From the research results, VN hard coating in this study can be a potential candidate of the lubricious materials for improving the machining performance at high speed with the dry cutting condition.

BP35 Selective Textured Deposition of Ti(C,N), ***L. von Fieandt*** *(linus.fieandt@kemi.uu.se), M. Boman*, Uppsala University, Sweden, *T. Larsson, O. Alm, J. Lauridsen*, Seco Tools AB, Sweden, *J. Persson, E. Lindahl*, Sandvik Coromant R&D Materials and Processes, Sweden

Multilayer hard coatings are used routinely for metal cutting because they can withstand the extreme conditions that usually prevail. Such coatings need to be hard, have a chemical inertness towards the working piece and they must have an excellent adhesion. In the case of CVD coated cutting tools multilayer coating system is usually used where one or more components is composed of Ti(C,N), often in combinations with Al_2O_3. It is of importance to understand the nucleation and growth of Ti(C,N) on different substrate surfaces. By increased knowledge and control of nucleation and growth of Ti(C,N), properties such as wear resistance and adhesion can be tailored.

In this work growth of MT-CVD Ti(C,N) on (001) sapphire substrates has been studied by means of X-ray diffraction and electron microscopy. The coatings were extremely fine grained and smooth and were found to have a preferred orientation of (211) despite a large lattice mismatch with the (001) oriented substrate. However, a low intensity peak originating from the (111) plane was observed by XRD suggesting that, at an initial stage, the growth of Ti(C,N) was affected by the substrate. At a later stage, the process switched to growth in the <211> direction.

The reason for this two-step transformation is probably kinetically driven where growth in the <211> direction was favored by a fast growth rate and growth in the <111> direction was favored by an initial matching epitaxy to the sapphire substrate. By changing the process parameters to lower the growth rate, the initial epitaxial growth direction of the T(C,N) could be maintained and coatings having a growth along the <111> direction could be grown.

BP36 Reduction of Coercivity in Graded X/FePt (X=CoPt, FePd, FePt) Thin Films with Perpendicular Anisotropy, ***S.H. Liu***, Feng Chia University, Taiwan, *S.N. Hsiao*, National Synchrotron Radiation Research Center, Taiwan, *S.K. Chen (Skchen.fcu@gmail.com)*, Feng Chia University, Taiwan, *H.Y. Lee*, National Synchrotron Radiation Research Center, Taiwan

In recent years, $L1_0$-FePt (001)-oriented films have been intensively investigated because of their high magnetocrystalline anisotropy (K_u=7×10^7 erg/cm^3). However, the high anisotropy causes an unfavorable increase in coercivity, which may exceed the writing field of magnetic head. In this paper, we reported that the reduction of coercivity in graded (001) X/FePt films with different top-layers (X=CoPt, FePd and FePt). The 5-nm-thick top-layers were deposited on preheated $L1_0$-FePt (001)-oriented films at 500 ^{o}C. XRD patterns, exploited by synchrotron radiation, reveal that uniaxial (001) orientation of X/FePt films, due to only appearance of (00l) reflections. Magnetic properties of the films are analyzed using a vibrating sample magnetometer (VSM). Fig. 1 shows the out-of-plane hysteresis loop for the single-layer FePt, and X/FePt films. The coercivity (H_c) of the single-layered FePt film is 10.2 kOe. For FePt/FePt, FePd/FePt and CoPt/FePt films, the H_c are reduced to 2.4, 3.4 and 3.7 kOe, respectively. In term of saturated magnetization (M_s), the M_s of single-layered FePt film is 441 emu/cm^3. The M_s are increased when the single-layered FePt films are deposited the top-layers at 500 ^{o}C to form graded X/FePt films, which are 606, 650 and 545 emu/cm^3 with FePt, FePd and CoPt layer, respectively. In addition, the K_u of X/FePt films are 8×10^6 erg/cm^3 with FePt and FePd layer smaller than that of single-layered FePt films (K_u = 1.2×10^7 erg/cm^3) and CoPt/FePt film (K_u = 1.1×10^7 erg/cm^3). Compared to single-layered FePt films, a significant reduction of maximum H_c ~ 72 %. The H_c is reduced, because the X/FePt films are formed graded structure films. Based on the results of secondary ion mass spectroscopy (SIMS), the formation of graded structure in X/FePt films due to interdiffusion of top-layer and FePt layer was found. Accordingly, the change of magnetic reversal mechanism due to the microstructural evolution results in the reduction of H_c, which will be discussed in the full article.

BP37 Effect Of The Concentration Of V In Corrosion Resistance Of Vanadium Carbide Coatings Deposited By The Thermoreactive Deposition Diffusion Process (Trd), ***A. Orjuela***, *J.E. Alfonso (jealfonsoo@unal.edu.co), J.J. Olaya*, Universidad Nacional de Colombia Bogotá, Colombia

Vanadium carbide coatings onto tool steel AISI H13 and AISI D2 were obtained using thermoreactive deposition/diffusion process (TRD). Four different percentages of ferroalloy were used and Corrosion resistance of vanadium carbide layers was evaluated using potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) in a solution with 3.0% of NaCl . The microstructure was characterized by X -ray diffraction (XRD) and scanning electron microscopy (SEM). The results show that the coatings thickness increases between 2µm and 10µm with vanadium content. The corrosion resistance increases with increasing the percentage of ferroalloy. Coatings with 20% of ferrovanadium on AISI D2 had the highest corrosion resistance with respect to the layers analyzed. These details are discussed in this research.

BP38 Thermal Effects On Steels At Laser Method Of Separation, ***D. Manas*** *(dmanas@ft.utb.cz),* Tomas Bata University in Zlin, Czech Republic, *M. Manas*, Tomas Bata University in Zlin, Faculty of Applied Informatics, Czech Republic, *M. Stanek, M. Ovsik*, Tomas Bata University in Zlin, Czech Republic

As regards material separation methods, more sophisticated and effective methods are used today beside the classical ones. The new everyday development and changes of modern electronic technology and machine tool engineering brings new generations of many different products. Global development of these methods plays a vital role in the industrial process.

The cutting of material is usually the first operation that has to be done when producing some component. There are different types and methods of steel cutting. The most common methods of material splitting are cutting by water jet, laser, plasma and flame. In some cases, the heat caused by cutting influences the outer layers of the processed material.

Among two other common methods of cutting there are cutting by tools with defined geometry and abrasive processing – such as grinding or sanding. Some progressive methods could be also applied using physical, electrical and chemical processes as well as other sources of energy for removal of the material.

All these methods of material splitting force us to explore their impact to the qualities of cut material, especially to the layer that is in direct contact with the cutting tool. Learning about changes in structure and qualities of processed materials could assist in development of material separation and processing technologies.

The submitted article describes the effects of a thermal separation of material on the properties of the surface layers. The separation of material is an integral part of a preparation of all final products. During cutting the surface layer of the separated material is effected, which then has an influence on the sequence of the following operations. Laser method of thermal separation of material was selected for the experiment described in the article. The material selected for laser method of separation was a common steel CSN 411 373, which is industrially produced and processed. The effect on the material was shown by measuring instrumented microhardness tests using a Micro Combi Tester, CSM Instruments (Switzerland) according to the standard CSN EN ISO 6507-1.

BP40 Production and Characterization of Vanadium Carbide Coatings on Gray Cast Iron by Termorreactive Diffusion / Deposition, *A.A. Amaya A. (aaamayaa@unal.edu.co), J.J. Olaya*, ***O.E. Piamba Tulcan***, Universidad Nacional de Colombia Bogotá, Colombia

Production research for industrial coatings from thermochemical processes plays an important role in materials science. Thermoreactive Diffusion deposition technique (TRD), points to obtain homogeneous coatings, continuous and resilient simple procedures at cost.

The coating was deposited in gray iron pearlitic matrix with randomly distributed lamellar graphite and 3.5% at total carbon. The process was carried out in a salt bath of molten borax at 940 ° C for 2 to 5 hours. Ferro-Vanadium is used as the carbide-forming element and aluminum as the reducing agent.

The coatings obtained were characterized by scanning electron microscopy (SEM), Auger Electron Spectroscopy (AES), and X-ray diffraction (XRD). SEM showed compact, continuous, homogeneous coatings and smooth interface. From XRD was observed with a composition consisting of VC, with preferential orientation in the (222) and (400). From AES was verified the presence of Vanadium at 471,8 eV and carbon in 266.8 eV. It also determined a significant increase in the Vickers hardness of 510 for a casting to 2506 ± 46 Vickers for Vanadium carbide coating. They found values of surface roughness of 694 microns.Finally it was found that the corrosion resistance and adhesion to the substrate increases, when evaluated by the technique of potenciodimnamic polarization and resistance by the Scratch.

BP41 Effect of the Concentration Of Nb In Corrosion Resistance Of Niobium Carbide Coatings Deposited by the Thermoreactive Deposition Diffusion Process (TRD), *A. Orjuela (faorjuelag@libertadores.edu.co)*, ***R. Rincón***, Fundacion Universitaria Los Libertadores, Colombia, *L. Ardila*, Universidad Nacional de Colombia Bogotá, Colombia

Niobium carbide coatings were deposited on low alloy steel AISI 1045, through thermoreactive deposition/diffusion technique (TRD). Corrosion resistance of niobium carbide coatings was evaluated using potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) in a solution of NaCl 3.0% varying the percentage of ferroniobium in the TRD process. The microstructure was characterized by X-ray diffraction (XRD) and morphology was characterized by scanning electron microscopy (SEM). Chemical analysis of the layers was obtained by X-ray Photoelectron Spectroscopy (XPS), observing the formation of Nb2O5 layers. The results show that thickness of the carbide coatings not change significantly with increasing ferroalloy. Carbide coatings improved corrosion resistance with respect to the substrates; however, those results were not affected by the percentage of ferroalloy in the salt bath.

BP42 Characteristic of Multiferroic $BiFeO_3$/$LaNiO_3$ Superlattice Structures Prepared by RF Sputtering, ***H.Y. Lee*** *(hylee@nsrrc.org.tw),* National Synchrotron Radiation Research Center, Taiwan, *Y.T. Liu*, National Chiao Tung University, Taiwan

Artificial superlattice structures consisting of alternating epitaxial layers of materials with dissimilar physical properties offer exciting new possibilities both in the investigation of fundamental physical phenomena and in the exploitation of novel properties for diverse applications. In this work, symmetric epitaxial superlattice structures of multiferroic $BiFeO_3$ (BFO) and conductive $LaNiO_3$ (LNO) sublayers were grown on a Nb-doped $SrTiO_3$ substrate with rf magnetron sputtering at temperature 660 ^{o}C. The superlattices contained 6 – 30 periods of BFO/LNO bilayers with a sublayer thickness in a range 1.7 – 8.5 nm; the total thickness of the films was fixed at ~ 100 nm. We characterized the structure of the interface and the surface morphology of these films by measuring X-ray reflectivity and diffraction. The formation of a superlattice structure was confirmed from the appearance of satellite features on both sides of the main feature in the X-ray diffraction pattern. The periods and thickness of the superlattice confirmed by XRD and XRR are consistent with the results of SIMS. X-ray measurements show that these superlattice films become subject to greater tensile stress along the c-axis and increased compressive stress parallel to the surface plane with decreasing thickness of the sublayer.

The BFO sulayer in the artificial superlattice is under biaxial compressive stress whereas the LNO sublayer is under biaxial tensile stress. The smaller is the thickness of the sublayer, the greater is the crystalline quality and the strain state. The hysteresis loops show a large leakage current at frequencies 0.5 and 1 kHz; the polarization decreases with increasing frequency. An intrinsic remanent polarization of the superlattices was observed at the thickness of a sublayer in the range 1.7 – 8.5 nm at 5 kHz. The rounded shape of the hysteresis loop at frequency ≦ 2 kHz resulted from large dc leakage and extrinsic interface effects.

BP43 Evaluation of the Erosion-corrosion of Nanocomposite (Fe, 25Cr, 5B, 6Mo, 15W, 3Mg, 4C, 12Ni, 2Si) Deposited on AISI-SAE 4340. Steel through Thermal Spray Arc, *F.A. Laverde (falaverdem@unal.edu.co), **J.E. Alfonso**, J.J. Olaya*, Universidad Nacional de Colombia Bogotá, Colombia

The thermal spray are a technique of deposit coatings in industrial application for the dimensional recovery surfaces, improve properties corrosives and properties of wear, this technique is easy to apply in different metallic substrates because; the aderencia is done by assembling mechanical by molten particle-propelled by an air stream to speeds of 150 m/s , which is applied after which a pair of wires are melted by an electrical arc. With this technique are deposited coatings from Low Carbon alloys to high engineering alloys as you contain nanocoposites; is important the surface preparation according the NACE 01 for adequate adherence. We studied erosion-corrosion of Nanocomposite coatings (Fe, 25Cr, 5B, 6Mo, 15W, 3Mg, 4C, 12Ni, 2Si) and, stainless steel (Fe, 0.3C, 1Si, 1mn, 13Cr) alloy iron and cobal (Fe, 15CO, 0.8 Mn, 0.2Si), deposited through arc thermal spraying deposited on steel AISI- SAE 4340, each separately and a nanocomposite coating mixing the stainless steel and iron cobalt, respectively. We used the manufacturer's recommended settings in individual coatings and made approximation to the optimal parameters for mixtures, depositing layers of 1mm with a base layer of 95Ni, 5Al. The erosion-corrosion test was conducted in suspension composed of 3.5% NaCl and 10% Si with particle size 50-70 AFS in deionized distilled water and varying the speed and angle of impact at room temperature, we determinated electrochemical parameters from potentiodynamic polarization curves TAFEL in static conditions and under the influence of the jet The mechanism of failure was evaluated through SEM analysis and the surface chemical composition was analyzed by spectroscopy of electrons Auger (SAE).

BP44 Morphological and Electrochemical Characterization of $V_XNb_YC_Z$ Coatings Produce by Thermo-reactive Diffusion, ***S.A. Castro Hermosa** (sacastroh@unal.edu.co), J.E. Alfonso, J.J. Olaya*, Universidad Nacional de Colombia Bogotá, Colombia

The transition metal carbides have an unusual combination of physicochemical properties, the among best known are high melting temperatures and hardness, for instance, the vanadium carbide (VC) is a hard transition metal and exhibit some other properties like good corrosion resistance. In the same way, Niobium carbide (NbC) studies have shown that it has a good corrosion resistance at high temperatures. Nevertheless, the studies in production and characterization of ternary carbides of these transition metals (VXNbYCZ) have been very few. Therefore, the aim of this work is to present an experimental study of the structural evolution of VXNbYCZ coatings produced by thermo-reactive diffusion (TRD). The treatments were carried out in a molten mixture constituted of borax, ferro-niobium, ferro-vanadium and aluminum, at 1313 K for 3 hours, using a resistance heating furnace. The crystallographic structure of the coatings was determinated by X-ray diffraction (XRD), the morphology of coatings was observed by cross-sectional optical microscopy and the corrosion resistance was analyzed by potenciodynamic polarization test (Tafel Extrapolation). The XRD analysis shows that the coatings are polycrystalline. The optical microscopy exhibited that the coatings grew in homogeneous form with a regular thickness, and potenciodynamic polarization evidenced that the resistance corrosion enhancement with respect than the bare substrate, because the corrosion current (icorr) is less, and the corrosion potencial (Ecorr) is approximately equal to the reference electrode (SCE).

BP45 Influence of Magnetron Sputtering Conditions on WTi and Ta Thin Films: Microstructure-stress-electrical Conductivity Relationship, ***P.O. Renault** (pierre.olivier.renault@univ-poitiers.fr), E. Le Bourhis, A. Le Priol*, University of Poitiers, France, *P. Muller*, Sofradir, France, *H. Sik*, SAGEM Défense Sécurité, France

This study reports on the influence of sputter-deposition conditions on the structural, electrical properties of two refractory metallic thin films, namely WTi and Ta, and, for two different thicknesses (10 nm and 180 nm for WTi and 20 nm and 100 nm for Ta). WTi (resp. Ta) thin films have been deposited using a planar DC Magnetron sputtering apparatus from WTi alloyed target (70:30 At%) (resp. pure Ta target 4N) in pure Ar working gas. The working pressure ranged from 0.14 to 1.4 Pa, at constant power discharge (150 W for WTi and 300 W for Ta films), without substrate bias and external heating. Both materials if elaborated by PVD techniques, may exhibit two different crystallographic structures: α-phase (b.c.c.) and β-phase (which is cubic A15 for WTi and tetragonal Ab for Ta). The WTi films only show a α-W structure with a strong {110} fiber texture. On the other hand, Ta films require a sublayer of WTi (superior at 4 nm) to show the b.c.c. phase only. For both WTi and Ta thin films, a residual stress transition from tensile-to-compressive stress state has been observed as the working pressure increases. Stress transition is unaffected by thickness reduction for WTi films. On the contrary, residual stress is almost constant with working pressure for Ta ultra-thin films. The measurements have been performed ex situ by using Stoney and X-Ray Diffraction. The stress transition for both materials which have similar atomic mass should happen at roughly the same working pressure. The difference of stress-transition-working-pressure could be attributed to the different power discharge and/or the presence of the WTi sublayer in case of Ta films. Influence of working pressure on electrical properties has been revealed. The evolution of the electrical conductivity is directly correlated to working pressure for both materials as well as to the residual stress state. Thin films microstructure has been highlighted by FIB-TEM observations. WTi and Ta ultra-thin and thin films process-structure-property relations are studied and discussed in relation with the state of the art.

BP46 Influence of Reducing Agent on Electroless (Ni-P) Coating Process and Optimization of Process Parameters using Taguchi Technique, ***M. Rajaraman**, E. Rasu (elansezhianr@pec.edu)*, Pondicherry Engineering College, India, *T. Balaji*, M. tech, SRM University, India

This paper reports on the improving nickel recovery of electroless Ni-P coating process. At present in electroless nickel coating process the nickel recovery efficiency is only in the order of 25%. Remaining 75% of unrecovered nickel is present in the electrolyte bath as waste. Due to poor nickel recovery from the bath the coating cost of electroless nickel is very high. Hence in spite of having unique advantages of electroless nickel coatings such as improved hardness, wear and corrosion resistance, uniform coating thickness etc., the coating process is not much popular among commercial coating industries. To overcome the above problem an attempt is made in the present study to improve the nickel recovery of electroless coating process. Earlier researchers had tried to recover nickel from the used bath and some of them got success in their attempt by further improving the nickel recovery from 25% - 60%. However no attempts have been made to recover nickel during the coating process. First time in the present study the nickel recovery was improved during the coating process by adding excess amount of reducing agent from 25% to 100% in the bath. In order to find out the influence of reducing agents at different coating intervals, the excess amount of reducing agent was added after 30 minutes, 60 minutes and 90 minutes of start of coating process. Nickel chloride and sodium hypophosphite were used as source of nickel and reducing agent respectively. Coating was carried out on mild steel specimens. Coating was done for two hours and volume of bath was fixed as 200ml. The coating parameter pH was varied at three different ranges as follows: 4-5, 6-7 and 8-9. Anionic surfactant sodium dodecyl sulphate was varied at three different concentrations such as before, at and after critical micelles concentration values and added in the bath. The influence of adding excess amount of reducing agent on nickel recovery efficiency, surface finish, micro hardness, coating thickness, rate of deposition and % of nickel and phosphorous on coated samples were investigated. The result showed that after adding 100% of excess amount of reducing agent at 90 minutes of start of coating the nickel recovery was significantly increased from 25% to 65%. The various coatings parameters used in the electroless bath were optimized using taguchi technique. The complete experimental details, their results and analysis are reported in this paper.

Keywords: electroless plating, nickel recovery efficiency, reducing agent, coating parameters, optimization, surfactant

BP47 Mechanical and Tribological Properties of Nanocomposite Ti-B-N-Si Films Deposited by High Power Impulse Magnetron Sputtering, ***J. Jang**, J. Kim, E. An, I.-W. Park (ipark@kitech.re.kr), D.-G. Nam*, Korea Institute of Industrial Technology (KITECH), Busan, South Korea, *K.H. Kim, I. Park*, Pusan National University, South Korea

Multifunctional nanocomposite, based on nanocrystalline and amorphous phases, films attract considerable interest to extend the lifetime of cutting tools, press-forming tools and various other mechanical components. Films for most tribological applications require combinations of properties such as a relatively high hardness, high fracture toughness, wear- and oxidation-resistance, and a low friction coefficient. The present work investigates the co-deposition of Ti-B, Ti-B-N, and Ti-B-N-Si nanocomposite films from a composite target of TiB_2 and a pure boron doped Si target using high power impulse magnetron sputtering in Ar/N_2 gas mixtures. The mechanical and tribological properties for the films were investigated in various N and Si

contents. The microstructures of the synthesized films were characterized by X-ray diffractometer (XRD), scanning electron microscope (SEM), X-ray photoelectron spectroscope (XPS), high-resolution transmission electron microscope (HRTEM), respectively. Nano-indentation was conducted to assess the hardness and Young's modulus of the films. Nanoindentaion was conducted to assess the hardness and Young's modulus of the Ti-B, Ti-B-N, and Ti-B-N-Si films. Wear resistance and coefficient of friction of these films were evaluated using a micro-tribometer. This paper will present the effects of Si content on the microstructure, hardness, and tribological properties of a high power impulse magnetron sputtered Ti-B-N-Si films.

BP48 Structural Investigation of Y- and Hf-Doped TiAlSiCN Coatings, ***Ph.V. Kiryukhantsev-Korneev*** *(kiruhancev-korneev@yandex.ru), K.A. Kuptsov, A.N. Sheveyko*, National University of Science and Technology "MISIS", Russian Federation, *C. Rojas, A. Fernandez*, Instituto de Ciencia de Materiales de Sevilla, Spain, *D.V. Shtansky*, National University of Science and Technology "MISIS", Russian Federation

Newly developed TiAlSiCN coatings with specific structure, in which TiAlCN columnar grains 10-30 nm wide are separated by a SiCN amorphous tissue, demonstrate combination of high hardness in a range of 40-50 GPa, elastic recovery >60%, good impact and wear resistance in different environments, corrosion resistance in alkaline solutions, and high thermal stability up to 1300^0C [1-4]. Even after annealing at 1500^0C TiAlSiCN exhibits acceptable hardness of 20 GPa, and crystallite size <50 nm. However practical application of TiAlSiCN is still limited by a relatively low oxidation resistance: complete oxidation at temperatures > 1000^0C [3]. Addition of optimal amount of Y drastically improves the oxidation behavior of the Ti-Al-N-based coatings and promotes grain refinement resulting in lower residual stresses in the coatings. Hf-alloyed TiN and Ti-Al-N coatings show improved oxidation resistance and high-temperature tribological characteristics. The aim of the present work is to study the structure of Y- and Hf-doped Ti-Al-Si-C-N coatings produced by magnetron sputtering and magnetron sputtering combined with metal ion implantation.

The TiAlSiCN composite target for sputtering was produced by self-propagating high-temperature synthesis. High energy bombardment by Hf^+ and Y^{n+} ions was implemented at the initial stage of deposition or assisted during the whole process. Accelerating voltage and current of the MEVVA type ion implanter were kept constant at 30 kV and 10 mA, respectively. Doped coatings were also produced using mosaic cathodes composed of TiAlSiCN and Y or Hf segments. The structure of coatings were studied by means of glow discharge optical emission spectroscopy, X-ray diffraction, X-ray photoelectron, Raman and electron energy loss spectroscopy, high-resolution transmission and scanning electron microscopy. Influence of Y and Hf additives on chemical and phase composition, texture, crystallites geometry, morphology, and topography of TiAlSiCN coatings are discussed. Preliminary results of structural investigation of alloyed coatings after air annealing at T> 1000^0C are also presented.

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BP49 Characterization of Double Stage Gas Nitrided 34CrAlNi7-10 Steel, ***I. Altinsoy***, *T. Yener*, Sakarya University, Turkey, *K.G. Onder (goker.onder@mikrosanmak.com)*, Mikrosan Makina ve Kalıp San. A.S. Heat Treatment Department, Turkey, *F.G. Celebi Efe*, Sakarya University, Vocational School of Karasu, Turkey, *C. Bindal*, Sakarya University, Turkey

The present study reports on characterization of double stage gas nitrided 34CrAlNi7-10 nitriding steel. Nitriding process was conducted in a two stage. First, steel samples were nitridied at 500°C for 10h and then at the second stage nitriding process were continued at 530, 540 and 550°C, respectively for 20h. Nitrogen activity on surface was controlled by the nitriding potential / (K_N) which is known as thermodynamical control parameter for controlled gas nitriding process during both stage and K_{N1} was kept constant as a value of 10 during first stage and K_{N2} wasranged from 3.2 – 0.2 for both nitriding temperatures at the second stage. The presence of nitrides formed on surface of test materials were determined by XRD analysis technique. The morphology and microstructures of nitrided layer were studied by optical microscope. The microhardness of surface of nitrided samples in HV_1 were observed between 955-1048. The measurements showed that the white layer thickness varies between 6.85-23.90 µm. The diffusion layer thickness of the nitrided samples were raised from 314 µm to 433 µm by increasing of the nitriding temperature and $K_N$values. The growth of the white layer, diffusion layer and the microhardness gradient were strongly affected by nitriding potential and temperature. The fracture tougness of the compound layer formed on surfaces of the samples were increased by descent of both nitriding potential and temperatures.

Keywords: Gas nitriding, nitriding steel, surface hardness, nitriding depth, nitriding potential (K_N), fracture toughness

BP50 Preparation and Characterization of (111)-oriented Ti1-xAlxN Thin Films on Monocrystalline Aluminium Nitride by Reactive Chemical Vapor Deposition, *H. Shimoda,* ***F. Mercier*** *(frederic.mercier@simap.grenoble-inp.fr), S. Lay, E. Blanquet*, SIMaP CNRS/Grenoble INP/UJF, France

In this work, we report on the preparation of Ti1-xAlxN thin films by a novel way, namely Reactive Chemical Vapor Deposition (R-CVD). Recently we have grown Ti1-xAlxN films by R-CVD from titanium tetrachloride, hydrogen and c-plane (0001) monocrystalline hexagonal aluminium nitride layers at varied temperature between 800°C and 1200°C. Onemicron-thick monocrystalline AlN layers have been prepared at 1500°C with a gas mixture of NH3 and AlCl3 on c-plane (0001) monocrystalline sapphire substrate1. The Ti1-xAlxN thin films have been analyzed by Field Emission Gun Scanning Electron Microscopy (FEG-SEM), Transmitting Electron Microscope (TEM), and X-ray Diffraction (XRD). Additionally,thermodynamic simulations have been carried out to predict the influence of the major operating parameters.

In this presentation, we focus on the chemical processes between the Ti1-xAlxN solid phase and the chlorine-based gaseous phase. The effect of the process conditions such as temperature, composition of the gas phase, deposition time on the thin films' properties (composition, thickness) will be discussed regarding both experiments and thermodynamic calculations. As a typical result, 70-nm-thick layer with (111)-oriented cubic Ti1-xAlxN ($0.1 \leq x \leq 0.45$) has been obtained. Work is going on to propose the best conditions for preparing Ti1-xAlxN thin films by reactive CVD.

BP51 Microstructure and Mechanical Properties of Carbon/carbon Composites with the Fiber Surface Modification by Carbon Nanofibers, ***J. Chen*** *(chenjiecsu@163.com), L. Huang, P. Xiao, X. Xiong*, Central South University, China

In order to surface modification, carbon nanofibers (CNFs) are uniformly dispersed on the fiber surface of the unidirectional carbon preform. The modified carbon preform was then densified to obtain CNF-C/C composite by chemical vapor deposition(CVD). The microstructure and mechanical properties of the CNF-C/C composite were investigated. Results show that CNFs on carbon fibers become the active points and induce the ordered deposition of PyC during CVD. There is an interface layer composed of CNFs and high texture PyC around them between the fiber and matrix in the CNF-C/C composite. After fiber surface modification by CNFs, the mechanical properties of C/C composite are adjusted. After modification, the fracture mode is changed and the flexural strength is enhanced in both vertical and parallel direction.

BP52 Effect of the Interlayer Thickness on the Adhesion Property of the CrZrN Coatings Deposited on AISI H13 Steel, ***K.-S. Kim***, *H.-K. Kim, J.H. La, S.-M. Kim, S.-Y. Lee (sylee@kau.ac.kr)*, Korea Aerospace University, Korea

Nanocrystalline CrZrN coatings with a Cr interlayer were deposited on AISI H13 steel substrate using unbalanced magnetron sputtering system. Although a metallic interlayer was generally used to improve adhesion property by reducing stress gradient between the coating and the substrate, the effect of the interlayer thickness on the adhesion property of the CrZrN coating has not been studied. In this work, the CrZrN coatings with various Cr interlayer thickness from 0 to 600 nm were deposited and the total thickness of the coating was 3 µm. The hardness, crystalline structure, microstructure, surface roughness, and adhesion property of the CrZrN coatings were evaluated by Fischer scope, X-ray diffraction (XRD), field-emission scanning electron microscopy (FE-SEM), atomic force microscopy (AFM), and scratch tester. The hardness of the CrZrN coatings, ranging from 32-34 GPa, did not show significant dependence on interlayer thickness. The preferred growth orientation of CrZrN coating without interlayer was CrZrN (111). As interlayer thickness increased, the growth orientation changed into CrZrN (220) and at the same time, the rms roughness of CrZrN coating increased from 2 nm with up to 450 nm thick interlayer to 7 nm with 600 nm. The critical load Lc3 showed the maximum value of 32 N at the interlayer thickness of 300 nm. The scratch failure mode changed from the buckling crack and spallation below 450nm to the wedging spallation at 600nm. This result could be attributed to that the shear failures at interlayer became dominant as the thickness of the soft metal interlayer increased.

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BP53 Effect of Gas Pressure and Exciting Voltage on the Plasma Stability of a Pulsed-DC Hollow Cathode Discharge, *A. Benkenstein (Andreas.Benkenstein@de.bosch.com)*, ***K. Böbel***, *Müller*, Robert Bosch GmbH, Germany, *B. Dzur*, Ilmenau University of Technology, Germany

A hollow cathode plasma discharge inside a blind hole has been evaluated concerning its electrical properties and its plasma stability. The governing parameters (i) gas pressure and (ii) exciting voltage were varied and conductivity curves were derived.

The experimental setup was an electrically contacted steel body that was isolated to the ground potential. The working gas Argon was supplied via a ceramic capillary. The dynamic pressure was measured at the end of the blind hole using a MEMS pressure sensor.

First experimental series investigated the relationships between gas flow rate, inner pressure and penetration depth of the capillary. Linear correlations were found (i) between gas flow rate and inner pressure and (ii) between capillary position and inner pressure. Furthermore, the experiments revealed the range of reliable, stable process and measurement conditions that were taken as experimental array for the subsequent investigations.

Oscilloscope measurements revealed the influence of the process input parameters frequency, duty cycle and voltage on the resulting ignition and stability behavior of the plasma. The maximum value of the voltage pulse was found to have the highest influence. This voltage pulse itself can be controlled by the average voltage, the off-time and the frequency.

Based on those results the conductivity curves for different capillary penetration depths, gas flows and voltages were established. The conductivity curves clearly revealed the range of the plasma stability: The lower limit is the transition to the normal glow discharge while the upper limit is the transition to the arc discharge that is detected by the power supply as a voltage drop. Additionally a strong influence of the capillary position not only on the pressure but also on the electrode surface area and hence on the resulting current was found.

BP55 Structure and Mechanical Properties of Ta Alloyed Cr-Al-N Coatings, ***R. Hollerweger*** *(robert.hollerweger@tuwien.ac.at)*, *L. Zhou*, Vienna University of Technology, Austria, *D. Holec*, Montanuniversität Leoben, Austria, *R. Rachbauer*, Oerlikon Balzers Coating AG, Liechtenstein, *P. Polcik*, Plansee Composite Materials GmbH, Germany, *P.H. Mayrhofer*, Vienna University of Technology, Austria

Transition metal alloying of $Cr_{1-x}Al_xN$ based coatings is commonly used to improve their mechanical properties and thermal stability. Recent reports show that Tantalum additions to $Ti_{1-x}Al_xN$ type coatings positively influence their properties, but only little information is available on the effect of Ta on $Cr_{1-x}Al_xN$ based coatings. Consequently, we have performed a combined experimental and *ab initio* based study on the influence of Ta additions (0, 2, 6, 12, and 26 at% on the metal sublattice) on structure and mechanical properties of arc evaporated $Cr_{1-x-y}Al_xTa_yN$ coatings with Al/(Cr+Al) ratios > 0.61. With increasing Ta-content the droplet number density decreases and coating surface smoothens, which is much more pronounced as with increasing the bias voltage from –40 to –120 V. Simultaneously, the columnar structure observed for Ta-free $Cr_{0.37}Al_{0.63}N$ significantly changes into a fine grained structure (crystallite size ~5 nm) with clearly reduced columnar character. Additionally, increasing the Ta content favors the formation of a preferred 200 growth orientation resulting in a reduction of the indentation moduli from ~500 to ~375 GPa, which is in agreement with *ab initio* calculations. As the hardness of our coatings remains at ~35 GPa with increasing Ta content, this indicates an increase in fracture toughness at still high resistance against plastic deformation.

BP56 Mechanical and Tribological Properties of TiAlSiN Nanocomposite Coatings Deposited by a High Power Impulse Magnetron Sputtering, ***M.K. Lei*** *(mklei@dlut.edu.cn)*, *B. Wu, Y.G. Li, Z.L. Wu, X.P. Zhu*, Dalian University of Technology, China

A series of TiAlSiN nanocomposite coatings were deposited by a high power impulse magnetron sputtering technique, as modulated pulsed power magnetron sputtering (MPPMS), using a N_2/Ar mixing gas on Si(100) wafer and stainless steel substrates at room temperature. The nitrogen partial pressure was used in the range from 10% to 37%, an approximately stoichiometric composition of (Ti,Al,Si)N was obtained with a similar Ti, Al, and Si contents. When the nitrogen partial pressure increased, the nanostructure of the (Ti,Al,Si)N coatings has changed from a nanocomposite of c-TiAlN/a-Si_3N_4 structure to that of c-TiAlN/h-AlN/a-Si_3N_4 structure due to little precipitation of h-AlN. A higher nanohardness was detected as about 33 Gpa for the c-TiAlN/a-Si_3N_4 nanocomposite coatings. With the fewer h-AlN precipitation, the nanohardness and Young's modulus of the (Ti,Al,Si)N nanocomposite coatings slightly decreased, whereas the residual stress generally increased. The friction coefficients of the (Ti,Al,Si)N coatings were observed around 0.8-0.9, and the specific wear rates were about 10^{-5} mm^3/N m, on a ball-on-disk tribometer against an Si_3N_4 counterface under a normal load of 0.5 N. A lower specific wear rate was obtained for the c-TiAlN/h-AlN/a-Si_3N_4 nanocomposite coatings due to the oxidation wear of the mixing phases including to the h-AlN precipitation.

BP57 Sputtered Thin Film Metallic Glass as Underlayer for Sn Whisker Mitigation, *W. Diyatmika*, ***J.P. Chu*** *(jpchu@mail.ntust.edu.tw)*, *Y. Yen, W.Z. Chang, C. Hsueh*, National Taiwan University of Science and Technology, Taiwan

The use of underlayer is one of the mitigation methods commonly used for preventing of the Sn whiskering phenomenon in electronic packaging. A proper underlayer prevents the intermetallic compound formation resulting from a Cu/Sn interaction. Ni underlayer has been extensively studied and industrially accepted. However, Ni underlayer suffers from its polycrystalline grain structure where grain boundaries act as a diffusion path for the Cu/Sn interaction. In this study, a 100-nm-thick $Zr_{46}Ti_{26}Ni_{28}$ thin film metallic glass (TFMG) is introduced to block the Cu/Sn interaction. Samples with and without TFMG underlayer were aged at elevated temperatures in ambient atmosphere. No Sn whisker is observed in the sample with TFMG underlayer after aging. In contrast, Sn whiskers are found in the absence of the underlayer and the whisker density increases with increasing aging time. It is found that TFMG underlayer plays an important role in effectively suppressing Sn whisker growth.

Keywords: Sn whiskers, electronic packaging, intermetallic compound formation, thin film metallic glass, underlayer

BP58 Tribocorrosion Properties of Duplex *MAO/DLC* Coatings on Ti6Al4V Alloys, *E.E. Sukuroglu (eedemirci@atauni.edu.tr)*, ***Y. Totik***, *E. Arslan, I. Efeoglu*, Atatürk University, Turkey

In the recent years, various technologies are being increasingly investigated for the surface modification of Ti and Ti alloys. Micro arc oxidation (MAO) is the one of the effective technique to improve the surface properties. However, it has some disadvantages for sliding wear applications and/or aggressive environments. In this study, the combined MAO and closed field unbalanced magnetron sputtering process was used to deposit duplex MAO/DLC coatings on Ti6Al4V alloy. The microstructures, morphology and crystallographic structure were analyzed by SEM, RAMAN and XRD. The wear, corrosion and tribocorrosion properties of the coatings were investigated by pin-on-disc wear test, potentiodynamic polarization test and combining tribocorrosion test unit, respectively. The results were show that duplex MAO /DLC coating exhibits a better wear, corrosion and tribocorrosion properties than the DLC or MAO monolayer on Ti6Al4V alloy substrate. MAO /DLC coatings exhibited dense structure, lower coefficient of friction and corrosion current density and the higher tribocorrosion resistance. The results were also showed that MAO /DLC duplex coatings on Ti6Al4V substrates increased the tribocorrosion resistance by acting as a barrier layer**.**

BP59 Effect of Coating Thickness on the Silt Erosion Properties of Ternary Metal Nitride Thin Films prepared by Magnetron Sputtering, *V. Arya (vivek@bhelrnd.co.in)*, BHEL R&D, India, ***P. Dubey***, *R. Chandra*, Indian Institute of Technology Roorkee, India

Silt erosion is a predominant phenomenon due to excessive silt present in water passing through under-water hydro turbine components affecting their life and efficiency. In recent years, binary and ternary transition metal nitride materials have played a crucial role in various engineering applications due to their remarkable physical and mechanical properties including high hardness, high melting point, chemical inertness and good thermodynamic stability. The role of nano composite thin films deposited by PVD techniques such as DC/RF magnetron sputtering is increasing prominently for combating silt and cavitation erosion. In the present study, ternary systems such as Titanium Silicon Nitride (Ti-Si-N) and 'Tungsten Zirconium Nitride (Zr-W-N) has been deposited on 13Cr-4Ni stainless steel substrate by DC/RF reactive magnetron sputtering. These thin films have been deposited with varied thickness in the range of 1-2 µm, 5-7 µm and 10-15 µm by varying coating parameters. The effect of coating thickness on silt erosion of these films, their damage mechanism and its correlation with mechanical properties are discussed in detail. The silt erosion resistance of these coatings has been compared with base material. It is observed that the silt erosion resistance of nano composite thin films has been improved significantly with increase in coating thickness.

Symposium C Poster Session

CP1 Computational Investigations of Stress Evolution during Thin Film Growth, ***X.X. Yu***, *W. Li, T. Kaub, G.B. Thompson (Gthompson@eng.ua.edu)*, The University of Alabama, US

A series of molecular dynamic simulations have been performed to elucidate the adatom mobility contribution to stress evolution during thin film growth. The simulations have explored intrinsic segregation of atoms to and from the surface and grain boundaries. The movement of these adatoms was found to assist in regulating either the tensile or compressive modes of growth. The computational results have been compared to experimental stress findings measured as the thin film grew. Case study metals, including Cu, Nb, Ni, and Fe have been investigated. The results revealed a preferential enrichment of specific atoms to the grain boundaries during growth. The preferential segregation of specific atoms to the boundaries appears as a means to tailor the stress within the film. The computational simulation results of the atomic placement of specific atoms are compared to analytical microscopy results of grain boundary structure and composition.

CP3 Effect of O_2 Plasma Treatment on Physical, Electrical, and Reliability Characteristics of Low Dielectric Constant Material, *Y.L. Cheng*, ***B.H. Lin*** *(s98323024@mail1.ncnu.edu.tw)*, National Chi-Nan University, Taiwan

The degradation induced by oxygen (O_2) plasma irradiation to the various low dielectric constant materials (low-*k* ; *k*=3.0~2.5) has been investigated in this study. The dielectric constant was observed to increase due to carbon atom depletion of the film surface, which is strongly influenced by the bonding structure of the low-*k* materials, and less related to the pore. Moreover, this damage can be suppressed by the low-*k* film surface densification using He/H_2 remote plasma treatment. Additionally, the role of ions, photons, and radicals in the plasma in inducing the low-*k* material degradation was clarify by using a special designed structure. The experimental results showed that all components in the plasma degrade low-*k* film electrical and reliability performance, and oxygen ions induce severe damage on the low-*k* material.

CP4 Gas Sensing of SnO_2 Nanoparticles and Pt/SnO_2 Nanoparticles by Thermal Decomposition Process, ***S.C. Wang*** *(scwang@mail.stust.edu.tw)*, *T.W. Yang, B.J. Huang*, Southern Taiwan University of Science and Technology, Taiwan

In this study, Gas sensing of SnO_2 nanoparticles by thermal decocomposition method is studied. The SnO_2 nanoparticles is prepared in this experiment, Sn(OA)x was prepared under inert atmosphere and high temperature by using tin oxide powder and oleic acid as the solvent, then $Sn(OA)_x$, surfactants of Tri-n-octylamine、oleic acid were reacted in the air atmosphere at high temperature to form SnO_2 nanoparticles, and transform into slurry. A layer of SnO_2 thick film was printed on the platinum comb electrodes of the alumina substrate, SnO_2 was then measured under different working temperatures on the sensitivity. Besides that, investigation on the influence of working temperature on sensing test, Sensing film annealed at different temperature and adding of metals, Pt/ SnO_2 thick film on the influence of gas sensing properties were done. The result showed that when the surfactant oleic acid was injected, the amount of oleic acid varied from 2 mmol~16 mmol, the average diameter of the powder increased from 5.5 nm to 12 nm。SnO_2 slurry was printed four times on the alumina substrate and the thickness of the thick film was about 38 μm. In the experiment of gas sensing resistance change, the optimal temperature for hydrogen (1000 ppm) was 300℃, and with Sensitivity up to 8600. The response and recovery speed can be increased by adding Pt. The repetitive of gas sensing circulation of air to hydrogen gas showed good results.

Keywords: Thermal Decomposition、Screen Printing、Gas sensor、Tin oxide、Pt

CP5 Ab Initio Evaluation of the Potential use of Sc-based III-Nitrides in Optoelectronics, *S. Zhang*, University of Cambridge, UK, ***D. Holec*** *(david.holec@unileoben.ac.at)*, Montanuniversität Leoben, Austria, *G. Fu, C. Humphreys*, University of Cambridge, UK, *P.H. Mayrhofer*, Vienna University of Technology, Austria, *MA. Moram*, Imperial College London, UK

Sc-based III-nitride semiconductors are of potential interest as new materials for short-wavelength optoelectronic devices and high-electron mobility transistors. In this work we employed density functional theory together with special quasi-random structure methodology to study their structural, elastic and electronic properties . $Sc_xAl_{1-x}N$ and $Sc_xGa_{1-x}N$ alloys are found to be stable in hexagonal phases up to $x\approx0.56$ and $x\approx0.66$, respectively, above which their rock-salt polymorphs are more stable. The elastic constants were calculated for hexagonal $Sc_xGa_{1-x}N$ and $Sc_xAl_{1-x}N$ up to $x=0.375$ using a stress-strain approach. The elastic constants C_{11}, C_{33}, C_{44} and C_{66} decreased while C_{12} and C_{13} increased slightly with increasing *x* for both alloys. The reduction in the bulk moduli and in most elastic constants of both alloys with increasing *x* is linked to a corresponding increas ing structural deviation from ideal tetrahedral bonding towards five-coordinate d local environments, and an increase in the average metal-nitrogen bond ionicity. The increase in Sc content expands the in-plane lattice parameter of $Sc_xAl_{1-x}N$ and $Sc_xGa_{1-x}N$ alloys, and leads to composition- and strain-tunable band gaps and polarization, and ultimately introduces ferroelectric functionality in $Sc_xGa_{1-x}N$ at $x\approx0.625$. Finally, we estimated critical thicknesses for stress relaxation by misfit dislocation s for several heterostructures using an energy balance model. These are greater than for the $In_xGa_{1-x}N$/GaN system at corresponding lattice mismatches.

Overall, our results indicate that Sc-based III-nitrides may be suitable for practical application in devices.

CP6 Field-enhanced Light Instability under Visible and Ultraviolet Light Irradiation on Amorphous In-Ga-Zn-O Thin Film Transistors, ***K.J. Liu***, *T.C. Chang (tcchang@mail.phys.nsysu.edu.tw), T.Y. Hsieh*, National Sun Yat-Sen University, Taiwan

This letter investigates the combined effects of gate-bias and visible or ultraviolet light on the instability in amorphous In-Ga-Zn-O thin-film transistors. Under the exposure to visible light, device exhibits stable characteristic without degradation, whereas UV light causes apparent subthreshold leakage and threshold voltage shift. This indicates that photon energy of visible light is not sufficient to induce trap-assisted photo-generation of electron-hole pairs within In-Ga-Zn-O bulk. In contrast, negative gate-bias illumination stress under visible and UV light both lead to a pronounced threshold voltage shift. The effects of visible light on the instability of device can be manifested only when negative gate-bias is applied, implying that perpendicular electric field can enhance photo-hole generation and lead to more inferior light stability. These phenomena are originated from the nature of thermionic-field emission process of photo-generated holes, and the light-induced instabilities are related to energy distribution of trap states within the In-Ga-Zn-O bulk as well as the applied electric field.

CP7 Modifications in Structure and Properties of Nickel Oxide Films after Argon Ion Beam Bombardment, *S.C. Chen, C.K. Wen (u93187022@mail2.mcut.edu.tw)*, Ming Chi University of Technology, Taiwan, ***T.Y. Kuo***, Institute of Materials Science and Engineering, National Taiwan University, Taiwan, *C.S. Wang*, Ming Chi University of Technology, Taiwan, *H.C. Lin*, Institute of Materials Science and Engineering, National Taiwan University, Taiwan

Nickel oxide (NiO) film has attracted a lot of attention recently, due to its good optical, electrical, magnetic properties and chemical stability. It can be fabricated by different physical and chemical vapor deposition techniques, including sputtering, plasma-enhanced chemical vapor deposition, and pulsed laser deposition. Recently, some researchers have reported that the as-deposited films can undergo further special treatment of the surface to enhance the stability of the films and to reduce the surface impurities. Using ion bombardment on the specimen is a promising way of modifying the surface properties, which is often effective in the enhancement of material properties [1].

In this study, the NiO-Ag composite films with Ag content of 6.17 at.% are deposited on corning 1737F glass substrate at ambient temperature by radio frequency (rf) sputtering of NiO-Ag composite target, with oxygen ion source assistance from direct current (dc) ion gun at a power of 150 W. Post-treatments were then performed by Ar ion beam (from ion gun at a power of 100 W) bombardment on the as-deposited NiO-Ag films in order to investigate the effect of various Ar ion bombardment times on the structures and optoelectronic properties of the films. The electrical resistivity of as-deposited NiO-Ag composite films obtained without ion beam bombardment is 1.5×10^{-2} Ω-cm. For the first 20 min of Ar ion bombardment, there is no marked change in electrical resistivity. However, it drops significantly to 7×10^{-3} Ω-cm and 3×10^{-3} Ω-cm when the bombardment time reaches 30 min and 40 min, respectively. On the other hand, the X-ray diffraction patterns show that the NiO-Ag films that are obtained without Ar ion beam bombardment only display weak NiO peaks. The crystallinity of NiO degrades greatly when the NiO-Ag composite films are post-bombarded with Ar ions. Furthermore, upon further increasing the Ar bombardment time to above 30 min, a (100) peak of Ni_2O_3 appears.

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CP8 Characterization and Properties of NiO Films Produced by RF Magnetron Sputtering with Oxygen Ion Source Assistance, *S.C. Chen, **C.K. Wen** (u93187022@mail2.mcut.edu.tw),* Ming Chi University of Technology, Taiwan, *T.Y. Kuo*, Institute of Materials Science and Engineering, National Taiwan University, Taiwan, *W.C. Peng*, Ming Chi University of Technology, Taiwan, *H.C. Lin*, Institute of Materials Science and Engineering, National Taiwan University, Taiwan

Nickel oxide is a wide band gap semiconductor with an energy gap in the range of 3.6-4.0 eV. Due to its good chemical stability, electrical and optical properties, the NiO film is a promising material for applications in electrochromic display devices, gas sensors, p-type conductive films etc. In the past, physical vapor deposition with ion beam assistance has been employed to deposit Transparent Conductive Oxide (TCO) films. Liu et. al. [1] reported that the electrical properties of indium tin oxide (ITO) films can be improved at ambient temperature by oxygen ion beam assisted electron-beam evaporation. Wang et al. have also reported that the electrical resistivity of NiO films by electron-beam evaporation is much lower than that of stoichiometric NiO films when oxygen ion source assistance is introduced [2]. However, the influence of oxygen ion beam assistance on the optoelectronic properties of the NiO films deposited by sputtering has not been explored yet.

In this work, the non-stoichiometric NiO films are deposited on glass corning 1737F substrates at ambient temperature through radio frequency (rf) sputtering of NiO targets with oxygen ion source by ion gun at various ion beam currents. An electrical resistivity that is too high and cannot be measured by four-point probe results when the NiO film is deposited without oxygen ion beam assistance. However, it drops significantly to 0.49 Ω-cm when an oxygen ion source is introduced from an ion gun set at a discharge current of 0.22 A. The electrical resistivity of the NiO films decreases continuously from 0.18 to 0.13 Ω-cm as the current is further increased from 0.28 to 0.42 A. The Hall measurements for all NiO films deposited with oxygen ion source assistance show p-type conduction. It is found that the crystallinity of the NiO films degrades when an oxygen ion beam is added during deposition. On the other hand, the transmittance of NiO films deposited without ion source assistance is around 69 %. It decreases significantly to 35 % when the discharge current of the oxygen ion gun is set at 0.22 A. Upon further increasing the current to 0.28 A, 0.33 A, and 0.42 A, the transmittance of the films drops further to 33 %, 28 %, and 22 %, respectively.

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CP9 Temperature Dependent Obliquely Deposited Anti-contamination Coating of HfO_2 for Glass Insulators, ***V. Dave**, A. Sanger, H.O. Gupta, R. Chandra (ramesfic@gmail.com),* Indian Institute of Technology Roorkee, India

In the present work, we report the fabrication of obliquely deposited hydrophobic coating of HfO_2 thin film on glass insulators as a function of substrate temperature. The main objective of this work was to prevent the outdoor glass insulators installed in a power system network from degradation through sunlight radiation and atmospheric contamination. The structural, optical, electrical and wettability characteristics of the coated thin film was investigated using XRD, AFM, FE-SEM/EDS, impedance analyzer, contact angle goniometry and four probe method.The XRD data reveals that all the deposited film exhibits a monoclinic structure with a change in the dominant peak orientation beyond 300 °C substrate temperature. A correlation was established between crystallite size and the deposition rate. The hydrophobicity of the deposited samples follows a linear trend not only with the roughness but also with the stoichiometric ratio. The packing density of the films evaluated from the transmission data dictated the electrical resistivity. The change in the bandgap with the deposition temperature was attributed to the defects in the samples. The dielectric constant evaluated by measuring capacitance was found out to be thickness dependent.

CP10 Resistive Switching Characteristics of Silicon Oxide Based RRAM with Titanium Doping, ***T.M. Tsai**, K.C. Chang, T.C. Chang (tcchang@mail.phys.nsysu.edu.tw), G.R. Liu, J.P. Jiang*, National Sun Yat-Sen University, Taiwan, *S.M. Sze*, National Chiao Tung University, Taiwan

In this study, we successfully produced bipolar resistive switching behaviors by titanium doped into silicon oxide at room temperature. The titanium element was doped into silicon oxide, which is a useful dielectric material in integrated circuit (IC) industries by co-sputtering technology. The resistive switching characteristics of the titanium doped silicon oxide thin films are carried out by XPS, fourier transform infrared spectroscopy, and IV measurement. Based on the proposed method, stable resistance switching behaviors can be demonstrated by DC sweep IV measurement and retention evaluation. We believe that the silicon oxide doped with nickel at room temperature is a promising method for resistive random access memory nonvolatile memory applications due to its compatibility with the IC processes.

CP11 Crystalline Structure of ZnO thin Films Grown on A-plane Sapphire Substrates Using High-temperature H_2O Produced by a Pt-catalyzed H_2-O_2 Reaction, *Y. Ohashi, T. Nakamura, N. Yamaguchi, T. Takeuchi, Y. Tamayama, **K. Yasui** (kyasui@vos.nagaokaut.ac.jp),* Nagaoka University of Technology, Japan

ZnO is highly useful for various applications such as short-wavelength optoelectronics and transparent conductive electrodes. In a previous paper, we reported a new growth method for preparing ZnO films by reacting dimethylzinc and high-temperature H_2O generated from the Pt-catalyzed exothermic H_2 and O_2 reaction [1]. The resulting ZnO films grown on a-plane sapphire substrates exhibited excellent optical and electronic properties [2]. From the thickness dependence of the electrical properties, the electron mobility at room temperature increased from 54 to 189 $cm^2V^{-1}s^{-1}$ with increasing film thickness from 200 nm to 2800 nm. The temperature dependences of the Hall mobility and carrier concentration of ZnO films with thinner than 500 nm and thicker than 500 nm were quite different. From these results, the existence of the layer with high-defect density near the film-substrate interface was estimated.

In this study, the crystalline structure of the ZnO film was observed using cross-sectional transmission electron microscopy (TEM). The dislocation density in the films was also evaluated under two-beam condition. The characterized ZnO epitaxial film was approximately 5 μm thick and the electron mobility at room temperature was 187 cm^2/Vs. Although contrast was observed in the image due to the interference of thickness fluctuation from focused ion beam (FIB) processing, no clear grain boundaries were evident, which indicates the ZnO film is a single crystal. The dislocation densities estimated using Ham's method [3] revealed lower density at the film surface than at the boundary between the film and substrate. The total dislocation density at the film surface was approximately 1.1×10^9 cm^{-2}, of which the edge, screw, and mixed dislocation densities were estimated to be 4.7×10^8, 5.0×10^8, and 1.6×10^8 cm^{-2}, respectively. On the other hand, the total dislocation density near the film-substrate interface was approximately 3.0×10^9 cm^{-2}, of which the edge, screw, and mixed dislocation densities were estimated to be 1.4×10^9, 8.2×10^8, and 8.2×10^8 cm^{-2}, respectively.

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CP13 Effects of Thickness on the Characteristics of p-type Cu_2O Thin Film for all Oxide Solar Cell using Reactive Sputtering, *Y.S. Jung, H.W. Choi, **K.H. Kim** (khkim@gachon.ac.kr),* Gachon University, Republic of Korea

The p-type Cu_2O thin film have been investigated many applications such as, thin film solar cell, thin film transistor, gas sensor and catalyst. The Cu_2O is a potential oxide semiconductor with a direct band gap of 2.1eV. The theoretical energy conversion efficiency of the Cu_2O solar cell is 20%. The Cu_2O is usually a p-type semiconducting material due to its native defects that are formed by Cu vacancies. The Cu_2O is a nontoxic material and all oxide candidates for low-cost photovoltaic applications. The Cu_2O has been considered to be an attractive transparent conductive oxide semiconductor, which is favorable for the fabrication of low-cost solar cells for terrestrial applications. In this study, We fabricated that p-type cuprous oxide thin films (Cu_2O) for absorber layer were deposited by reactive sputtering using Facing Targets Sputtering method. As the results, the resistivity, hole concentration and mobility of the p-type semiconductor Cu_2O thin film at 500nm exhibited 166 Ω.cm, 9.758×10^{16} cm^3 and 0.38 cm^2/V.s.

CP14 Characteristics of SiH4-containing Plasma Generated by ICP-CVD Mixed with H2, B2H6 and PH3, *J.H. Hsieh (jhhsieh@mail.mcut.edu.tw), **H.S. Lin***, Ming Chi University of Technology, Taiwan, *C. Li*, National Central University, Taiwan

A Langumir probe and an OES was used to characterize various SiH4 plasmas generated by an ICP-CVD system attached with four internal antennas. SiH4-containing gases used in this study were mixed with H2, B2H6 and PH3 gases. The plasmas were generated under 10 mtorr with 3000 W (RF) power. The use of the plasma probe provided information that included electron temperature (Te), plasma pontential (Vp), plasma density. The goal of this study was aimed at understanding the effects of various

SiH4-containing gases on these plasma parameters. The results showed that Te and Vp would decrease with the increased partial pressure of the additional gases. SiH4+H2 plasma showed the highest Te, compared with other mixed gases. Plasma density was not affected by the partial pressure of added gases. SiH4+H2+B2H6 have the highest plasma density up to 2.2 x 1017 m-3. With the addition of B2H6 or PH3, the crystalline volume fraction would increase by 5 %, which would be caused by the increase of plasma density. The results of OES showed that ISiH* decreased with the increase of H2 or doping gases. This would cause the decrease of deposition rate. The effects of these plasma parameters on the electrical properties of Si:H films were also discussed.

CP15 Low Contact Resistance Carbon Thin Films as Current Collectors for Lithium Ion Batteries, *S.K. Chen, K.-F. Chiu (kfchiu@fcu.edu.tw), S.-H. Su, S.H. Liu, K.-H. Hou,* ***C.-C. Hsiao***, Feng Chia University, Taiwan

The carbon films have been synthesized by chemical vapor deposition (CVD) on AISI304 stainless steel (304SS) sheets with various C_2H_2/H_2 flow ratios at 810 °C. The films exhibit three different morphologies: filament, sphere and transition types at different C_2H_2/H_2 flow ratios, as characterized by scanning electron microscopy, X-ray diffraction and Raman spectroscopy. It was found that the degree of graphitization increased with decreasing C_2H_2/H_2 flow ratios. $LiMn_2O_4$ materials were plated on different types of carbon coated 304SS sheets as the cathodes for lithium ion batteries. The electrochemical properties of these $LiMn_2O_4$ cathodes were investigated. The capacity of the $LiMn_2O_4$ electrode with the transition type carbon film current collector is 55% higher than that of the electrode without carbon film. The results also indicate that the transition type carbon film efficiently improves the performances of high current density charge-discharge, which can be attributed to the reduction of contact resistance measured by electrochemical impedance spectroscopy.

CP16 Effects of Temperature on Instabilities Caused by Charge-trapping Phenomenon in Dual Gate Amorphous In-Ga-Zn-O Thin-film Transistors, ***P.Y. Liao***, *T.C. Chang (tcchang@mail.phys.nsysu.edu.tw)*, National Sun Yat-Sen University, Taiwan

The temperature effects on instabilities caused by hot-carrier stress (HCS) and negative gate bias illumination stress (NBIS) in dual gate amorphous In-Ga-Zn-O thin-film transistors (TFTs) are reported. After HCS, devices exhibit on-state current decrease and threshold voltage (V_T) shift. In contrast, the on-state current increases without V_T shift under NBIS. To have deeper insight into these phenomena, the effects of temperature on the degradation behaviors are analyzed. The degradation behaviors are found to follow Arrhenius equation and imply that the origin of instability is activated by heat. Both for HCS and NBIS, the dominant degradation mechanism is due to charge trapping through thermionic-field emission into etch-stop layer. Furthermore, experimental results specify that electron-trapping and hole-trapping dominate the instabilities caused by HCS and NBIS, respectively. Through extraction of activation energies, the trapping efficiencies of electron and hole are analyzed. Evidences indicate that the energy band structure between In-Ga-Zn-O and SiOx is the root cause responsible for different deteriorating rates under HCS and NBIS. Furthermore, dynamic stresses are carried out to investigate the trapping response time, with results showing that electron-trapping process is more rapid than hole-trapping.

CP17 Effects of Uniaxial Mechanical Strain on Amorphous In-Ga-Zn-O Thin Film Transistors Fabricated on Flexible Polyimide Substrates, ***B.W. Chen***, *T.C. Chang (tcchang@mail.phys.nsysu.edu.tw)*, National Sun Yat-Sen University, Taiwan

This work investigates the impacts of mechanical strain on flexible back-channel etched In-Ga-Zn-O thin film transistors fabricated on a polyimide substrate. The flexible thin film transistors are exposed to mechanically tensile or compressive bending with different bending radii of 30, 40 and 50 μm. Device parameters such as threshold voltage, carrier mobility, sub-threshold swing, and gate leakage current are extracted from drain current-gate voltage characteristics. Also, the strain-induced trap state generation and distribution of density-of-state within energy gap are investigated utilizing capacitance-voltage measurements. By investigating the transfer as well as output characteristics of devices, variation of carrier mobility and trap states are discovered. Such phenomena indicate that the molecular bonding structures are altered after mechanical strain. Furthermore, strains are applied along the device channel width or length directions to clarify the strain effect on electrical instability.

CP18 Correlation Between Temperature-dependent Carrier Transport Behavior and Self-heating Effect in Amorphous In-Ga-Zn-O Thin Film Transistors, ***T.Y. Hsieh***, *T.C. Chang (tcchang@mail.phys.nsysu.edu.tw), P.Y. Liao*, National Sun Yat-Sen University, Taiwan

Drain current-induced self-heating effect in amorphous In-Ga-Zn-O thin film transistors is investigated in this work. Current-induced Joule heating phenomenon is found to enhance drain current and lead to overestimation of channel current in conventional dc measurement. To suppress or even eliminate self-heating during characterization process, fast pulsed-measurement is carried out to probe the intrinsic characteristics of current conduction in amorphous In-Ga-Zn-O thin film transistor. Pulse operations with different frequencies are utilized to estimate the critical time for self-heating to fully take place in In-Ga-Zn-O semiconductor film. Results reveal that heat generation as well as heat dissipation efficiency both determines the amount of accumulated heat. Temperature effect on carrier transport behavior is also investigated through extracting the activation energy, with results showing a heat-activated nature of channel current conduction. Such carrier transport behavior explains the enhanced drain current in conventional dc measurement which self-heating effect misleads the drain current measurement.

CP19 Effect of Selenization Temperature on the Formation of $Cu(In,Ga)(Se,S)_2$ Phtovoltaic Absorber by Selenization and Sulfurization of CuGa/In/Se Metal Precursors, *J. Koo, S. Lee,* ***W.K. Kim*** *(wkim@ynu.ac.kr)*, Yeungnam University, Republic of Korea

Reactive annealing of metallic Cu-Ga-In precursors under H_2Se and/or H_2S ambient has been employed as a promising method for high-performance $Cu(InGa)Se_2$ thin film solar cell absorber formation. It is, however, often observed that Ga is accumulated near the Mo side of glass/Mo/CIGS structure during or after the selenization of Cu-Ga-In precursors yielding the lower energy band gap at the junction of CIGS/CdS and thus low open-circuit voltages of device. One way to compensate for the loss of energy band gap near surface region is the sulfurization of film using H_2S gas. It is reported that the Ga depth homogeneity was improved by adopting 2-step selenization/sulfurization process.

In this paper, the effect of selenization step with different temperatures on sulfurization process of preformed CIGS by H_2S was investigated with a particular emphasis on the phase evolution and compositional depth profile. The CuGaIn metal precursors were prepared by sequential sputtering of CuGa and element In target, followed by thermal evaporation of Se. The reactive annealing of metal precursors was performed in a rapid thermal process system consisting of a quartz tube reactor with an inner diameter of 62 mm, quartz sample tray and infrared heater. Selenization of precursors was carried out by Se layer at various temperatures of 250~570°C, followed by the sulfurization under flowing H_2S gas at higher temperature of 600°C. In-situ phase evolution during sulfurization was observed by high-temperature X-ray diffraction scan. Compositional depth profile was measured by transmission electron microscope-energy dispersive X-ray spectroscopy. The results showed that sulfurization could drive Ga to move toward the surface region of CIGS layer, and increase the band gap. Low temperature selenization at 250~350°C resulted in the formation of Cu_xSe secondary phase, but better incorporation of sulfur and Ga into chalcopyrite structure.

CP20 Effect of the Sputtering Conditions of Co-sputtered Cu-In-Ga Precursors on $Cu(InGa)Se_2$ Photovoltaic Absorber Formation, ***J. Park***, *W.K. Kim (wkim@ynu.ac.kr)*, Yeungnam University, Republic of Korea

For a few of decades, chalcopyrite $Cu(InGa)Se_2$ (CIGS) thin film has been considered as one of most promising candidate for light absorber, recently achieving over 20% cell efficiency ($0.5cm^2$, AM1.5, 2013). Among several processes which have been developed for the production of reliable CIGS absorbers, 2–step metallization–selenization process is widely accepted as a scalable process. Cu-In-Ga metal precursors were generally deposited by sputtering technique.

In this paper, the effect of the sputtering conditions in co-sputtered Cu-In-Ga precursors on morphology, phase evolution and reaction kinetics of selenization was investigated. The precursors were deposited onto Mo-coated glass with a thickness of 1.8 mm by DC sputtering a CuGa alloy(28 wt.% Ga) and pure In target simultaneously under an Ar gas at an operating pressure of 5×10^{-3} Torr at room temperature, yielding more consistent morphology and cross-sectional structure of precursors and selenized films than typical multi-stacked precursors. Precursors were intended to have a total thickness of 500 - 600 nm by controlling sputter power and time. Using the different sputtering conditions, i.e., CuGa / In powers of 15/40W(Case I), 35/80W (Case II) and 60/120W (Case III) is expected to vary the density and morphology of precursors. To recognize the composition effect of Cu/III and Ga/III of the samples prepared with different sputtering conditions, the compositions varied slightly per each sputtering case. The precursors were selenized in a rapid thermal process

system composed of a quartz tube reactor with a diameter of 62 mm, sample tray, and infrared heater.

By using the X-ray diffraction (XRD), grazing incidence XRD (GIXRD) with $CuK_{\alpha 1}$ incident radiation, and field emission scanning electron microscopy (FE-SEM), the crystal structures and morphologies of the precursors and CIGS absorbers were analyzed in detail. The reaction pathways and kinetics of each precursor were observed by in-situ high-temperature XRD (HT-XRD). The compositions of precursors and CIGS absorbers were measured by inductively coupled plasma–atomic emission spectroscopy (ICP-AES).

The XRD data revealed that three types of precursors have common peaks corresponding to intermetallic compounds such as Cu_3Ga, Cu_2In and an elemental In. As the sputtering power increases, the size of nodules on the precursors is likely to increase with maintaining the thickness constant. It was found that increase in the sputtering power has advantage with respect to the Ga distribution of precursors during selenization, issued in CIGS solar cell. More results concerning precursor concentration effect will be discussed as well.

CP21 Structural Characteristics and Properties of Gallium Nitride Thin Films Prepared by Radio Frequency Magnetron Sputtering, *Y.K. Cho,* ***J.H. Kim*** *(joohan@cbnu.ac.kr)*, Chungbuk National University, Republic of Korea

The structural characteristics and properties of gallium nitride (GaN) thin films prepared by radio frequency (RF) magnetron sputtering were investigated. The GaN thin films were deposited on silicon and fused quartz substrates at room temperature in a pure nitrogen atmosphere. Auger electron and X-ray photoelectron spectra showed that the films were mainly composed of gallium and nitrogen. Small amount of oxygen was observed in the films and found to be incorporated into the films during the deposition. The value of the refractive index of the GaN films was measured to be 2.36 at a wavelength of 633 nm. The optical bandgap of the GaN films was determined to be approximately 3.31 eV. From the grazing incidence x-ray reflectivity measurements, the density of the GaN films was estimated to be 5.827 g/cm^3. X-ray diffraction analysis revealed that the crystalline phase of the GaN films changed from wurtzite to zinc-blende as the working gas pressure was reduced. It was found that the phase change was accompanied by an increase in the lattice parameters in the direction perpendicular to the film's surface. These results suggest that the observed phase change of the GaN films was strongly correlated with the biaxial compressive stress.

CP22 N_2O Plasma Treatment Suppression of Temperature-dependent Point Defect Formation in Amorphous Indium-Gallium-Zinc-Oxide Thin Film Transistors, ***J.C. Jhu***, National Chiao Tung University, Taiwan, *T.C. Chang (tcchang@mail.phys.nsysu.edu.tw)*, National Sun Yat-Sen University, Taiwan, *G.W. Chang, Y.H. Tai*, National Chiao Tung University, Taiwan

An abnormal sub-threshold leakage current is observed at high temperature in amorphous indium-gallium-zinc-oxide thin film transistors (a-IGZO TFTs). To confirm this phenomenon's dependence on the defects in the a-IGZO active layer, this paper proposes devices with N_2O plasma treatment on the a-IGZO film. Experiments verify that the N_2O plasma treatment enhances the thin film bonding strength and therefore suppresses the formation of temperature-dependent point defects which occur from oxygen atoms leaving their original sites at temperatures above 400K. The N_2O plasma treatment devices have better stability performance than as-fabricated devices. The results suggest that the point defect state for a-IGZO TFTs with N_2O plasma treatment is much lower than in as-fabricated devices. The N_2O plasma repairs the point defects to suppress temperature-dependent sub-threshold leakage current. In addition, positive and negative gate bias stresses at high temperature were applied to both devices, with N_2O plasma treatment devices exhibited a reduced threshold voltage shift under positive bias stress, and ….. under negative bias stress. Furthermore, we provided energy diagram to illustrate conduction carrier behavior and explain the dominant mechanism during applied bias stress at high temperature.

CP23 Properties of CNTs/PEDOT:PSS (spin-coated) Thin Films as Flexible Transparent Electrodes, ***B.J. Kim***, *S.H. Han, J.S. Park (jinsp@hanyang.ac.kr)*, Hanyang University, Republic of Korea

Indium tin oxide (ITO)-based transparent conductive films (TCFs) have been widely used as transparent electrodes for electronic devices including liquid crystal displays, solar cells, and touch screen panels. ITO-based TCFs, however, have several limitations in applications of next-generation flexible electric devices because they are easy to crack and their sheet resistances are significantly increased under bending or other stresses due to their brittle nature. Recently, several materials, which include metal meshes, conducting polymers, and nano-structured carbon materials such as carbon nanotube (CNT) and graphene, and other metal-oxide films, have been introduced to replace the ITO-based TCFs. Among those, CNTs have much attraction for flexible TCFs because of their superior properties such as chemical stability, thermal conductivity, mechanical strength, and flexibility. Furthermore, in order to improve the electrical properties of CNT-based TCFs, composite materials which are made by mixing CNTs with poly-ethylenedioythiophene:poly-styrenesulfonate (PEDOT:PSS) have also been suggested . However, the CNTs/PEDOT:PSS composite may cause the visibility problem because PEDOT:PSS naturally shows blue color.

In this study, we fabricated the CNT-based TCFs, which have low sheet resistance (< 100 Ω/sq), high transmittance (> 80 %) in the visible wavelength range, and low yellowness (b* < 2), by coating PEDOT:PSS on CNTs. The CNTs were deposited on the polyethylene terephthalate (PET) substrates by spray coating and then PEDOT:PSS layers were coated by spin coating. The morphologies and sheet resistances of the three kinds of materials, such as CNTs, PEDOT:PSS layers, and PEDOT:PSS-coated CNTs, were measured via field-emission scanning electron microscopy (FESEM) and four point probe methods respectively. The transmittances and color properties of PEDOT:PSS-coated CNTs were measured using a UV-VIS spectrometer. Also, the flexibilities of PEDOT:PSS-coated CNTs were tested using a bending machine (more than 10,000 times) with the angle and distance fixed. The experimental results confirmed that the fabricated CNTs/PEDOT:PSS TCFs would satisfy the requirements for flexible transparent electrodes of touch screen panels.

CP24 Effects of Substrate Corona-pretreatment on Properties of Flexible Transparent CNT Electrodes, ***S.H. Han***, *B.J. Kim, J.S. Park (jinsp@hanyang.ac.kr)*, Hanyang University, Republic of Korea

Despite the exceptional optoelectronic properties of indium-tin-oxide (ITO) thin films as transparent conductive (TC) electrodes, they suffer from considerable drawbacks under bending or other stresses due to their brittle nature. This has motivated the researches for alternative flexible TC materials. Carbon nanotubes (CNTs) have been considered to be one of the promising flexible electrodes. For flexible applications, plastic substrates, such as polyethylene terephthalate (PET), polyethylene (PE), and polypropylene (PP), can be used for the deposition of CNTs. Also, the indirect methods such as spray coating, dip coating, bar coating, and inkjet printing are favored when the CNTs are deposited on the plastic substrates. These methods, however, have common problems regarding the weak adhesion between the substrates and the CNTs. For obtaining the enhanced CNT-substrate adhesion, surface modification techniques, by which plastic substrates are pre-treated using plasma, corona-discharge, and ultraviolet light prior to the deposition of CNTs, have been suggested recently. Among those, corona-discharge treatment may be commercially favorable because it can be carried out at atmospheric pressure and room temperature.

In this study, we investigate the effects of corona-discharge pre-treatment on the properties of CNTs which can be used as flexible transparent electrodes. The CNTs were deposited on PET substrates using a spray coating method. Prior to the deposition of CNTs, the PET substrates were corona-treated by varying the directions (such as vertical, horizontal, and diagonal) and numbers of treatments as well as the discharge powers. The variations in the surface morphologies of the PET substrates due to corona-treatment were characterized via atomic force microscopy (AFM). Dynamic contact angles (DCAs) of the corona-treated PET substrates were measured and analyzed as functions of the treatment conditions. Also, the sheet resistances and visible-range transmittances of the CNTs deposited on PET substrates were measured before and after bending test. The experimental results obtained in this study provided strong evidences that the adhesive forces between CNTs and PET substrates would substantially be enhanced by corona-discharge pretreatment.

CP25 Effects of Hot-pressing on Structural, Optical, and Electrical Properties of Silicon-incorporated Zinc Oxide Thin Films, ***K.W. Cha***, *S.H. Lee, W. Kim, J.S. Park (jinsp@hanyang.ac.kr)*, Hanyang University, Republic of Korea

Amorphous oxide materials have been potentially applied to thin film transistors (TFTs) for flat panel displays due to their superior electrical characteristics compared to hydrogenated amorphous silicon (a-Si:H) as well as the transparency in the visible wavelength range. Most of the currently-developing oxide-TFTs adopt indium (In)-incorporated zinc-oxide (ZnO)-based thin films such as indium-zinc-oxide (IZO) and indium-gallium-zinc-oxide (IGZO) because they exhibit high electron mobilities even when they are deposited at room temperature. However, the In element is expensive and relatively rare on Earth. Recently, silicon (Si)-incorporated zinc-oxide (SZO) films have been suggested as one of the candidates for substituting the In-incorporated oxide films because Si can act as a donor in ZnO. Also, post-annealing process is generally used to improve electrical properties of oxide films. However, post-annealing may increase the surface

roughness of oxide films, deteriorating the device characteristics of oxide-TFTs.

In this study, we suggest a hot-pressing method that can produce SZO films with excellent qualities which are desirable for channel layers of oxide-TFTs. The SZO films were deposited at room temperature by co-sputtering two separate targets of Si (60 W of power) and ZnO (100 W of power). After deposition of SZO films, the hot-pressing process was carried out at 0.5~3 Mpa of pressure and at room temperature~250 ºC of temperature. The variations in the electrical, structural, and optical properties of SZO films due to hot-pressing were characterized using four-point probe, X-ray diffraction (XRD), UV/visible spectrophotometer, atomic force microscope (AFM), and X-ray photoelectron spectroscopy (XPS). The experimental results indicated that hot-pressing resulted in the improvement of the SZO films' electrical properties and at the same time ensured the stabilization of surface roughness. The effects of hot-pressing on device characteristics of SZO-TFTs were also examined.

CP26 Effects of Air Exposure and Thermal Treatment on Properties of SZO Films and Characteristics of SZO-based Thin Film Transistors, ***S.H. Lee***, *K.W. Cha, W. Kim, J.S. Park (jinsp@hanyang.ac.kr)*, Hanyang University, Republic of Korea

Amorphous oxide semiconductor (AOS)-based thin film transistors (TFTs) have been intensively investigated for various electronic applications including active-matrix organic light emitting diode (AMOLED) and active-matrix liquid crystal display (AMLCD) due to their high field-effect mobility than that of conventional hydrogenated amorphous silicon (a-Si:H) TFT. AOS materials also have good optical transparency in the visible light region. Most of the successful AOS-based TFTs incorporate indium (In), which is relatively rare on Earth, such as indium-zinc oxide (IZO) and indium-gallium-zinc oxide (IGZO). This makes those technologies easily subject to a material shortage. Recently, the experimental results, which demonstrate new oxide semiconductors free of In, have been reported. Also, several studies have suggested that silicon (Si) atoms may act as effective donors in zinc oxide (ZnO) lattices and silicon-incorporated zinc oxide (SZO)-based TFTs can be one of alternative candidates replacing the In-incorporated oxide-TFTs. Until now, however, there has been a scarcity of comprehensive studies on the SZO-based TFTs.

In this study, we present experimental results regarding the effects of air exposure and thermal treatment on the material properties of SZO thin films and the device characteristics of SZO-based TFTs. The SZO films, which were used as the channel layers of TFTs, were deposited using an RF magnetron co-sputtering method by varying the power of Si target. The SZO-TFT was fabricated with a bottom gate structure. As a gate, a highly doped n-type Si substrate with a low resistance ($\leq 2\times10^{-3}$ Ωcm) was used, and a gate insulator (300 nm) was formed by thermally oxidizing the Si substrate, and then the SZO-channel layer was deposited. Photolithography was performed to form the pattern, and Al electrode (source/drain) was deposited via RF sputtering. Then, lift-off was carried out to remove photo-resist (PR). The various methods, including four-point probe, X-ray diffraction (XRD), UV/visible spectrophotometer, secondary ion-mass spectrometer (SIMS), were used to investigate the effects of air exposure and thermal treatment on the electrical, structural, and optical properties of the SZO films. The device characteristics of the fabricated SZO-TFTs were measured in a dark environment using a semiconductor parameter analyzer to monitor the variations of device parameters, such as threshold-voltage and field-effect mobility, due to air exposure and thermal treatment. Also, the roles of Si in determining the device characteristics of the SZO-TFTs were discussed in detail.

CP27 Effect of Molecular Structure of the Starting Precursor Materials over the Crystallization, Growth and Luminescence of ZnO Coatings, ***S. Brahma***, National Cheng Kung University, Taiwan, *S.A. Shivashankar*, Indian Institute of Science Bangalore, India, *J.-M. Ting (jting@mail.ncku.edu.tw)*, National Cheng Kung University, Taiwan

We report large scale fabrication of zinc oxide (ZnO) nanorods on Si(100) substrate by using metal–organic complex of zinc (Zn) as the precursor, and microwave irradiation assisted chemical synthesis as a process. The coatings are uniform and high density ZnO nanorods (1.5 -2 μm length) grow over the entire area (625 mm^2) of the substrate within 1–5 min of microwave irradiation. In addition to the regular metal organic complex of zinc (zinc acetylacetonate), we have also employed two relatively new precursors for ZnO deposition. The shape of the nanorods vary significantly with the variation of the molecular structure/molecular weight of the precursors. The precursors in addition with the surfactant and the solvent are widely used to obtain desired coating on any substrate including flexible polymers. ZnO coatings obtained by solution phase deposition yield strong UV emission. The position of the chromaticity coordinates in yellow region of the color space gives an impression of white light emission from these coatings by exciting with a blue laser. The primary growth mechanism of ZnO over Si(100) including the initial nucleation and the schematics of the growth process are discussed in detail.

CP28 High Electrical Conductivity of Orientedly-assembled Sb_2Se_3 Nanostructured Films, *H.C. Chang*, ***T.H. Chen***, *K.S. Ke, C.H. Chen (chunhuachen@mail.nctu.edu.tw)*, National Chiao Tung University, Taiwan

Antimony selenide (Sb_2Se_3) has received considerable attention in recent years due to its excellent Seebeck coefficient (~1800 μVK^{-1}) which is at least 6-fold higher than that of the optimized bismuth telluride (Bi_2Te_3). However, the relatively low electrical conductivity (10^{-6}~10^{-2} Sm^{-1}) seriously deteriorates the thermoelectric figure of merits and possible applications. Here, we fabricated a series of unusual Sb_2Se_3 nanoassembles including nanorods (400 ºC), nanodecks (450 ºC), nanotwizers (550 ºC), and nanotubes (600 ºC) with a distinct c-axis preferred orientation by pulsed laser deposition. The optimized electrical conductivity is 10^4 times higher than that of the Sb_2Se_3 bulks and films, indicating that controlling the orientation and alignment of the nanostructured films is an effective solution for fundamentally resolving high resistance of Sb_2Se_3.

CP29 A Germanium/Silicon Heterojunction Field Effect Transistor Photodetector Fabricated on Silicon-on-insulator, *H. Mohammed, M. DeBerry, U. Obahiagbon, O. Akpa, M. Awaah,* ***N. Korivi*** *(nkorivi@mytu.tuskegee.edu), K. Das*, Tuskegee University, US

We report on the development of a germanium/silicon heterojunction field effect transistor (HJFET) photodetector. One novel aspect of this device is the use of radio frequency sputtering to grow hetero-epitaxial thin films of germanium (Ge) as active device material. Another novel aspect is the device fabrication on a silicon-on-insulator (SOI) substrate by a multi-step standard ultraviolet light photolithography which allowed the patterning of the sputtered Ge thin films. The HJFET photodetector was fabricated with several different Ge gate widths – 5 μm, 10 μm, 15 μm, 25 μm, 50 μm, 75 μm, and 100 μm respectively. All the different width gates had the same length. The HJFET photodetector was electrically characterized (current-voltage characteristics) by connected its source and drain contacts to a semiconductor parameter analyzer and illuminating the device's Ge/silicon junction to infrared illumination in the wavelength of 900, 940 and 1550 nm respectively . As a baseline, the device was also probed in dark. Voltage was swept between the range of -0.5V to +0.5V and the measured current was recorded in real-time using Labview 8.2 software. The Ge/Si HJFET photodetector demonstrated a dark current of 22 nA; a photogenerated current of 0.6 μA and sensitivity of 0.55 A/W at -10 mV for the smallest gate width (5 μm). It was observed that the sensitivity decreased as gate width increased, with the smallest gate being most sensitive and the largest gate being the least sensitive. The developed HJFET photodetector is being integrated with an on-chip silicon waveguide coupled to an optical fiber capable of bringing in light from a 1.55 μm source. The development of this Ge/silicon HJFET photodetector for the 1.55 μm wavelength range is essential for silicon photonics integration. The development of this Ge/silicon HJFET device potentially allows for the reduction of silicon area in CMOS devices. Also, the use of a standard photolithography process to pattern sputtered thin films of Ge active material offers possibilities for cost-effective manufacturing.

CP34 Influence of Pre-metal / Post-metal Annealing on Reliability with High-k/Metal Gate Metal-oxide Semiconductor Field Effect Transistors, ***Y.H. Lu***, *T.C. Chang (tcchang@mail.phys.nsysu.edu.tw)*, National Sun Yat-Sen University, Taiwan

This study investigates the influence of pre-metal / post-metal annealing on reliability with High-k/metal gate metal-oxide-semiconductor feild effect transistors. After positive and negative bias temperature instability (P/NBTI), the amount of high-k bulk and interface traps increases, leading to electric characteristic changed. To f urther analysis in fast I-V measurement , the threshold voltage shift in positive direction after PBTI with post-metal annealing device is smaller than that with pre-metal annealing device. In addition, the transconductance and subthreshold swing are slightly decayed. This is because that the n itrogen of TiN metal gate diffuses to high-k layer to passivate the shallow traps. On the other hand , the interface traps measured by the charge pumping technique with pre-metal annealing device is almost similar to that with post-metal annealing device under initial. This phenomenon indicates that the n itrogen do not diffuse from metal gate to interface layer.

CP36 The Effect of Hydrogen Ion on Resistance Switching Characteristic of Hf-doped Silicon Oxide RRAM, ***T.J. Chu***, *T.C. Chang (tcchang@mail.phys.nsysu.edu.tw), T.M. Tsai, K.C. Chang, Y.E. Syu, M.C. Chen*, National Sun Yat-Sen University, Taiwan

The resistive switching behaviors of hafnium doped silicon oxide by co-sputtering technology at room temperature were investigated in this study. Although non-doped SiO_2 based device has no switching phenomenon,

silicon oxide with a few Hf dopants can successfully be used as switching layer in resistive random access memory (RRAM). The reliability were exhibited by good endurance and retention in the Hf-doped silicon oxide ($Hf:SiO_x$) RRAM.

On the other hand, we also presented the special role of hydrogen ions in $Hf:SiO_x$ RRAM. In addition to the more typical oxygen ion-dominated resistive switching, hydrogen ions were also observed to trigger a resistance transformation phenomenon. Unlike a normal RRAM device, a hydrogen plasma-treated RRAM device is operated with a reversed voltage polarity, and the direction of hydrogen ion migration results in the chemical bonds breaking and repairing. This particular hydrogen-induced switching behavior suggests a different RRAM switching mechanism and is finally explained by our model.

CP37 Dynamic Gate-Induced-Drain-Leakage Stress Associated Hot Carrier Degradation in HfO_2/TiN n-channel Metal-Oxide-Semiconductor Field-Effect Transistors, ***J.Y. Tsai***, *T.C. Chang (tcchang@mail.phys.nsysu.edu.tw)*, National Sun Yat-Sen University, Taiwan, *C.E. Chen, S.H. Ho*, National Chiao Tung University, Taiwan

This work investigated the contribution of dynamic gate-induced-drain-leakage stress (GIDLS) associated dynamic hot carrier stress (HCS) in HfO_2/TiN n-channel metal-oxide-semiconductor field-effect transistors. In this work, the individual dynamic GIDLS and dynamic HCS show band-to-band hot hole injection at the drain side and interface states generation, respectively. However, there is no change in Sub-threshold swing (S.S.) after dynamic GIDLS associated HCS due to band-to-band hot hole injection at the drain side which acts to diminish the lateral electric field. Moreover, t he impaired lateral electric field causes most of interface states are mainly concentrated on shallow states. This result in ON state current and transconductance decreases but no significant S.S. degradation after dynamic GIDLS associated HCS. The proposed model is confirmed by one-side charge pumping measurement and gate-to-drain capacitance at varying frequencies.

CP38 Investigation of Hot Carrier Stress in p-channel Double Diffused Drain Metal-Oxide-Semiconductor Transistors with Different Shallow Trench Isolation Structures, ***C.E. Chen***, National Chiao Tung University, Taiwan, *T.C. Chang (tcchang@mail.phys.nsysu.edu.tw)*, National Sun Yat-Sen University, Taiwan, *H.M. Chen*, National Chiao Tung University, Taiwan, *B. You*, National Sun Yat-Sen University, Taiwan, *T.Y. Tseng*, National Chiao Tung University, Taiwan

This paper investigates the effects of liner oxide and nitride layer in shallow trench isolation (STI) on hot carrier stress (HCS) issue for p-channel double diffused drain metal-oxide-semiconductor (DDDMOS) transistors. It was found that abnormal off-current behavior after HCS in p-channel DDDMOS transistors with no optimized STI structure. According to ISE-TCAD simulation, the electric field at the corner of n-type substrate, or in the STI edge is strong than in the main channel. Moreover, there is a nitride layer for buffer in STI. Therefore, the electrons are generated by impact ionization in STI edge can be easily trapped in the nitride layer, or at the interface between liner oxide and nitride layer. Furthermore, the electron trapping in STI can be extended from drain to source during HCS, and then the conductive path for off-current is formed. From the charge pumping measurements at different operation conditions, this path formation is confirmed by the comparisons of charge pumping measurements between initial state and after HCS. For further analysis, the different thicknesses of liner oxide and nitride layer in the STI to demonstrate the origin of abnormal off-current after HCS in p-channel DDDMOS transistors.

CP39 Anomalous Degradation Behaviors under Illuminated Gate Bias Stress in a-Si:H Thin Film Transistor, ***M.Y. Tsai***, *T.C. Chang (tcchang@mail.phys.nsysu.edu.tw), A.K. Chu, T.Y. Hsieh, K.Y. Lin*, National Sun Yat-Sen University, Taiwan

This letter investigates the impact of gate bias stress with and without light illumination in a-Si:H thin film transistors. It can be observed that the I-V curve shifts toward the positive direction after negative and positive gate bias stress due to interface state creation at the gate dielectric. However, this study found that threshold voltages shift negatively and the transconductance curves maxima are anomalously degraded under illuminated positive gate bias stress. In additional, threshold voltages shift positively under illuminated negative gate bias stress. These degradation behaviors can be ascribed to charge trapping in the passivation layer dominates degradation instability and are verified by dual gate a-Si:H device.

CP40 Investigation on Degradation Behavior with UV Light Treatment under Negative Bias Illumination Stress in a-InGaZnO Thin Film Transistor, ***H.M. Chen***, National Chiao Tung University, Taiwan, *T.C. Chang (tcchang@mail.phys.nsysu.edu.tw), M.Y. Tsai*, National Sun Yat-Sen University, Taiwan, *Y.H. Tai*, National Chiao Tung University, Taiwan

Comparing the devices with and without ultraviolet (UV) light treatment, the threshold voltage shift of devices with UV light treatment under negative bias illumination stress (NBIS) in a-InGaZnO thin film transistor is less than that without UV light treatment. Under NBIS, the origin of degradation contains oxygen vacancy generation and hole trapping in gate insulator or the interface between gate insulator and a-InGaZnO layer. Excluding the oxygen vacancy generation, the degradation behavior of devices with UV light treatment is the same as that without UV treatment. The result indicates that the vacancy-induced degradation is constant in the devices with and without UV treatment and part of oxygen vacancy was generated by UV light treatment. Therefore, during NBIS, the less vacancy-induced degradation is generated in the devices with UV light treatment. In another word, oxygen vacancy generated by previous UV light treatment in a-InGaZnO layer causes the threshold voltage instability.

CP41 Hydrolysis-Induced Abnormal On-Current Degradation and Current Crowding Behavior under Negative Gate Bias Stress in a-InGaZnO Thin Film Transistors, ***K.H. Liu***, National Chiao Tung University, Taiwan, *T.C. Chang (tcchang@mail.phys.nsysu.edu.tw), M.C. Chen*, National Sun Yat-Sen University, Taiwan, *W.C. Chou*, National Chiao Tung University, Taiwan

This research investigates the electrical instability induced by surface hydrolysis effect under negative gate bias stress (NGBS). Different from the conventional stable characteristics under NGBS, a-IGZO TFT electrical characteristics exhibit instability after NGBS, with on-current degrading and current crowding phenomenon arising. When negative gate bias is applied on the TFT, hydrogen ions dissociate from ZnO-H bonds. Further, the dissociated hydrogen ions cause degradation of the interface between a-IGZO film and source/drain terminals. The obtained results of Fourier transform infrared spectroscopy (FTIR) also reveal the hydrolysis effect of the back surface of a-IGZO TFTs. According to the experimental results, the hydrolysis effect on the back surface of a-IGZO film plays an important role in the electrical reliability of a-IGZO TFTs.

CP43 Effect of Annealing Temperature on the Optical, Electrical and Thermoelectric Properties of MOCVD Grown ZnO, ***K. Mahmood*** *(khalid_mahmood856@yahoo.com), M. Asghar*, The Islamia University of Bahawalpur, Pakistan, *L. Na, Y. Raja, I. Ferguson*, University of North Carolina, US

Thin films of ZnO were grown on sapphire substrate by MOCVD growth technique. The grown ZnO thin films were annealed in oxygen environment at 500°C – 1000°C, keeping a step of 100°C for one hour. Photoluminescence study revealed that the intensity of band edge emission increased and defect emission decreased as annealing temperature increased because the density of oxygen vacancy related donor defects decreased with annealing temperature. This argument was further justified by the Hall measurements which showed that carrier concentration is inversely related with annealing temperature. Room temperature Seekbeck measurements showed that Seebeck coefficient increased from 222 to 415 μV/K as annealing temperature increased from 500 to 900 ^{0}C. and then decreased at 1000 ^{0}C. The power factor also obeys the increasing trend with annealing temperature

CP44 One Step Synthesis of Cobalt Ferrites ($CoFe_2O_4$) Nanoparticles by Hydrothermal Method and Optical Properties, ***A. Al-Shihri***, *A. Kalam (abul_k33@yahoo.com)*, King Khalid University, Saudi Arabia, *G. Du*, Zhejiang Normal University, China

Nanocrystalline cobalt ferrites ($CoFe_2O_4$) were synthesized in one step by hydrothermal process, using sodium hydroxide as precipitating agent and polysaccharides like cellulose and starch. The samples were labeled as HT-1a (blank), HT-1b (cellulose) and HT-1c (starch), respectively, where the molar ratios of Co : Fe was 1:2. The effect of NaOH, cellulose and starch on structural, morphological and optical properties of nanocrystalline cobalt ferrites were investigated by X-ray diffraction (XRD), transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM), Fourier transform infrared spectroscopy (FTIR) and ultraviolet visible spectroscopy (UV-vis). The infrared spectroscopy studies confirm the presence of metal oxide. By means of the above mentioned investigations, it is found that the using of cellulose decrease the crystallite size but starch increases the crystallite size of cobalt ferrites therefore, band gap increases with cellulose. We hope that the procedure mentioned can be suitable for the high–grade synthesis of $CoFe_2O_4$ nanoparticles and may have potential applications in waste water treatment, electrode, sensors, catalysts etc. The objective of this work is to compare the structure, size and

optical properties of $CoFe_2O_4$ nanoparticles obtained by the hydrothermal method.

CP45 Effect of Electron Beam Radiation on Electrical and Optical Properties of Multilayered Tin Oxide Thin Films, ***K.I. Maddani*** *(ki_maddani@rediffmail.com)*, SDMCET, India, *J.S. Bhat*, Karnatak University, India

Effect of electron beam radiation on electrical and optical properties of sol-gel spin coated tin oxide multilayered thin films are reported in the present article. The multilayered tin oxide films were synthesised using hydro-alcoholic solution [1]. Electric properties are investigated in terms of sheet resistance / resistivity [1, 3] and optical properties through UV absorption method [2, 5]. Variation in the transport properties of the film are recorded after exposing to electron beam radiation of different dosage.

Films exposed to electron beam radiation of 8Mev energy show significant change in the electrical and optical properties; resistivity of the films increase and optical absorption edge shifts towards higher energy region. The resistivity of single layer films before irradiation was $2.653x10^{-3}$ Ω – cm and increases 2.741x100 Ω – cm. The absorption edge of single layer film before irradiation occurs at 3.731 eV and after irradiation shifts to 3.865 eV. Similar, but less variations were recorded in the multilayered coatings.

In conclusion, the observed effects of irradiation may be due to elastic collisions of energetic electron beam with the nuclei of the thin film, which may cause further increase in disorders and scattering in the lattice structure of the deposited films.

CP46 TiO_2:Nb Transparent Conductive Thin Films Treated by a Post Hot-wire Annealing in a Reducing H_2 Atmosphere, *M.V. Castro, L. Rebouta, P. Alpuim, M.F. Cerqueira*, University of Minho, Portugal, *E. Alves, N.P. Barradas*, Ion Beam Laboratory (ITN), Portugal, ***C.J. Tavares*** *(ctavares@fisica.uminho.pt)*, University of Minho, Campus Azurém, Portugal

Transparent and electrically conductive niobium-doped TiO_2 thin films have been deposited on glass surfaces by d.c.-pulsed reactive magnetron sputtering from a composite Ti:Nb target, using oxygen as reactive gas. A rapid 1 min annealing at 500 ºC in an atomic hydrogen rich atmosphere, obtained by flowing H_2 on a Ta filament resistively heated to 1750ºC in vacuum (hot-wire), proved to be very efficient in enhancing the electrical properties of these ~100 nm thick TiO_2:Nb (2at.%) thin films. Dark conductivity (σ_d) and its activation energy was measured as a function of (inverse) temperature and the value of σ_d at room temperature was used to assess the effect of the H_2 annealing on the transport properties. A 5-order of magnitude increase in electrical conductivity was observed for optimised treatment conditions at a hydrogen pressure of 10 Pa. A maximum value of σ_d in the range of $\sim 1.4 \acute{} 10^3$ S/cm was attained for optimised conditions, where a level of ~6 at. % of H doping was measured close to the film surface. X-ray photoelectron spectroscopy, elastic recoil detection analysis, Rutherford backscattering and Raman spectroscopies were used to access information of composition and film structure for the explanation of the strong enhancement of the film's electrical conductivity and band-gap widening to 3.45 eV following hot-wire treatments. These thin films can be used as transparent conductive oxide contact layers for photovoltaic applications.

Keywords: Nb doping; titanium dioxide; hot-wire; TCO; electrical properties; reactive sputtering.

CP47 Thermo-mechanical Behavior of Die Attach Film on Flexible PCB Substrate for Multi Chip Package, ***J.-O. Bang***, Sungkyunkwan University, Republoic of Korea, *K.S. Kim*, Sungkyunkwan University, Republic of Korea, *Y.M. Lee*, Samsung Electro-Mechanics Co., Republic of Korea, *S.B. Jung (sbjung@skku.ac.kr)*, Sungkyunkwan University, Republic of Korea

Die attach film (DAF) has been widely used as an adhesive layer in electronic packaging industry, on account of its high cohesive strength and low moisture absorption. These characteristics of DAF are preferred for good adhesion between a die and a printed circuit board (PCB). However, DAF delamination might occur by voids which are induced during a post process for multi-stacking package. Therefore, the study on the correlation between the voids and mechanical properties of DAF is one of the challenging issues for development of multi-chip package (MCP). The various types of specimen were prepared using different solder resist conditions and tested for interfacial adhesion. All the samples were manufactured using 50-μm-thick dies and 20-μm-thick DAFs with optimal bonding conditions. After infrared heating, voids and delamination at the films' interfaces with the PCBs were measured by C-mode scanning acoustic microscopy, which showed void volume percentages of approximately 2%-6%. Peel testing and lap shear testing showed that the adhesion of the DAF to the PCB and delamination under stress were greatly affected by voids.

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CP48 Optimization of n-Oxide Thin-film Formation in Heterojunction Solar Cells Using Thermally Oxidized p-Cu2O Sheets, ***Y. Nishi***, *T. Miyata (tmiyata@neptune.kanazawa-it.ac.jp)*, *T. Minami*, Kanazawa Institute of Technology, Japan

Recently, we reported a substantial improvement in conversion efficiency in Cu2O-based p-n heterojunction solar cells fabricated by forming an n-type oxide semiconductor thin film on a thermally oxidized p-type cuprous oxide (Cu2O) sheet [1]. In this paper, we describe the optimization of formation conditions for various n-oxide thin films, including multicomponent metal oxide semiconductors, in order to achieve further improvement in obtainable photovoltaic properties in heterojunction solar cells using the p-Cu2O sheet. Thermally oxidized polycrystalline p-Cu2O sheets were prepared with a low resistivity, on the order of 100-103 Ωcm (Hall mobility above roughly 100 cm2/Vs), for use in this work. The evaluation of photovoltaic properties was conducted under simulated AM1.5G solar illumination. All of the n-oxide thin films were prepared with a thickness of 30-70 nm on non-intentionally heated Cu2O sheets by a magnetron sputtering deposition or pulsed laser deposition (PLD). It was found that the obtained photovoltaic properties in Al-doped ZnO (AZO) transparent electrode/Ga2O3-based multicomponent oxide/Cu2O heterojunction solar cells tended to improve as the Ga content was increased in the multicomponent oxide thin films prepared by PLD. For example, the values of open circuit voltage, short-circuit current density, fill factor and conversion efficiency obtained in AZO/(GaXIn1-X)2O3/Cu2O heterojunction solar cells all decreased as the Ga content (X) was decreased. However, in heterojunction solar cells with either Ga2O3-ZnO or Ga2O3-Al2O3 thin films, the highest efficiency was obtained by adding an amount of ZnO or Al2O3 that was small relative to that of Ga2O3. In AZO/(GaXAl1-X)2O3/Cu2O heterojunction solar cells with (GaXAl1-X)2O3 thin films prepared by varying X with a thickness of 50 nm, an AZO/(Ga0.975Al0.025)2O3/Cu2O heterojunction solar cell exhibited the highest efficiency of 5.72%.

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CP49 Study on Aluminum Hot-dip Copper Process and the Interface Microstructure of Copper-clad Aluminum Bimetallic Material, ***X. Chen***, Georgia Institute of Technology, US, *X. Tang, Z. Wang (wangzd@mater.ustb.edu.cn)*, *X. Hui*, University of Science and Technology Beijing, China, *M. Li*, Georgia Institute of Technology, US

The Copper-clad aluminum bimetallic material not only has the good electric conductivity, high thermal conductivity, low contact resistance of copper, but also has the light weight and economic advantages of aluminum. However, some problems still exist in the current various production methods of copper-clad aluminum composite materials, such as the difficulties to control the process, the thickness of composite layer and the weakness of composite strength. To address the problems, the hot dip method was conducted to produce the copper-clad aluminum thin wire. The experimental results show that the best process of scribbling fluxing agent is bathing the aluminum wires in 1.8% KF aqueous solution at 35℃ for 30s. The best parameters of hot dip process is hot dip aluminum wires in 1085℃~1090℃ copper liquid for less than 1s. The success of aluminum hot dip in copper has achieved the low melting point metal hot dip in high melting point metal liquid, which is of significance for the further development and application of production of copper-clad aluminum bimetallic thin wires in hot dipping methods.

Keywords: A. Hot dip; B. Copper-clad aluminum bimetallic thin wire; C. Fluxing agent; D. Interface

Coatings for Biomedical and Healthcare Applications
Room: Town & Country and San Diego - Session DP

Symposium D Poster Session

DP1 Biocompatibility and Antimicrobial Performance of TiZrCN Coatings, *H.L. Huang*, China Medical University and Hospital, Taiwan, *Y. Chang (yinyu@mail2000.com.tw)*, ***Y.C. Yang***, National Formosa University, Taiwan, *C.H. Lai*, *T.M. Shieh*, China Medical University and Hospital, Taiwan

Commercial pure (CP) titanium (Ti) is widely used as metallic biomaterials. However, pure Ti still fails to meet some requirements for clinically uses of implant applications due to its poor wear resistance and a lack of antimicrobial performance. Better antimicrobial and wear-resistant abilities of Ti implant are beneficial for avoiding the infection and inflammation after surgery. In this study, a new TiZrCN film was deposited on a bio-grade pure Ti material. A cathodic-arc evaporation system with plasma enhanced duct equipment was used for the deposition of TiZrN and TiZrCN coatings. Reactive gas (N_2) and C_2H_2 activated by the titanium and zirconium plasma in the evaporation process was used to deposit the TiZrCN coatings with different carbon and nitrogen contents. Characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy (RS), field emission scanning electron microscopy (FESEM), and transmission electron microscopy (TEM), the crystal structure, bonding state and surface morphology of the deposited TiZrCN films were studied. The chemical composition was evaluated by wavelength-dispersive x-ray spectroscopy (WDS). M echanical properties, such as the hardness and elastic modulus, were measured by means of nanoindention. To evaluate the wear performance of the deposited coatings, an impact test was performed using a cyclic loading device with a hard tungsten carbide indenter as an impact probe. The microbial activity of the films was evaluated against ***Staphylococcus aureus*** and ***Actinobacillus actinomycetemcomitans*** are *Gram-positive* and Gram-negative bacteria, respectively, that exhibit physiological commensalism on the human skin, nares, and mucosal and oral areas. Both bacteria were chosen as the model for ***in vitro*** anti-bacterial analyses by a fluorescence staining method employing Syto9. The cell compatibility and morphology related to cell-line human skin fibroblast cells (CCD-966SK) on the coated samples were also determined by using the MTT assay, reverse transcriptase–polymerase chain reaction (RT-PCR), and scanning electron microscopy (SEM). The results suggested that the TiZrCN film can improve antibacterial performance with compatible soft-tissue biological response.

DP2 Biocompatibility and Electrochemical Behavior of Nanotubular Anodized TiO2 Layer for Implant Applications, *E. Mundaray*, ***L. Gil*** *(lindaegil@gmail.com)*, Universidad Nacional Experimental Politécnica (UNEXPO), Venezuela (Bolivarian Republic of), *F. Alvarez*, Fundación Instituto de Estudios Avanzados (IDEA), Venezuela (Bolivarian Republic of), *L. Hernandez*, Universida Nacional Experimental Politécnica (UNEXPO), Venezuela (Bolivarian Republic of)

Titanium (Ti) and its alloys, due to their self-organized oxide layer, which protects the surface from corrosion and prevents ion release, are widely accepted as biocompatible metal implants. However, when Ti and Ti alloys are implanted in bone, the bonding of the implant with living bone often does not develop, and a long time of several months is required to achieve the integration of the implants with bone tissue. Recently, researchers have started to focus on surface modification of the implant in the nano-scale regime because of the natural physiological environment to which bone cells are accustomed to. Synthesis of nanostructured titanium dioxide (TiO2) such as nanotubes has raised interest lately due to their high surface-to-volume ratio and the ability to provoke a greater degree of biological plasticity compared to conventional microstructures. A physical advantage of a TiO2 nanostructured surface is that it is composed of and created directly from the underlying native Ti oxide and this can eliminate the tendency of delamination that occurred prevalently in the bioactive coating. Another aspect to consider is that in the case of implants, the selection of the electrochemically stable materials with effective long-term corrosion resistance in the body is also essential. In this study, the bioactive and the electrochemical properties of titanium implant materials with a nanotube surface treatment were evaluated. Disks of Ti6Al4V were used as substrate and anodized at 20V in two electrolytes (HF + H_3PO_4, and NH_4F:H2O: glycerol) with three anodization times for each electrolyte at room temperature. The nanotubes morphology was examined by FE-SEM. The biocompatibility was evaluated in *vitro* through cultivation of mesenchymal stem cells (MSCs) and the determination of these metabolic activities. The experimental results show that the diameter of the nanotubes was markedly influenced by the anodization times and it was not influence by the electrolytes solution. The best electrochemical behaviour and biocompatibility response were obtained for an anodization time of 4 hour and a NH4F:H2O: glycerol electrolyte solution

DP3 Low Temperature Pasteurization via High Density Plasma Oxidation, ***T. Aizawa*** *(taizawa@sic.shibaura-it.ac.jp)*, Shibaura Institute of Technology, Japan, *Y. Sugita*, YS-Electric Industry, Co. Ltd., Japan

A sterilizer with use of ethylene oxide gas (EOG) has been widely utilized in hospitals or large-scaled clinics. Although this gas-phase system provides us a powerful means to sterilize medical tools for operation, its poisonous nature is often harmful and time-consuming in practical use. Various kinds of plasmas have been applied as a promising method to make low-temperature pasteurization instead of those conventional sterilizers. For an example, the hydrogen peroxide plasma sterilizing system is utilized in market since it works in relatively low temperature; however, its effectiveness in sterilization is often limited by the presence of peptidoglycan on the eubacteria cell membrane. That is, eubacteria is still alive after sterilizing because of this protection. This issue is never solved even by using ICP or micro-wave induced oxygen plasmas.

Authors have been concerned with research and development of high density oxygen plasma generators. Owing to high electron density and ionized oxygen flux, carbon-base films on the substrate can be removed with fast ashing rate. In the present study, this system is applied to pasteurization to solve the above issues related to plasma sterilizing. As a bio-indicator, the geobacillus stearothermophilus sample with the sporophyte content of 104 and 105 is employed as a target for sterilizing experiment. This gram-positive bacteria is shielded by peptidoglycan; without direct oxidation and bombardment against this shield layer, this bacteria could be alive to germinate during long-term cultivation culture. In the sterilizing experiment, this bacteria sporophyte is enclosed by the glassine paper to make a test-piece. Plasma parameters are varied to find that no bacteria is cultured from the sporophyte at 323 K after cultivation time of 604.8 ks or one week when 3000 kw is applied to this test-piece. This assures that generated oxygen atoms and ions should penetrate the glassine paper and sporophyte membrane and to make direct interaction with bacteria for pasteurization.

DP4 Biomolecular Modification of Zirconia Surface for Enhenced Biocompatibility, *S.K. Hsu*, *H.C. Hsu*, Central Taiwan University of Science and Technology, Taiwan, *W.F. Ho*, Da-Yeh University, Taiwan, *K.H. Lee*, ***S.C. Wu*** *(scwu@ctust.edu.tw)*, Central Taiwan University of Science and Technology, Taiwan

Yttria-Tetragonal Zirconia Polycrystal(Y-TZP) is a preference material used as biomaterials due to its good mechanical properties. In order to improve the biocompatibility of zirconia, RGD-peptide derived from extracellular matrix proteins was employed to modify the surface of YTZP to promote cell adhesion.

In this study, the surfaces of YTZP were modified using hydrothermal method at different periods. The topographies of modified YTZP were analyzed by contact angle, XRD, FTIR, AFM and FE-SEM, as well as the mechanical properties were evaluated by Vickers hardness, fracture toughness and three point bending. The RGD-peptide was immobilized on the surface of YTZP by chemical treatment. This RGD-peptide immobilized YTZP were characterized by FTIR, AFM and FE-SEM, and then were cocultured with MG-63 osteoblast cells for the biocompatibility assay. The cell morphology and proliferation were evaluated by SEM, WST-1 and ALP activity assay.

The XRD results indicated that the phase transformation, from tetragonal phase to monoclinic phase, was increased with increasing the incubation time of hydrothermal treatment. However, there are no significant differences in mechanical strengths after RGD-peptide was successfully grafted onto the YTZP surface. The SEM images showed that the MG-63 cells appeared polygonal, spindle-shaped, and attached on the RGD-peptide modified YTZP. The proliferation and cellular activities of MG-63 cells on the RGD-peptide modified YTZP were better than that on the YTZP.

From the above results, the RGD-peptide can successfully grafted onto the hydrothermal modified YTZP surface. The RGD-peptide immobilized YTZP can increase the cell adhesion, thus, improve the biocompatibility of YTZP.

DP5 Surface Modification of Blood-contacting Biomaterials by Plasma-Polymerized Super-Hydrophobic Films, *C.R. Hsiao*, Feng Chia University, Taichung, Taiwan, *C.W. Lin*, Central Taiwan University of Science and Technology, Taiwan, *C.M. Chou (cjchung@ctust.edu.tw)*, Taichung Veterans General Hospital, Taiwan, ***C.J. Chung***, Central Taiwan University of Science and Technology, Taiwan, *J.L. He*, Feng Chia University, Taiwan

Due to the increasing cardiovascular diseases, it has a significant impact on human's life and thereby raises the demand of blood-contacting

biomaterials. In this study, the film composed of plasma-polymerized hexamethyldisiloxane (HMDSO) containing silica nano-particles as the main layer and a very thin plasma-polymerized fluorocarbon layer over the top was developed to exhibit super-hydrophobic property. The polyurethrane (PU), a broadly used biomaterial for medical applications such as vascular grafts, catheters and prostheses was used as substrate. A pulsed-dc plasma polymerization process was employed by adjusting the precursor flow rate and the power input. The deposited films were examined their microstructure, water contact angle, cytotoxicity and *in vitro* platelet adhesion tests.

Experimental results show that the deposited films are amorphous with randomly dispersed silica nanoparticles exposed to the surface of the deposited films. Water contact angle of the obtained film, after optimizing deposition parameters, was measured at 153.4^{o}, namely super-hydrophobicity, which shall attribute to the synergistic effect of both nano-structural surface morphology (resulting from the inserted silica nano-particles) and low surface energy (resulting from surface flourocarbon groups). Results of *in vitro* cytotoxicity and platelet adhesion tests showed satisfactory fibroblasts cell proliferation and decreased platelet adhesion on the coated specimens. These quantitative indications as revealed above imply that such films may have the potential to avoid thrombosis and possibly provide an alternative for surface modification of blood-contacting biomaterials.

Keywords : super-hydrophobic; plasma-polymerization; polyurethrane (PU); blood-contacting biomaterials.

DP6 Influence of Non-Photoresist Lithography on Cell Activity of Titanium, ***J.-H. Kang***, *M.-H. Lee (mhlee@kicet.re.kr), W.-S. Seo,* Korea Institute of Ceramic Engineering and Technology, Korea, *S.-W. Lee,* Kyung Hee University, Korea, *H.-J. Choi*, Yonsei University, Korea

Titanium and its alloys are widely useful materials for the fabrication of dental and orthopedic implants, on account of their favorable combination of properties such as high corrosion resistance and excellent general biocompatibility by surface oxide layer. Also, in biomedical systems, formed microgroove on titanium substrate influenced to increase of cells adhesion, proliferation and cell guidance. However, microgroove on titanium surface should be formed by various processes, such as photoresist to establish microgroove and subsequent acid etching process. However, micropattern using ultraviolet (UV) on titanium substrate can easily formed by only photomask without photolithography and etching process. Also, UV wavelength influenced to improve the cell adhesion and proliferation of titanium surface by variation of electrostatic property and chemical composition. This research examined the effect of micropattern size formed by UV wavelength with various pattern size of photomask on cell proliferation. The UV-micropattern of titanium surface were formed using photomask of various pattern size (30 ~ 300um) in UV irradiation condition during 24hr. The treated titanium substrate was characterized by XPS, wetting angle and CLSM. The activity of Human Primary Ligament Cells (PLCs) on the UV-micropattern was analyzed after 14days of osteogenic culture using the ALP activity test. Through these results, the relationship between the wavelength of UV light source and the variation of surface characteristics and HPCs activity are discussed.

DP7 Investigation of an a-TiC_x Film as the Interlayer of Fluorinated DLC on a Ti6Al4V Substrate- an Approach to the Anti-corrosive and Mechanical Properties, *C.-C. Chou (cchou@ntou.edu.tw), H.-Y. Chen,* ***M.-K. Hsu***, National Taiwan Ocean University, Taiwan, Republic of China

Amorphous titanium carbide (a-TiC_x) was deposited on Ti6Al4V substrates as an interlayer of functional diamond-like carbon (DLC) to improve the corrosive drawback of the silicon interlayer by radio frequency plasma enhanced chemical vapor deposition (rf PECVD) technique. The a-TiC_x thin films were obtained by using a mixture of titanium tetrachloride ($TiCl_4$) and methane (CH_4) gases. Fluorinated amorphous DLC (F-DLC) was then coated on the samples by the same CVD system from the precursors of tetrafluoromethane (CF_4) and CH_4. The structure and surface properties of a-TiC_x interlayers, prepared by various $TiCl_4$ flow ratios, were investigated by using X-ray diffraction spectroscopy, Raman spectroscopy, Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy, and scanning electron microscopy. The mechanical properties were evaluated by nano-indentation and the adhesion, by micro-scratch. The corrosion behavior was studied in a physiological solution. An F-DLC coating with a 100 nm Si interlayer prepared by physical vapor deposition process was also implemented as a benchmark. The results showed that the anti-corrosion capability and the adhesive strength of the F-DLC coatings with an a-TiC_x interlayer is much better than that with an a-Si one.

DP8 Effects of the Plasma Electrolytic Oxidation Method in the CaP Enriched Titanium Oxide Layer Physicochemical and Corrosion Properties, ***C. Laurindo*** *(carlos.laurindo@pucpr.br), R.D. Torres, P. Soares,* Pontificia Universidade Católica do Paraná, Brazil, *S. Mali, J. Gilbert,* Syracuse University, NY

The Plasma Electrolytic Oxidation (PEO) is a traditional technique that promotes the transformation of the titanium substrate into a high hardness ceramic layer by the interaction of anodic oxide growth and plasma channel shock caused by the dielectric break down at high voltages, taking place in an aqueous electrolyte. There are two principal methods used in anodic oxidation, the potentiostatic mode, which the voltage is maintained constant and the galvanostatic mode, which the current density is maintained constant. However, the differences between these two methods are unclear. The aim of this work is to evaluate the influence of the PEO method and time on the surface and corrosion properties. Titanium samples were submitted to potentiostatic PEO at 250, 300, 350 and 400V and galvanostatic PEO at 200, 400, 600 and 800 mA/cm² for 1 and 3 min. The surface properties were evaluated by scanning electron microscopy (SEM), X-Ray Diffraction (XRD), roughness and surface wettability measurements. The corrosion properties were evaluated by open circuit potential, electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization. The oxide layer is significantly altered with the applied voltage, while there is no change for different applied current densities. Pore size, contact angle, and the amount of rutile phase increased with applied voltage in the potentiostatic PEO. In the galvanostatic PEO, the oxide surface properties remain practically the same. Corrosion resistance is improved with applied voltage, and with anodization time for current densities.

DP9 Silicon-substituted Hydroxyapatite Coating on Biomedical Ti-Nb-Zr Alloy Using Cyclic Electrochemical Deposition Method, ***Y.H. Jeong***, *W.A. Brantley*, The Ohio State University, US, *H.C. Choe (hcchoe@chosun.ac.kr)*, Chosun University, Korea

The usage of biomedical implant has been gradually increased for couple of decades due to replace for injuries and old aged diseases. The metallurgical implant materials is one of the most frequently used to restore for damaged hard tissue such as dental and orthopedic field, which should be have non-toxic and high biocompatibility. The surface modification and alloy development of implant materials have been encouraged to have more successful and higher biocompatibility between replacement materials and human tissue. Regarding these reasons, Hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$, HA] is used as a bio-ceramic coating on metal implant surface due to their bioactivity and osseoconductive properties in vivo. To be more effective HA coating layer, the silicon substitution of HA (Si-HA) coatings are greater than single HA coating for bone on-growth. As a coating substrate of implant materials, β phased Ti-Nb-Zr alloy system has significant low elastic modulus and has non-toxic elements than that of conventional alloys such as pure titanium or Ti-6Al-4V alloy, Ti-35Nb-10Zr alloy has appropriate properties with reasonable mechanical and chemical properties to be used as a Si-HA coating substrate. The objective of this study was to investigate the silicon-substituted hydroxyapatite coating on biomedical Ti-Nb-Zr alloy using cyclic electrochemical deposition method.

The Ti-Nb-Zr alloy was manufactured with 35 wt.% of Nb and 10 wt.% of Zr by arc melting furnace to be a β phase. Electrochemical deposition of Si substituted Ca/P was performed by pulsing the potential with a method of cyclic voltammetry, and changed cyclic time between 10 and 150. The electrolyte was prepared by dissolving the reagent-grade chemicals: $Ca(NO_3)_2$, $NH_4H_2PO_4$, and $Na_2SiO_3 . 9H_2O$ to be 1.67 of Ca/P ratio and Si contents were controlled to be 1 - 2.5 wt.% in the total portion. The surface characteristics were observed by field-emission scanning electron microscopy, X-ray diffractometer, Fourier transform infrared spectroscopy, electrochemical corrosion test (potentiodynamic and AC impedance test). Analysis of variance (ANOVA) was performed to compare the variation of corrosion parameters and significance was $p<0.05$. As results, more cyclic time of coatings layer could be have increased corrosion potential and decreased current density, also has more plate like structure than that of less cyclic time. (NRF: R13-2008-010-00000-0; hcchoe@chosun.ac.kr [mailto:hcchoe@chosun.ac.kr])

Keywords: Silicon substitution, Hydroxyapatite, Electrochemical Deposition, Corrosion, Biomaterials

DP10 Nanotube Shape and Morphology Control of Ti-6Al-4V by Various Applied Potential for Drug Doping and Bioactive Materials Coating, ***H.C. Choe*** *(hcchoe@chosun.ac.kr)*, Chosun University, Republic of Korea

CP Ti and Ti-6Al-4V alloy has been widely used for implant materials such as dental and orthopedic implants due to a good mechanical property, corrosion resistance, and biocompatibility. Even though these advantages,

many researchers have focused on the surface modification for improvement of biocompatibility on interface between implant and bone.

Especially, one of surface modification methods is nanotube formation on the alloy for improvement for biocompatibility. It is possible to form nanotubes on the surface of the implant alloy under the conditions of constant voltage in general. However, in this study, given the gradual change of the various applied potential, to nanotube formation, was studied how nanotubes form would change accordingly for drug dopping and bioactive materials coating.

In this study, nanotube shape and morphology control of Ti-6Al-4V alloy by various applied potentials for drug dopping and bioactive materials coating have been researched by using electrochemical methods in 1 M H_3PO_4 with small amounts of fluoride ions. The nanotube formation was carried out by DC power supply with applied voltage variation in range of 10~40V after washing three times with distillation water for 15 minutes. Nanotube shape and morphology was observed by FE-SEM, EDS, XRD, STEM, AFM, XPS. Nanotube shape can be controlled by applied potential for drug dopping and bioactive materials coating(hcchoe@chosun.ac.kr [mailto:hcchoe@chosun.ac.kr]).

Keywords: Ti-6Al-4V alloys, Applied potential, Nanotube shape, Drug dopping, Coating

DP11 Electrochemically Hydroxyapatite-precipitated Nanotubular Ti-35Ta-xNb Alloys, ***C.I. Jo***, Chosun University, Korea, Republic of Korea, *H.C. Choe (hcchoe@chosun.ac.kr)*, Chosun University, Republic of Korea

The β-type titanium alloys are advantageous for the development of titanium alloys with low Young's modulus for biomedical applications. Young's modulus of dental implant is important to osseointegration of human bone for decreasing the stress shielding. In such conditions, bone atrophy occurs and leads to the loosening of the implant and refracting of the bone. In order to forming β-type titanium alloys, titanium alloys have encouraged the search for new Ti-based biomaterials non-toxic and non-allergic element such as Nb, Ta, Zr, Hf, Mo, and Sn. Hydroxyapatite (HA) coatings on the implant biomaterials have many biological benefits such as direct bonding to bone and enhancement of new bone formation around it due to its chemical similarity with hard tissues. Many Electrochemical deposition method is one of the many coating methods for dental implant, electrochemical coating method on titanium alloys is an attractive process because highly irregular objects can be coated relatively quickly at low temperatures. Additionally, the thickness and chemical composition of coatings can be well controlled through adequate conditions of the process. Also, nanotube formation is observed that the size of the nanotubes can affect cell proliferation and adhesion.

In this study, we were researched electrochemically hydroxyapatite-precipitated nanotubular Ti-35Ta-xNb alloys for biomedical application. The Ti-35Ta-xNb alloys contained from 0 wt. % to 15 wt. % Nb contents were manufactured by arc melting furnace. The surface treatment was performed using anodizing electrolyte of 1 M H_3PO_4 containing 1.2 wt. % NaF for 1 h. HA thin film coatings were prepared by electrochemical deposition that was carried out using cyclic and voltammetry (CV) method at 85 ℃ in 5 mM $Ca(NO_3)_2$ + 3 mM $NH_4H_2PO_4$. The coated surface morphology of nanotube structured Ti-35Ta-xNb alloy was examined by FE-SEM, EDS and XRD. It was found that HA coating surface on the nanotube structured Ti-35Ta-xNb alloys have good biocompatibility and good corrosion resistance for biomedical application. (Supported by NRF: 2013 R1A1A 2006203 & NRF: R13-2008-010-00000-0; hcchoe@chosun.ac.kr [mailto:hcchoe@chosun.ac.kr]).

DP12 Nanotube Formation Phenomena on Ti-25Nb-xZr Alloys with Zr Content and Applied Potential, ***I.S.Byeon. Byeon***, *H.C. Choe (hcchoe@chosun.ac.kr)*, Chosun University, Republic of Korea

Cp-titanium and Ti-6Al-4V alloys are metallic materials used as a dental implants and orthopedic implants. However, there are some problems of Ti-6Al-4V alloy such as Alzheimer's disease of aluminum, toxicity of vanadium, high elastic modulus, and low corrosive-wear resistance. These concerns have led to the development of new type titanium alloys without aluminium and vanadium. It has been reported that, β rich Ti-Nb-Zr alloys are better substitutes, as these materials possess low modulus and consists of non-toxic elements. The Nb present in these alloys, a known β stabilizer reduces the modulus of the alloy. Further, the presence of β phase in the microstructure enhances the ability of the alloys to harden on subsequent aging. The addition of Zr to implant alloy leads to better corrosion resistance due to the formation of stable oxide layer. Also, for the improvement of biocompatibility of Ti alloy, we need the nano-scale surface modication, for bioactivity and osteoblast adhesion. The nanotubular surface with nano-scale on the native oxide will result in very strong reinforcement of the bone response for the formation of nano-scale surface.

Therefore, the objective of the present study was to research on nanotube formation phenomena on Ti-25Nb-xZr alloys with Zr content and applied potential. The Ti-25Nb-xZr ternary alloys contained from 0 wt. % to 15 wt. % contents were manufactured by vacuum arc-melting furnace. The ingots of Ti-25Nb-xZr alloys were homogenized in Ar atmosphere at 1000 ℃ for 12 h followed by quenching into 0 ℃ water. The formation of nanotubular film was conducted by electrochemical method in mixed electrolytes with 1 M H3PO4 + 0.8 wt. % NaF at 30 V for 2 h. The surface characteristics were investigated using field emission scanning electron microscopy (FE-SEM), x-ray diffractometer (XRD), X-ray fluorescence (XRF) and energy dispersive X-ray spectroscopy (EDS). Microstructures of Ti-25Nb-xZr alloys were shown needle-like structure to equiaxed structure as Zr content increased. Nanotube formed on Ti-25Nb-xZr alloys show two types of nanotube structure. (Supported by NRF: 2013 R1A1A 2006203 & NRF: R13-2008-010-00000-0; hcchoe@chosun.ac.kr).

Keywords: Nanotube, Ti-25Nb-xZr alloy, anodization, Biocompatibility.

DP13 The Tribocorrosion of CoCrMo Alloys Coated with TiAlPtN/TiAlPt Multilayers, ***M. Flores (martin.flores@red.cucei.udg.mx)***, Universidad de Guadalajara, Mexico, *E. Andrade*, Universidad Nacional Autónoma de México, Mexico, *O. Jimenez*, Universidad de Guadalajara, Mexico

The tribocorrosion phenomenon is present in biomedical alloys that are used in artificial implants to replace natural joints. This damage limit the service life of such implants, the hard coatings can improve the resistance of wear and corrosion. The multilayers of TiAlPtN/TiAlPt were deposited on CoCrMo alloys by magnetron sputtering. In this work we study the wear mode of the samples coated and alone in a simulated body fluid with an ion concentration similar to that in the human blood. The structure of coatings was studied by means of XRD and the composition by RBS and EDS techniques. The tribocorrosion behavior of CoCrMo alloys alone and coated with TiAlPtN/TiAlPt multilayers was studied in simulated body fluid. The tribocorrosion was performed using a ball on plate reciprocating tribometer, the tests were conducted at 37 ℃ of temperature. The loads used were between 0.25 N to 2N, the oscillating frequencies was 1Hz. The corrosion and tribocorrosion were studied using open circuit potential (OCP) and potentiodynamic polarizations. The potentiodynamic polarization was used to estimate the change in the corrosion rate due to wear and the potensiostatic polarization in the passive region to measure the change in the wear rate due to corrosion. In order to study the wear mechanisms, the debris, the topography and composition of worn surfaces were analyzed by means of SEM and EDS. For the CoCrMo alloy the corrosion augmentation factor was greater than the wear augmentation factor. The coatings improve the corrosion and tribocorrosion resistance of CoCrMo alloys.

DP14 Enhanced Corrosion Resistance and Hemocompatibility of Biomedical NiTi Alloy by Atmospheric-pressure Plasma Polymerized Fluorine-rich Coating, ***P.H. Li***, City University of Hong Kong, Hong Kong Special Administrative Region of China, *L.M. Li*, City University of Hong Kong, China, *W.H. Wang*, The University of Hong Kong, China, *W.H. Jin*, City University of Hong Kong, China, *X.M. Liu*, Hubei University, China, *K.W.K. Yeung*, The University of Hong Kong, China, *P.K. Chu (paul.chu@cityu.edu.hk)*, City University of Hong Kong, Hong Kong Special Administrative Region of China

To improve the corrosion resistance and hemocompatibility of biomedical NiTi alloy, hydrophobic polymer coatings are deposited by plasma polymerization in the presence of a fluorine-containing precursor by an atmospheric-pressure plasma jet. This process takes place at a low temperature in air and can be used to deposit fuoropolymer films using organic compounds that cannot be achieved by conventional techniques. The composition and chemical states of the polymer coatings are characterized by Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS). The corrosion behavior of the coated and bare NiTi samples is assessed and compared using polarization tests and electrochemical impedance spectroscopy (EIS) in physiological solutions including simulated body fluids (SBF) and Dulbecco's Modification of Eagle's Medium (DMEM). The corrosion resistance of the coated NiTi alloy is evidently improved. Protein adsorption and platelet adhesion tests reveal that the adsorption ratio of albumin to fibrinogen is increased and the number of the adherent platelets is greatly reduced on the coating. The plasma polymerized coating produces better hemocompatibility and is promising as a protective and hemocompatible coating on cardiovascular implants.

DP15 Enhanced Osteogenic Activity on Platform of Titanate Nanotube Arrays, ***X.M. Zhang***, *L.M. Li, W.H. Jin, P.H. Li*, City University of Hong Kong, Hong Kong Special Administrative Region of China, *L.Z. Zhao*, The Fourth Military Medical University, China, *K.F. Huo*, Huazhong University of Science and Technology, China, *P.K. Chu (paul.chu@cityu.edu.hk)*, City University of Hong Kong, Hong Kong Special Administrative Region of China

Titanium (Ti)-based dental and orthopedic implants are widely used clinically, but insufficient osseointegration and associated infection may occur after implantation. Hence, materials improvement is necessary. Highly ordered titania nanotubes (TiO_2-NTs) fabricated on Ti implants by electrochemical anodization have attracted increasing attention. TiO_2-NTs have a lower elastic modulus of approximately 36-43 GPa which is much closer to that of natural bones and are expected to have better biomechanical compatibility than other artificial biomaterials. They are also promising bioactive coatings that can induce direct bone-implant bonding and enhanced host defense on the implant surface. More importantly, the hollow structure in the TiO_2-NTs with the proper dimensions not only alter the cell behavior and foster the growth of nano-structured hydroxyapatite in simulated body fluids, but also act as an excellent drug delivery platform, particularly for inorganic bioactive elements. Our previous work shows that the hierarchically hybrid TiO_2-NTs and silver particles are stable and can generate long-lasting delivery effects. Elements such as strontium (Sr) and zinc (Zn), have aroused clinical interests because of the pronounced effects in reducing the bone fracture risk in osteoporotic patients, antibacterial ability, as well as anabolic effects on bone metabolism by stimulating osteoblast proliferation and mineralization. However, it is challenging to achieve stable and long-lasting trace element release. Here, we report a more efficient delivery platform capable of controlled trace element release by transforming the TiO_2-NTs into titanate-NTs and the nanotubular structure is preserved despite the hydrothermal treatment. Our results show that a titanate-NT coating incorporated with the optimal element (Sr and Zn) and dose allows proper release rate for enhanced osteointegration and antibacterial ability. The titanate-NT coating loaded with the proper element has large potential in biomedical applications due to the prevention of implant-associated infection and enhanced osseointegration without the need to apply foreign complex biomolecules. The materials are easy to fabricate and have good stability enabling large-scale industrial production and suitable for storage, transport, sterilization, and clinical use.

DP16 The Effect of PEO Process Parameters on the Tribocorrosion Properties of TiO_2 Coatings, *E.E. Sukuroglu (eedemirci@atauni.edu.tr), H. Farzi*, Atatürk University, Turkey, ***S. Sukuroglu***, Gümüşhane University, Turkey, *Y. Totik, E. Arslan, I. Efeoglu*, Atatürk University, Turkey

TiO_2 coatings are suitable materials for use as implants due to their good mechanical properties and their bio-compatibility features. Plasma electrolytic oxidation (PEO) method due to its low cost and ability to achieve high thickness is a proper method for deposition of TiO_2 coating. In this study, TiO_2 coating was deposited on Ti6Al4V substrates with different voltages and frequencies as the coating process parameters. The mechanical properties of coatings were investigated by scanning electron microscopy (SEM), XRD and EDS analysis. Tribocorrosion behavior of the coating was also measured.

Tribology & Mechanical Behavior of Coatings and Engineered Surfaces
Room: Town & Country and San Diego - Session EP

Symposium E Poster Session

EP1 Tribology of Hydrogenated and Hydrogen-free Diamond-like Carbon Coatings in Biofuel Systems at Elevated and at Higher Temperatures, ***A. Dorner-Reisel*** *(a.dorner-reisel@fh-sm.de), R. Lieberwirth, S. Svoboda*, University of Applied Sciences Schmalkalden, Germany, *K. Günther*, University of Applied Sciences Mittweida, Germany, *C. Himcinschi*, Technische Universität Bergakademie Freiberg, Germany, *S. Weißmantel*, University of Applied Sciences Mittweida, Germany, *G. Irmer*, Technische Universität Bergakademie Freiberg, Germany

Hydrogenated and hydrogen-free diamond-like carbon coatings show different suitability for use in bio-fuel under elevated or enhanced temperatures. The key element for low friction and minor wear is a layer between moving counter faces that restricts interaction and sticking between them. For tetrahedral amorphous carbon without hydrogen, a passivation of the surface by adsorbates from the environment is elementary to reach a very low coefficient of friction. Hydrogenated diamond-like carbon already delivers elementary hydrogen for forming less interacting hydrogen-carbon chains during sliding. However, species from intermediate fluid changes the top layer of the surfaces which even could result in worsening of the friction.

Bio-diesel contains a complexity of different components. It tends to degrade very quickly and needs stabilization. In the present study, different kinds of bio-diesel, like Soja-Methyl-Ester (SME) without stabilization, SME with 200 mg/kg stabilizer, SME with 1000 mg/kg stabilizer, Raps-Methyl-Ester (RME) without stabilization and REM with 1000 mg/kg stabilizer were used as an intermediate fluid. The diesel fuels were completely characterized according to the standard DIN EN 590. The HFRR (high frequency reciprocating rig) is measured. For gaining further information, Infrared spectroscopy is used. The–CO signal at 1750 cm^{-1} can be used to measure the fraction of FAME (**F**atty **A**cid **M**ethyl **E**ster) according to DIN EN 14078. Wear tests were carried out according to DIN 51834, parts 2 and 3 using the translatory oscillation test machine SRV III with the software of SRV IV of the company Optimol Instruments GmbH, Germany at room temperature and at 150 °C. In the present study, samples are made of hardened steel and coated with pure hydrogenated diamond-like carbon (a-C:H) and N- or Si-doped hydrogenated diamond-like carbon coatings by PE-CVD. The fraction of Si- and N in the hydrogenated carbon coatings were changed between 5 and 15 wt.-%. Friction and wear behaviour in the above mentioned bio-diesel is compared to hydrogen-free tetrahedral carbon coatings at room temperature and at 150 °C. The wear tracks were examined by Raman spectroscopy.

EP2 Optimizing Wear and Hydrophobic Properties of Cr-N/Al-N Multilayer Coatings, ***Y. Yang*** *(yusen@nkfust.edu.tw)*, National Kaohsiung First University of Science and Technology, Taiwan

The Cr-N/Al-N Multilayer coatings are deposited on high-speed tool steels and silicon wafers using an unbalanced magnetron sputtering process. In the experimental design, L18(21x37) orthogonal array experiments were used for the statistical purpose and the eight process control factors selected in order to study their contributions to the properties. The wear and hydrophobic properties were evaluated by means of the wear rate and water contact angle (WCA), respectively. For optimizing and balancing the performance of these two properties, a grey relational analysis is applied to combine the two signal-to-noise ratios of single property in a performance index. With the grey Taguchi multi-objective optimization approach parameter which were Argon cooling time 20 min、bias voltage -125V、the Chromium target current 1A、the Aluminum target current 3A、Ion bombardment -300V、work distance 7 cm、Nitrogen flow rate 48%、rotation speed 9 rpm. The total film thickness is controlled around 1.5μm. Multi-objective optimization result shows that the wear rate decreased from the initial design 4.76E-06 to 9.97E-07, the water contact angle increased from the initial design 91.43 ° to 95.81°.

EP3 Microstructure and Properties of WC-Co-(Cr) Coatings Modified by Sub-microcrystalline Carbides Obtained by Different Methods of High Velocity Spray Process, *K. Szymański, G. Moskal (grzegorz.moskal@polsl.pl)*, ***H. Myalska***, Silesian University of Technology, Poland

In this paper microstructure and basic mechanical properties of WC-Co coatings obtained by HVOF and HVAF technique were shown. Standard powder of WC-Co 83-17 (Amperit 625.074) was used for coating deposition on steel substrate. Sub-microcrystalline TiC powder was used to modify coting deposited from Amperit 625.074.The aim of investigations was to compare microstructure and some mechanical properties of coatings deposited by different methods of high velocity spray process. An influence of sub-microcrystalline additions on basic mechanical properties of coatings was analyzed. Deposited coatings were characterized. Theirs overall quality, porosity, adhesion of coatings to substrate and theirs tendency to making cracks were analyzed.

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EP5 Thermo-mechanical Stability Analysis of Sputtered DCB on Al_2O_3 for Aerospace Hybrid Power Converter, ***J.-S. Jeong*** *(jjseicp@keti.re.kr)*, Korea Electronics Technology Institute, Republic of Korea

This study is investigates about thermal stability of sputtered DCB (direct copper bonding) on Al_2O_3 substrate for aerospace/space general power converter purpose based on PoF (physics of failure). Sputtered DCB on Al_2O_3 substrate was made for electrical circuit board which is applied to the bare die base Hi-Rel (high reliability) hybrid power converter module. The thickness of Al_2O_3 substrate is 780 um and width is 80mm x 70mm. The thickness of deposited Cu is 100 um and patterned minimum line width by chemical etching is 200 um. The test was required to see whether the completed sputtered DCB secured enough reliability and robustness which

can be applied to Hi-Rel hybrid power converter. Effective stress factors and failure modes by them was produced through FMEA(failure mode & effect analysis) in the field. Critical failure mode of sputtered DCB among potential failure modes is delamination, void and crack damage caused by the fatigue of thermo-mechanical stress. To demonstrate the failure mechanism, a thermal shock test was designed by operating and storage condition of Hi-Rel hybrid power converter and conducted on a sputtered DCB. The temperature shock conditions are -55 ℃ to 165 ℃, -55 ℃ to 125 ℃ and -55 ℃ to 85 ℃ and the dwell time is 15 min. Measurements were carried out every 100 cycles monitoring the shear strength through shear tester. To visualize the thermal stability of the sputtered DCB, deformation by temperature change with Moiré interferometry was analyzed before and after the aging. Microstructure analysis about the junction between sputtered DCB and Al_2O_3 was conducted before and after the aging.

EP6 Wear and Friction Behavior of Fe2B Layers Formed According to a Mathematical Model of the Growth Kinetics, ***E.E. Vera Cardenas*** *(evera@upp.edu.mx), M. Ortiz-Dominguez,* Universidad Politécnica de Pachuca, Mexico, *R. Lewis,* University of Sheffield, UK, *J.L. Bernal Ponce,* Universidad Politécnica de Pachuca, Mexico, *F. Nava Leana,* Universidad Politecnica de Pachuca, Mexico, *M.A. Flores-Rentería,* Universidad Politécnica de Pachuca, Mexico

The study of the growth kinetics of boride layers is an important tool to determine the suitable process parameters for obtaining an adequate boride layer thickness. In this study, the mathematical model of the growth kinetics of the layers on steels substrates was proposed for powder-pack boriding treatment. The boriding of the steels substrates was developed at temperatures of 1123 and 1223 K with exposure times of 2 and 8 h respectively. The tribological characterization was performed to determine the effect of the set of experimental parameters of the boriding process. The sliding wear tests were performed using a reciprocating wear test machine. All tests were conducted in dry conditions with a room temperature between 293 K and 296 K and 45% to 50% relative humidity. A velocity of 10 Hz and 15 mm sliding distance were used. The applied Hertzian pressure was 2.01 GPa. Optical microscopy and scanning electron microscopy (SEM) were used to observe and analyze the wear mechanisms. Additionally, the variation of the friction coefficient versus the number of cycles was obtained. It was possible to know the wear life of the Fe_2B layers and possible causes of its variation.

EP7 Dimensioning Indentation and Scratch Tests for Thin Films, ***M. Fuchs*** *(m.fuchs@siomec.de), N. Schwarzer, N. Bierwisch,* Saxonian Institute of Surface Mechanics, Germany

Although it is a well known fact meanwhile, that a standard Rockwell test or high-load Vickers test does not give any relevant information about thin films, dimensioning indentation or scratch tests for such surface structures is still difficult – if not impossible for more complex structures (e.g. multi-layer, graded, or nano-structured coatings). Hence, well-dimensioned indentation or scratch experiments are quite uncommon. As a result, indenter tips break away on, for instance, hard coatings rather often or measurement results do not correlate with practical experience.

Indentation measurements, scratch tests and tribology experiments should be well dimensioned in order to prevent such damage to measurement equipment, learn as much as possible about a coating (e.g. elastic modulus, yield strength, hardness, tensile strength, …), and reproduce the failure happening in a certain quality assurance test or even in real life.

Even though the basic principle has been outlined yet [1], the procedure of dimensioning such mechanic contact test is still quite difficult. Therefore, an quick and easy method to dimension indentation and scratch tests for thin films with respect to maximum normal force, indenter tip type, radius, and tip rounding will be shown in this work. This method, which is based on the „Oliver & Pharr method extended for coatings“ [2], is even accessible on the Internet enabling one to do the dimensioning virtually anywhere within just 2 minutes.

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EP8 A Comparative Study About the Wear Resistance of Hard Coatings Obtained by Three Different Hardening Diffusion Processes at the Surface of AISI 4140 Steel, *J. Hernández-Sánchez,* ***E. Hernández-Sánchez*** *(enhernandezs@ipn.mx),* Instituto Politecnico Nacional, Mexico, *Y. Domínguez-Galicia, M.E. Rosales Peña Alfaro,* Instituto Politecnico Nacional-UPIBI, Mexico, *J.J. Coronel-Hernández,* Universidad Autónoma de Querétaro, Mexico

The resistance to abrasive wear of thermo and thermochemically treated steels is strongly related with the surface hardness of mechanical components, nevertheless, wear resistance is affected not only by surface hardness but also by nature and properties of surface layer of metallic materials.

In this study the abrasive wear resistance of surface layers obtained by three different hardening processes was evaluated. The layers were formed at the surface of AISI 4140 steel, by applying the boriding process, nitriding process and carburizing process. Wear resistance was evaluated by means of a standardized tribologic machine for abrasive wear with a dry sand/rubber wheel. Wear tests were developed according with the limits established by the ASTM G65 "Standard Test Method for Measuring Abrasion Using the Dry Sand/Rubber Wheel Apparatus".

According with results, borided layers exhibited the highest wear resistance in comparison with carburized and nitrided layers. In contrast, nitrided layers presented the highest loss of volume. Scanning Electron Microscopy (SEM) revealed the presence of the four mechanisms of wear, which are characteristic of abrasive wear in all samples.

Finally, SEM examination revealed that micro-crackinghe damage is the precursor mechanism of wear in this kind of hard layers.

EP9 The Corrosion Resistance and the Adhesion Strength of Double Layered Zn-Mg Thin Films, ***J.H. La,*** *K.S. Kim, S.-Y. Lee (sylee@kau.ac.kr),* Korea Aerospace University, Republic of Korea, *J.J. Lee,* Seoul National University, Republic of Korea, *W.Y. Jeung,* Korean Institute of Science and Technology, Republic of Korea

Recently, the Zn-Mg films have been studied extensively to enhance the corrosion resistance of steel. The Zn-Mg coated steel exhibits excellent corrosion resistance compared to the pure Zn coated steel, which was postulated to relate to the presence of the Mg. The Mg in Zn-Mg films enhanced the corrosion resistance of coated steel by the formation of dense microstructure which obstructed the direct pathway between a corrosive environment and the steel. However, the dense microstructure of Zn-Mg coating suppressed the formability of the coated steel and consequentially it reduced the adhesion strength of films. Therefore in this study, double layered Zn-Mg films were designed and synthesized using unbalanced magnetron sputtering process with various Mg contents. The surface and cross-sectional morphology, the chemical composition, and crystal phase of synthesized coatings were investigated by field emission scanning electron microscopy (FE-SEM), glow discharge optical emission spectroscopy (GDOES), and X-ray diffractometer (XRD) with Cu Kα radiation (λ=0.15418nm), respectively. And the corrosion resistance and the adhesion strength of the Zn-Mg film were examined as well. Preliminary results indicated that the double layered Zn-Mg films could be synthesized successfully and the adhesion strength of the double layered Zn-Mg films was improved compared to the films with high Mg content. Also the corrosion resistance of the double layered Zn-Mg films was better than that of the films with low Mg content. Detailed experimental results will be presented.

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EP10 Scratch and Wear Behavior of AlTiN/TiN Nanolayer Coatings, *H. Çalışkan (halilcaliskan06@yahoo.com),* Bartın University, Turkey, ***M. Panjan****, P. Panjan, M. Čekada,* Jozef Stefan Institute, Slovenia, *A.C. Karaoğlanlı*, Bartın University, Turkey

Nanolayered AlTiN/TiN hard coatings are known to have superior performance in protection of surfaces at hard working conditions due to their properties such as low thermal conductivity, high wear resistance and high oxidation resistance. In the present study, scratch and wear behavior of nl-AlTiN/TiN nanolayer coating was investigated. The coatings were deposited on AISI D2, AISI H11, K600 and cemented carbide substrates by CC800/9 sinOx ML (CemeCon) industrial magnetron sputtering system. CSM Revetest scratch tester was utilized for the adhesion measurements. The scratch tests were performed under progressive load. The adhesive strength of the coatings was measured by microscopic observation, acoustic emission detection and friction force recording. Surface failures were analyzed by using optical microscope. Wear tests were performed on CSM tribotester using alumina balls at low and high sliding speeds, and friction coefficient and wear rate data were recorded. Wear traces were investigated by scanning electron microscope. It was found that the highest value of the critical load is obtained in the nl-AlTiN/TiN coating on cemented carbide substrate, and it is much higher than that of single layer TiN and TiAlN coating. Spalling, chipping, conformal cracking and tensile cracking are the failures of the nanolayered coating. Although wear rate of nl-AlTiN/TiN coating is higher than that of TiN coating at low sliding speed, its wear rate decreases with the increasing sliding speed and becomes lower.

EP11 The Friction and Wear Properties at Room Temperature and Vacuum Atmosphere of $Ti/TiB_2/MoS_2$ Graded-Composite Coatings Deposited by CFUBMS, *Ö. Baran (obaran@erzincan.edu.tr)*, Erzincan University, Turkey, *F. Bidev*, ***H. Cicek***, Atatürk University, Turkey, *L. Kara*, Karadeniz Technical University, Turkey, *I. Efeoglu*, Atatürk University, Turkey, *T. Küçükömeroğlu*, Karadeniz Technical University, Turkey

MoS_2 coatings is effectively used in vacuum and in water vapor-free environments because of increased friction coefficient and decrased service life in room temperature. To increase friction and wear resistance of MoS_2 coatings are used different alloys elements (e.g., Ti, Nb, Cr) and materails (e.g., TiN, TiB_2). Therefore, in this study $Ti/TiB_2/MoS_2$ graded-composite coatings (GCC) were deposited by the closed-field unbalanced magnetron sputtering (CFUBMS). The structural properties of the coatings were analyzed by scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and X-ray diffraction (XRD). The hardness of the coatings was measured using a microhardness tester. The tribological properties of coatings were determined in room temperature (RT) and vacuum atmosphere. $Ti/TiB_2/MoS_2$ (GCC) have MoS_2 (002) and TiB_2 (100) reflections. The coatings exhibited a dense and non-columnar structure. Tribological properties of coatings in RT and vacuum atmosphere significantly affected from hardness,thickness and stoichiometric ratio of elements in the structure .

Key Words: Friction,Wear, $Ti/TiB_2/MoS_2$, graded-composite, CFUBMS

EP12 Instrumented Indentation Hardness and Sliding Wear Characteristics of a Sequential Plasma Process of AISI 316L Austenitic Steel, after Pre-shot Peening, *M.R. Menezes*, Universidade Federal de Minas Gerais, UFMG, Brazil, *J.C. Avelar-Batista Wilson*, Tecvac, Ltd., UK, ***M.V. Auad***, Auad Godoy Consultants, Brazil, *A.C. Bozzi*, Universidade Federal de Espirito Santo, UFES, Brazil, *C. Godoy (cristinagodoyufmg@gmail.com)*, Universidade Federal de Minas Gerais, UFMG, Brazil

Austenitic stainless steels exhibit excellent corrosion resistance, but relatively poor wear resistance. Preceding studies of sequentially plasma carburized and nitrided AISI 316 steel [1] indicated an increase of wear resistance without a deterioration of corrosion resistance. As it is known that mechanical treatment prior to nitriding can lead to significant increase in the thickness of the nitrided layer [2], in this work we have investigated the effect of shot peening on sequential plasma processed AISI 316L.The sequential plasma treatment, which was performed at temperatures of 673K and 748K, consisted of a 2h carburization step followed by nitriding for 2h.

The structure of the evolved surface layers was analyzed by X-ray diffraction (XRD), scanning electron microscopy (SEM) and nanoindentation and was correlated with the wear behavior. XRD patterns of plasma-processed specimens indicated the presence of two distinct surface layers with expanded austenitic structure, one rich in nitrogen and another rich in carbon. In addition, some chromium nitrides were found for the specimen processed at 748K. SEM micrographs showed that the nitride layer is thinner than the carburized layer. The thinner nitride layer might be explained by the trapping of nitrogen due to the chemical binding with chromium [3]. The nanoindentation hardness profiles demonstrated three regions of hardness: the first one correlated with the nitrided layer, the second with the carburized layer and the third one with the substrate material. Higher hardness values were found for the nitrided layer formed at 673K, probably due to a higher concentration of nitrogen in solid solution, since chromium nitrides are present only in the sample nitrided at 748K. Relative to an untreated sample, the pre-shot peening had decreased the nanoindentation hardness in the nitrided layer, but not in the carburized layer. The curves of coefficient of friction also indicated regions of distinct behavior. The shot peening process smoothed the coefficient of friction curves on dry sliding wear test. The worn volume, evaluated by 3-D profilometry, showed that sequential plasma treatment at 748K after pre-shot peening leads to the best wear resistance.

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[3] Moskalioviene Surf. & Coat. Technol. 205 (2011) 3301-3306

EP13 Tribological Properties of Solid Lubricant W-S-N Coatings, ***P. Mutafov***, *T. Polcar (t.polcar@soton.ac.uk)*, Czech Technical University in Prague, Czech Republic, *M. Evaristo, A. Cavaleiro*, SEG-CEMUC, University of Coimbra, Portugal

Transition metal dichalcogenides (TMD) are suitable as solid lubricants due to their anisotropic layered structure, where the adjacent lamellae with strong covalent bonding interact through relatively weak van der Waals forces. Pure sputtered TMD films are sensitive to environmental attacks, which limits their mechanical properties and wear resistance. Alloying of TMD with other element could improve their properties, such as adhesion, hardness and load bearing capacity. Recently, we have deposited amorphous W-S-N coating showing ultra-low friction during sliding in dry nitrogen (lower than 0.003). TEM analysis of the tribolayer adhered on the ball revealed tungsten oxide combined with tungsten disulphide; this observation was confirmed by XPS and Auger electron spectroscopy (AES). Thus, we decided to deposit this film with wide range of composition and tests its tribological properties in various atmospheres including humid air.

In present study the tribological behavior of W-S-N coating with different nitrogen content is sputtered from WS2 target in Ar/N_2 atmosphere. Besides the usual physical, chemical and mechanical characterization, including the evaluation of the chemical composition by electron probe microanalysis, the structure by X-Ray diffraction (XRD), the chemical bonding by X-Ray photoelectron spectroscopy (XPS), the morphology by Scanning electron microscopy (SEM), the hardness and the cohesion/adhesion, special attention was paid to the friction and wear behaviour in dry nitrogen.

The nitrogen content varied from 8 to 25 at.%, the hardness increased with nitrogen content from 5 GPa to 10 GPa. XRD spectra showed broad peaks typical of nanocrystalline WS_2. The friction was quite low even in humid air; the values were typically 0.2 to 0.3 in humid air. Investigation of the wear track and the ball wear scars by electron microscopies and by Raman spectroscopy shed light on the formation of low-friction tribolayer on the worn surfaces.

EP14 Characterisation of Amorphous Carbon Coatings for Tribological Applications in Challenging Environments, ***J. Cooper*** *(mtp11jc@sheffield.ac.uk)*, University of Sheffield, UK, *DA. Stewart*, Rolls Royce, UK, *A. Leyland, A. Matthews*, University of Sheffield, UK

For manufacturing mechanical components in tribological contact it is often useful to employ liquid lubricants to increase the performance and reduce degradation of the interacting materials. However, unforeseen challenges can arise when the conventional boundaries are exceeded and components are exposed to extremes of environmental condition; significant variations in the temperature, pressure, and/or chemical media present can all act to drastically affect the behaviour of the materials or lubricants involved. For some of these applications a possible solution could lie with the optimisation of amorphous carbon film systems.

Potential attractive properties of amorphous carbon films include high hardness, low friction, chemical inertness, and self-lubrication. Such characteristics are useful in situations where low friction conditions are required, but lubrication retention is low (or corrosive media lead to changes in material properties in the tribological contact). In this work we explored the architecture, dopants and properties in a variety of commercially available amorphous carbon coating systems to assess how the material properties and adhesion evolve in-situ. Evaluation of films in actual operating conditions indicated their suitability for wear at elevated temperatures and/ or corrosion, thereby allowing new amorphous carbon coating formulations to be designed to resist these challenging environments more effectively.

In order to successfully characterise these thin amorphous carbon films we subjected samples to simulated environmental conditions to provide experimental data that supports the theoretical optimal compositions. For amorphous carbon we conducted these experiments alongside specific characterisation techniques, performed before and after (and, if possible during) environmental exposure. These techniques include scanning electron microscopy (SEM), Raman, and surface profilometry to determine the thickness and structure of the film, nano-indentation to determine changes in hardness, mechanical wear testing to measure tribological performance, and methods to determine the hydrogen content of the film like elastic recoil detection analysis (ERDA).

EP15 Analysis of Sliding Wear Tests of Plasma Processed AISI 316L, *M.C.S. Duarte*, Universidade Federal de Minas Gerais, UFMG, Brazil, *A.C. Bozzi*, Universidade Federal do Espírito Santo, UFES, Brazil, ***C. Godoy*** *(cristinagodoyufmg@gmail.com)*, Universidade Federal de Minas Gerais, UFMG, Brazil

In this study we investigate the influence of different plasma treatments on the wear resistance of AISI 316L austenitic stainless steel. The chosen plasma treatments include carburizing at 475°C for 3 hours, nitriding at 450°C for 5 hours, and a sequential process composed of carburizing at 475°C for 3 hours followed by nitriding at 450°C for 5 hours. In order to correlate wear behavior and structure as well as the concentration of carbon and nitrogen at the surface, the plasma treated samples were thoroughly investigated by means of scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), X-ray diffraction (XRD), glow discharge optical emission spectroscopy (GDOES), ball-on-disc dry sliding wear tests, micro- and nanoindentation.

Each plasma treatment led to a modified surface layer of the AISI 316L steel. It was shown that these surface layers had different thicknesses for

each of the three different treatments and two expanded austenitic structures without precipitates. Post the initial running-in period of the sliding wear tests, sharp transitions were observed, probably due to the plasma modified surface layers. After identifying the sliding distances corresponding to these transitions, the tests were stopped at these points and EDS compositional maps of the wear tracks were taken. The depth of wear tracks and the worn volumes were measured by 3D profilometry. The significant drops in carbon and/or nitrogen concentrations of each wear track indicate that the modified layers were almost worn out at these positions. Comparing the worn volumes, the sequentially plasma treated sample showed the best wear resistance. For this system three defined regimes were identified: the first probably correlated with the upper nitrided layer, the second with the carburized layer and finally the third one with the substrate. Micro- and nano hardness measurements demonstrated that the wear behavior can be related to the different mechanical properties of these three different layers.

This study shows that the wear behavior is strongly related to the particular structure of the modified surface. A steady-state wear will be only observed for long sliding distances, when the worn material already corresponds to substrate bulk material.

EP16 Comparision of the Tribological Behavior of VN-Cu and MoN-Cu Coatings at High Temperature, *G. Ramirez (jramirez@anl.gov), **T.A.L. De Lima Burgo**, O.L. Eryilmaz, A. Erdemir*, Argonne National Laboratory, US

VN-Cu and MoCu-N nano-composite coatings were prepared using a reactive magnetron sputtering technique. A pure vanadium or molybdenum target was sputtered using a HIPMS power supply and the copper doping was made using a copper target attached to a DC power supply. Along with argon, nitrogen gas is used as a reactive gas during the deposition. HIPIMS was also used for metal ion etching on the steel substrate in order to improve the adhesion of the coatings. The films are grown on 440C stainless steel flat and 3/8" diameter ball samples for tribological tests and Si wafer samples are coated for other coating characterization studies. The microstructural properties are studied using thin film X-ray diffraction; the compositions of the films before and after tribological tests are evaluated by using X-ray photoelectron spectroscopy (XPS). The mechanical properties of composite coatings were assessed using a nanoindentation technique.

The tribological tests were conducted using a high temperature ball on disk system in open air environment. The samples were tested at room temperature, 350°C and 650°C. The results show that the coefficient of friction (COF) has a strong dependence on test temperature. For both VN-Cu and MoN-Cu coatings, COFdecreased with increasing temperature and the lowest COF (i.e., 0.4) was attained at 650C due to the formation of the lubricious metallic oxides on sliding surfaces. The wear resistance of coatings also improved with increasing temperature. The nature of lubricious oxides is studied using Raman and x-ray photoelectron spectroscopy techniques and correlated with the friction and wear performance of coated surfaces.

EP17 Microstructure Characterization and Mechanical Properties of Multicomponent CrAlSiTiVN Hard Coating, ***Y. Chang** (yinyu@mail2000.com.tw)*, National Formosa University, Taiwan

Abstract Transition metal nitrides, such as TiN and CrN, have been used as protective hard coatings due to their excellent tribological properties. In this study, multicomponent CrAlSiTiVN coatings were synthesized by cathodic-arc evaporation. The coatings were deposited onto SKD61 tool steels (HRc 50~52) and tungsten carbides. TiV and CrAlSialloy cathodes were used for the deposition of CrAlSiTiVN coatings. During the coating process of multicomponent CrAlSiTiVN, TiN was deposited as an interlayer to enhance adhesion strength between the coatings and substrates. The cathode current and pulse frequency of both TiV and CrAlSi cathodes were controlled at 50~ 100A and 0~500Hz, respectively. With different cathode current ratios ($I_{[CrAlSi]}/I_{[TiV]}$) of 05~1.5, the deposited multicomponent CrAlSiTiVN coatings possessed different chemical contents and periodic thicknesses of CrAlSiN and TiVN layers. The multilayer thickness and alloy content of the deposited coating were correlated with the evaporation rate of cathode materials. The microstructure of the deposited coatings was investigated by a field emission gun high resolution transmission electron microscope (FEG-HRTEM, FEI Tecnai G^2 20 S-Twin), equipped with an energy-dispersive x-ray analysis spectrometer (EDS), operated at 200 keV for high-resolution imaging. Glancing angle X-ray diffraction was used to characterize the microstructure and phase identification of the films. The composition and depth profile were evaluated by wavelength-dispersive x-ray spectroscopy (WDS). Mechanical properties, such as the hardness and elastic modulus, were measured by means of nanoindention. To evaluate the correlation between impact fracture resistance and hardness/elastic modulus ratio of the deposited coatings, an impact test was performed using a cyclic loading device with a tungsten carbide indenter as an impact probe. The design of multicomponent CrAlSiTiVN coatings is anticipated to inhibit the grain growth, and leads to grain refinement effect, which expected to increase the hardness and impact resistance of coatings.

EP18 Investigation of Hard Coatings with the Instrumented Indentation Test, ***T. Haas** (tanja.haas@helmut-fischer.de), B. Binder, G. Bosch, H.P. Vollmar*, Helmut Fischer GmbH, Germany

During the last years the instrumented indentation test has been established as a common analysing technique for the material characterisation. Beside the hardness value these technique provides further important material properties. In the recent years the thickness of new developed industrial coatings decreased constantly. Due to the high force resolution and the ability to apply very low loads, the instrumented indentation test also offers the possibility to measure such thin coatings without an influence from the substrate.

For different reasons coatings are getting thinner recently. A coatings thickness well below one micrometer is standard and coatings in the order of 100 nanometers are nothing unusual, depending on the application. Hard coatings like PVD or DLC are also following the trend. But those coatings often tend to have an uneven surface with roughness values in the order of the coating thickness. The combination of a small coating thickness and a high roughness is a challenge to the instrument and the user.

The poster shows different ways to analyse such samples. Sometimes an increased number of measurements allow comparing the mean values of different samples. Measuring a cross section of the sample can also improve the results. A high precision of the XY-positioning is mandatory for this. Using an AFM can give additional information about the sample which is not available by standard nanoindentation measurements.

EP19 Glassy Carbon Coatings Deposited on Hybrid Structure of Composite Materials, *A.. Posmyk, J. Myalski, **B. Hekner** (bartoszhekner@gmail.com)*, Silesian University of Technology, Poland

During designing and manufacturing machinery and equipment (e.g. components for automotive or food and medicine industry), one of the development directions is substituting and eliminating liquid lubricant by solid lubricant. The solid lubricant predominantly are built into a surface of construction materials working in friction conditions. An application of solid lubricant constituting integral part of structure leads to decrease of frictional resistance and wear of couple of friction. Reliable long-term cooperation while maintaining the desired efficiency can be obtained by applying less quantity of liquid lubricant.

This paper presents a method of production metal matrix composites with aluminum oxide foam covered by glassy carbon used as a reinforcement. The glassy carbon surface was formed for decreasing of friction coefficient and reduction the wear. The glassy carbon acts as solid lubricant in this case. In first step of technology liquid glassy carbon precursor is deposited on ceramic foam, subsequently cured and carbonated at elevated temperature. In this way ceramic foam is covered glassy carbon coating with 2 ÷ 8 μm of thickness. It provides desirable amount of glassy carbon in the structure of the material. In the next step, porous shapes with carbon coating are infiltrated by liquid matrix of Al-Si-Cu alloy. Thereby, equable distribution of glassy carbon in composite volume is achieved. Moreover, typical problems for composites reinforced by particles like sedimentation, agglomeration and clustering of particles are avoided. Tribological characteristics in friction in air conditions with cast iron as a counterpart were made. Produced composites with glassy carbon layer are characterised by friction coefficient between 0.08 ÷ 0.15, thus meeting the typical conditions for solid lubricants.

EP21 Tribological and Corrosion Properties of Ni/MWCNT Nanocomposites Produced by Pulse Electro Co-deposition, ***M. Kartal** (kartal@sakarya.edu.tr)*, Sakarya University, Turkey, *H. Gul*, Duzce University, Gumusova Vocational School, Turkey, *M. Uysal, A. Alp, H. Akbulut*, Sakarya University, Turkey

Nanostructured materials have attracted many researchers due to their outstanding mechanical and physical properties. For example, carbon nanotubes (CNTs) or carbon nanofibres (CNFs) are considered to be attractive reinforcement materials for light weight and high strength metal matrix composites. The inclusion of a reinforcement phase into electrodeposited coatings to form a composite has been shown to be useful for many tribologically aggressive applications. Composite coatings containing solid particles of carbides, oxides, diamonds, and polymers are rapidly increasing in importance in modern engineering application due to their enhanced hardness, wear resistance, self-lubrication and corrosion resistance when compared to metal or alloy. The improved properties of composites coatings heavily depend on the nature and content of particles in the coatings.

In the present work, Nickel /multiwalled carbon nanotube (MWCNT) metal matrix composite coatings were deposited by pulse electro co-deposition

method from a Watt's type electrolyte. The influence of the MWCNT content in the electrolyte and peak current density on the particle co-deposition and distribution, the surface morphology, microstructure, microhardness, tribological features and corrosion resistance of nanocomposite coatings were studied. Copper substrates were used for electro co-deposition of Ni matrix/MWCNTs with the diameter of 50–60 nm and length of 10 mm carbon nanotube reinforcements. The electrodeposited Ni matrix coatings were characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD) analysis and Raman spectroscopy. The tribological behaviors of the electro co-deposited Ni/MWCNT nanocomposite coatings sliding against an M50 steel ball (Ø 10 mm) were examined on a tribometer. All the friction and wear tests were performed without lubrication at room temperature and in the ambient air (with a relative humidity of 55–65 %). A comprehensive worn surface analysis was performed using SEM, XRD, Raman and 3D surface profilometer facilities. Corrosion tests were performed in aqueous NaCl (3.5 wt.%) using electrochemical measurements for pure nickel coating and Ni/MWCNTs composite coating.

EP22 Wear Behavior of CBN Coated Carbide Tools in Milling of Ti6Al4V Alloy, ***H. Çalışkan*** *(halilcaliskan06@yahoo.com), B. Kurşuncu, A.C. Karaoğlanlı*, Bartın University, Turkey

Hard machining and high speed cutting are challenging machining processes demanded for high productivity for several decades. Cubic boron nitride (CBN) solid tools are widely used in these processes due to their high hardness, low friction coefficient and thermal stability at high temperature. However, its low toughness limits the usage of CBN tools in milling operations where cutting forces change during machining. Therefore, in this study, CBN was deposited on carbide cutting tools by magnetron sputtering, and thus cutting tools with high toughness and high surface hardness were obtained. TiN coating was used as interlayer in order to improve the adhesion of the CBN coating on carbide tools. Wear behavior of these CBN coated carbide tools were investigated in face milling operation of Ti6Al4V alloy. Microhardness of the coating was determined by nanoindentation. Before and after cutting tests, the structure of the coated tools was determined by scanning electron microscopy (SEM) in combination with energy-dispersive X-ray spectroscopy (EDS). The results obtained from the CBN coated carbide tools were compared with commercial coated tools in order to highlight the influence of CBN coating on the performance of the carbide cutting tools.

EP25 Reactively Sputtered Chromium Carbide/Carbon Glass-like Films for Sliding Electrical Contact Applications, ***K. Nygren*** *(kristian.nygren@kemi.uu.se),* Uppsala University, Sweden, *M. Samuelsson, A. Flink, H. Ljungcrantz,* Impact Coatings AB, Sweden, *A.K. Rudolphi, U. Jansson*, Uppsala University, Sweden

Sliding electrical contacts are commonly used, and the contact material should maintain stable properties over the course of several thousand cycles. Most electrical contacts are coated with noble metals to prevent formation of insulating metal oxides, although in tribological systems such coatings wear down and shorten the lifetime of the product. It is also known that e.g. Ag coatings suffer from tarnishing. Transition metal carbide/carbon nanocomposite films, with carbide grains embedded in an amorphous carbon matrix, have been suggested as alternative to noble metals. The carbide phase provides high conductivity, high corrosion resistance, and high hardness, while the carbon matrix improves wear properties and reduces friction.

We demonstrate use of chromium carbide glass-like films in a rocking motion sliding electrical contact setup, capable of in situ contact resistance measurement and life time simulation. Amorphous Cr-C-H films were grown by reactive direct current and high power impulse magnetron sputtering from a Cr target. An industrial scale PVD system allowed for growth rates from 0.1 to 0.5 $\mu m \cdot min^{-1}$. Film structure and properties were studied by XPS, Raman spectroscopy, XRD, TEM, SEM, nanoindentation, unlubricated reciprocating sliding experiments, and by the novel sliding electrical contact setup. The films were relatively soft for being carbide-based, with hardness values of 8 - 12 GPa, which can be explained by the amorphous structure. Coefficients of frictions vs. steel bearing balls were $\mu = 0.13 – 0.60$, correlated to the fraction of amorphous carbon. Films grown on SS316L were tested as sliding electrical contacts, and major differences in useable life time as electrical contact were observed depending on the chemical bonds present in the films. The best films demonstrated performance comparable to industry standard Ag for up to 10 000 cycles.

EP26 Mechanical and Tribological Characterization of ZrN Coatings on Titanium Modified Austenitic Stainless Steel, ***M.F. Wani*** *(mfwani@nitsri.net)*, National Institute of Technology Hazratbal, India

Reliability and availability of mechanical components at operational stage is reduced due to tribologial failures. In order to reduce tribological failures due to wear, application of hard coatings on mechanical components is considered one of the most appropriate and feasible alternative. In this research study, mechanical and tribological behaviour of ZrN coatings deposited on titanium modified austenitic stainless steel (alloy D- 9) substrates has been investigated. The coatings were deposited in the deposition temperature range 300–873 K, using the pulsed magnetron sputtering technique. Scratch adhesion tests were carried out using Rock well indenter under various conditions of load. Hardness of these coatings were determined using Vicker indenter. Detailed tribological studies were conducted to understand the friction and wear behaviour of these coatings under various conditions of load and sliding velocity. For all tribological studies steel and ceramic balls were used as counter face material. 3D-Surface profiles of all wear tracks was carried out using 3D universal profiler.

Surafce profiles indicated propagation of Hertz cracks leading to brittle fracture of ZrN coatings. Higher coeffcient of friction was observed in case of ceramic ball against ZrN coated disc, as coampared to steel ball against ZrN coated disc. However, a lower value of coefficent of frction was observed in case of coatings deposited at higher tempearture. Wear increases with the increase in normal laod. The failure of coatings, variation in the coefficient of friction and wear with the steel and ceramic balls is further discussed in relation with morphology and elemental distribution in the wear tracks of the ZrN coatings.

EP27 Application of a DLC-coating for Improving Hydrostatic Piston Shoe Bearing Performance under Boundary Lubrication Conditions, *S.-M. Kim, S.-R. Lee,* ***S.-Y. Lee****, Y.S. Hong (yshong@kau.ac.kr), C.-H. Kim*, Korea Aerospace University, Korea

The pumps of electro-hydrostatic actuators are frequently subject to boundary lubrication, since they operate as a control element compensating for position control errors. Therefore, their tribological performance should be capable of enduring the extreme conditions to which they are subject to compared to conventional pumps operating constantly at high speeds. When conventional swash plate type piston pumps are applied to electro-hydrostatic actuators, their performance under boundary lubrication conditions should be examined and supplemented. The frictional power losses, as well as the wear rate of the sliding components such as piston shoes, can significantly increase under boundary lubrication conditions. In this paper, a DLC-coating was applied to the swash plate and ball joint of pistons, and its ability to reduce the power losses from the frictional solid-to-solid contact and the leakage flow rate of the hydrostatic piston shoe bearing was investigated. The DLC-coated swash plate was able to effectively reduce the friction force on the piston shoe, while the leakage flow rate could also be reduced using the DLC-coated ball joint. Using the DLC-coated ball joint and swash plate together the total power loss from the hydrostatic piston shoe bearing could be reduced by more than 40% in the pump speed range from 10rpm to 100rpm

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EP28 The Effect of Deposition Parameters on the Tribological Properties of TiAlCrNbN Thin Films, *L. Kara (lkara@ktu.edu.tr),* Karadeniz Technical University, Turkey, *Ö. Baran,* Erzincan University, Turkey, *T. Küçükömeroğlu,* Karadeniz Technical University, Turkey, ***I. Efeoglu***, Atatürk University, Turkey

Tribological behaviour of bearing surface of extrusion dies has an important technological and economic importance since it affects the tolerance and surface quality of extrudate and increases manufacturing cost and determines the service life of dies. Extrusion dies are usually made from hot work tool steels such as AISI H13. In order to increase the service life, they are always surface treated by various forms of nitriding. Surface-coating by physical vapour deposition (PVD) or chemical vapour deposition (CVD) is currently being introduced as a means to further improve the wear resistance.

In this study, TiAlCrNbN nanocomposite thin films were deposited on AISI H13 steel substrate by Pulsed Dc Closed Field Unbalanced Magnetron Sputtering, and the effect of frequency, bias voltage and working pressure on the mechanical and tribological properties were investigated. The coatings have been characterized by X-ray diffraction, scanning electron microscopy and energy dispersive spectroscopy. The lowest amount of wear were attained at lowest frequency and highest bias voltage and working pressure.

EP29 Improvement of Fatigue Property of Magnesium Alloy by Coating Thin Film Metallic Glass, ***C.H. Chang***, *J.P. Chu (jpchu@mail.ntust.edu.tw),* National Taiwan University of Science and Technology (NTUST), Taiwan, *P.K. Liaw*, University of Tennessee, US

It is well known that fatigue performance is a related to the residual stress level at the surface of a component and, therefore, coating techniques inducing compressive residual stresses can potentially enhance fatigue behavior. The mechanisms of enhances fatigue properties as following: (i) high hardness to prevent the surface roughening, (ii) good ductility and toughness to prevent crack initiation from the place where persistent slip bands intersect the film, (iii) high compressive residual stresses to retard the crack propagation into the substrate, and (iv) good adhesion with the substrate to prevent coating delamination. Recently, beneficial effects of TFMGs on fatigue-properties of crystalline metallic substrates have been reported.

In this study, Zr-based thin film metallic glass (TFMG) is deposited on the magnesium alloy by magnetron sputtering. Fatigue tests are performed using four-point-bending fatigue testing machine operating at a frequency of 10 Hz. It has been found that fatigue lifetime of magnesium alloy can be considerably improved by coated. Compared to uncoated sample, the fatigue limit is also enhanced. It reveals that the reduction of the surface roughness after film deposition, good adhesion between the film and the substrate, and the high hardness, strength, and good ductility of TFMG, are the major factors for the fatigue properties enhancements.

New Horizons in Coatings and Thin Films
Room: Town & Country and San Diego - Session FP

Symposium F Poster Session

FP1 Preparation of *n*-ZnO and *p*-CuO Films and Their Heterojunctions by Chemical Bath Deposition Based Technique, ***T. Terasako*** *(terasako.tomoaki.mz@ehime-u.ac.jp), T. Murakami, S. Shirakata*, Ehime University, Japan

Zinc oxide (ZnO) has the wide band gap energy of 3.37eV and exhibits *n*-type conduction. ZnO is one of the most conceivable candidates for the alternative materials for tin doped In_2O_3 (ITO) widely used in the window layers of solar cells and in transparent electrodes of the flat panel displays. On the other hand, copper (II) oxide (CuO) with the narrow direct band gap energy of ~1.2 eV exhibits *p*-type conduction derived from copper vacancies (V_{Cu}s). According to the Shockley-Queisser limitation assuming single *p-n* junction solar cells, the maximum energy conversion efficiency is expected to be achieved at the band gap energy of ~1.4 eV, which is close to that of the direct band gap energy of CuO. To clarify the possibility of the solar cell applications, we will discuss the preparations and characterizations of *p*-CuO and *n*-ZnO films and their heterojunctions by chemical bath deposition (CBD) based technique in this paper.

Zinc acetate dihydrate and copper (II) nitrate trihydrate were used as Zn and Cu sources, respectively. The pH values of the aqueous solutions were adjusted to 10-10.5 by the use of ammonia solution. The Au/Ti/Si(100) wafers and glass substrates were used as the substrate materials. The bath temperature was changed in the range of 70-90 ℃. Growth times for the CuO and ZnO layers were 60 and 20 min, respectively. After each CBD process, post-annealing treatment was carried out at 250 ℃ in the air.

The X-ray diffraction patterns of the CuO/glass films were dominated by the (002) peaks. It was confirmed that as-deposited CuO films do not exhibit *p*-type conduction without the post-annealing treatment. For the CuO/glass films, Hall mobilities were distributed in the range of 8.9-33.6 cm^2/Vs, and the carrier concentration *p* varied in the range from 2.9×10^{16} to 3.6×10^{18} cm^{-3}.

SEM observations revealed the successful growth of ZnO nanorods with 500-1400 nm in length and 270-700 nm in width on the top of the CuO layers composed of the columnar grains with approximately 400 nm in width. The current density-voltage curves for the *p*-CuO/*n*-ZnO heterojunctions exhibited rectifying characteristics. However, the extremely large ideality factors of 3.17-4.15 have been obtained so far, indicating that there is a lot room for improvement of the interface states between the *p*-CuO layer and the *n*-ZnO layers. With respect to this problem, the effect of the insertion of the intermediate layer between the *p*-CuO layer and the *n*-ZnO is also under investigation.

FP2 Low Temperature Atomic Layer Deposition of ZnO Thin Films on Cellulose Nanofibers for low Cost Dye-Sensitized Solar Cells, ***K.N. Ha***, Korea Institute of Industrial Technology (KITECH), Korea, *E. An*, Korea Institute of Industrial Technology (KITECH), Busan, South Korea, *W.-J. Lee*, Pusan National University, South Korea, *I.-W. Park (ipark@kitech.re.kr),* Korea Institute of Industrial Technology (KITECH), Busan, South Korea, *S.-H. Kwon, Y. Park*, Pusan National University, South Korea

Dye-sensitized solar cells (DSSCs) have attracted attention because of their low cost, eco-friendliness, low incident-light-angle dependence, and high efficiency. In DSSCs, nanostructured ZnO or TiO_2 photoanode layers are essential part to increase the dye adsorption and photoconversion efficiency by enhancing electron transfer. Several attempts have been made to improve the electron transport efficiency of those photoanode layers using one-dimensional (1D) nanostructures or 3D porous structures with a thin shell (i.e., the inverse opal structure) to provide fast electron transport paths. For the preparation of the nanostructures, atomic layer deposition (ALD) has many advantages, including excellent step coverage and conformality, accurate thickness control, exceptional composition control for nanostructures, and uniformity over large areas. Herein, a simple and versatile template assisted approach was investigated to prepare ZnO nanostructured photoanodes on large area for low cost dye-synthesized solar cells (DSSC). As a low cost nanostructured template, the paper that composed of cellulose nanofibers was utilized. After the low temperature atomic layer deposition (LT-ALD) of ZnO on the paper followed by calcination, the porous and fibrous nanostructures of paper was able to be successfully replicated. Due to the low thermal stability and complex interconnected nature of cellulose nanofibers in the paper, the use of LT-ALD process of ZnO was inevitable. In the presentation, the optimization of both LT-ALD ZnO and calcination processes will be discussed in terms of the microstructure and photoelectrochemical characteristics. Also, the feasibility of using our approach will be demonstrated by fabricating DSSCs.

FP3 Characterization of ZnO Nanotubes Grown by Supercritical CO_2 Fluid Mixed with Ethanol Solution, ***K.C. Chang***, *T.M. Tsai, T.C. Chang (tcchang@mail.phys.nsysu.edu.tw), G.R. Liu, H.C. Huang, T.F. Young, D.S. Gan*, National Sun Yat-Sen University, Taiwan

In this work, we applied a novel treatment of supercritical fluid to fabrication ZnO nanotubes and successfully demonstrated that using supercritical CO2 fluid mixed with ethanol solution can oxidize and transform the DC-sputtered zinc film for synthesizing ZnO nanotubes. The treatment process was kept at 60 ^oC and 3000 psi for 1 hour. The morphology of ZnO nanotubes was uniform with diameter of 10 nm and 3-nm thickness of tube, which observed in the images of scanning electron microscopy and transmission electron microspore. Besides, the distribution of ZnO nanotubes was clustered and high density, fully grown on the surface of subtract. These ZnO nanotubes were analyzed by the N & K analyzer, photoluminescence (PL), scanning electron microscope (SEM) and Transmission electron microscope (TEM) to investigate the characteristics of the optical, morphology and crystal structures.

FP4 High Power Impulse Magnetron Sputter Deposited IGZO on Flexible Substrate and its Thin-film Transistor Performance, ***Y.H. Chen*** *(tieamo2002@gmail.com), R.C. Ke, J.L. He*, Feng Chia University, Taiwan

Indium gallium zinc oxide (IGZO), with high transparency, remarkable saturation mobility (μ_{sat}), low operation voltage and low density-of-states (DOS), has been utilized as a substitute for poly-Si in thin-film transistor (TFT). Even though the amorphous IGZO that fabricated by conventional dc magnetron sputtering as well as many other coating methods are satisfactory in its properties for practical application, literatures have shown that additional substrate heating or post-annealing can enhance the saturation mobility, operational stability and electrical conductivity. For fulfilling the flexible display purpose, as the aim of this study, high power impulse magnetron sputtering (HIPIMS) technique known to provide high density plasma is employed so as to form high-quality IGZO film on polymeric flexible substrate at a relatively low substrate temperature. By regulating the output waveform of the HIPIMS power supply, the optical and electrical characteristics of the obtained IGZO were investigated to associate with film microstructure.

Experimental results reveal that the as-prepared IGZO film is very morphologically dense. The saturation mobility, the electrical conductivity and the optical transmittance are dependent on the output waveform and are discussed. The characteristics of the TFT device using IGZO layer as the channel layer is also explored.

FP5 Measurement of Ionized Metal Flux Fraction in HiPIMS by Retarding Field QCM Analyzer, ***T. Kubart*** *(Tomas.Kubart@angstrom.uu.se)*, Uppsala University, Angstrom Laboratory, Sweden, *M. Cada, Z. Hubicka*, Institute of Physics of the ASCR, v.v.i., Czech Republic

In this contribution, we describe measurements of the ionized metal flux fraction, the ratio between ionized and neutral metal species, arriving to the substrate in High Power Impulse Magnetron Sputtering (HiPIMS). The ionized metal flux fraction is determined from the deposition rate of ions and neutrals. In order to determine the respective rates, a combination of a retarding field and by a quartz crystal microbalance (QCM) was used. Two different sensors were tested. A standard QCM equipped with a set of grids and an alternative grid-less sensor which was developed in order to increase the sensitivity. The grid-less sensor uses magnetic field to repel electrons and the bias voltage is applied directly to the QCM top electrode.

We report results for two materials, Ni and Ti. Ti was characterized both in nonreactive (Ar) and reactive (Ar+O2) atmosphere. Measurements with the QCM analyzer showed an ionized fraction of up to 50% for Ni. Somewhat higher values, exceeding 60%, were measured for Ti. In this case, shorter on times lead to higher ionized fraction at the same deposition rate and average discharge power. In reactive sputtering of Ti, substantially higher ionized fraction was observed in the oxide mode as compared to the metal mode. Already at lower values of the peak power, there was a significant fraction of Ti ions in the oxide mode.

FP6 Improving the Absorption of Visible Light of Iron Silicide Thin Film by Pinhole Fabrication, ***H.F. Hsu*** *(hfhsu@dragon.nchu.edu.tw), Y.T. Chang, G.Y. Li*, National Chung Hsing University, Taiwan

Semiconducting iron disilicide (β-$FeSi_2$) is expected strongly as a novel photovoltaic material with theoretical energy conversion efficiency about 16-23%. Increasing the roughness of the surface is another useful method to improve the light absorption of the solar cell device. Reactive deposition epitaxy (RDE) is a common method for growing epitaxial β-FeSi2 films on Si substrate. Many studies of improving the crystal quality of β-$FeSi_2$ films have been reported. However, effects of the surface morphology on the light absorption properties of β-$FeSi_2$ films were scarcely investigated. In this study, iron silicide films were directly grown on Si substrate by RDE, and the effects of process parameters such as substrate temperature and deposition rate on the properties of iron silicide films were investigated.

The results show that Fe, (CsCl)FeSi or γ-$FeSi_2$ and β-$FeSi_2$ phases were observed at 350 and 400ºC deposition. Then, when the substrates temperature was at 450 and 500ºC, Fe was reacted with Si substrate completely, and the silicide films contained (CsCl)FeSi or γ-$FeSi_2$ and β-$FeSi_2$ phases. The iron silicide film grown at 450˚C has lowest reflection of visible light due to the formation of pinholes on the iron silicide surface. Furthermore, increasing the deposition rate caused that the size and density of pinholes reduced and increased, respectively. When the porosity iron silicide film annealed at 600 and 800ºC further, the pinholes were still existent, and the silicide phase was transformed to β-$FeSi_2$. These porosity β-$FeSi_2$ films still have low reflection of visible light comparing with the pinhole-free ones. It would be beneficial to use porosity β-$FeSi_2$ films for solar cell device.

FP7 Synthesis, Structure and Optical Properties of Tungsten Oxynitride Thin Films, ***C. Ramana*** *(rvchintalapalle@utep.edu), A.J. Moreno-Tarango, E. Rubio, R. Vemuri*, University of Texas at El Paso, US

Tungsten oxide (WO_3), one among the transition metal oxides, exhibits excellent physical, chemical and electronic properties. Recently, cationinc and anionic doping of WO_3 is gaining significant attention since such doped W- oxides are considered to be attractive for application in photo-electrochemical cells. In this talk, we present our recent approach on the controlled modification of electronic structure and optical properties of W-oxide doped with nitrogen (N). The emphasis is to demonstrate tailoring of the structure and electronic properties of the resulting materials via crystal phase-size-composition correlation. N-doped W-oxide films were grown using RF sputtering. Nitrogen concentration was varied by varying the nitrogen gas flow rate from 0 to 20 sccm keeping the growth temperature fixed at 450 ºC. While nitrogen doping significantly influences the structure-property relationships, specific approach based on stabilizing tetragonal (t) phase WO_xN_y films with N-incorporation leads high quality and best optical performance. Structural analysis revealed that the progressive nitrogen-incorporation induces tetragonal (t-WO_3) to monoclinic (m-WO_3) phase transformation. The approach adopted in this work indicates a structure dependent optical band gap variation leading to the lowest optical band gap (~2.12 eV) at 0.7 at.% of nitrogen the films. Results will be presented and discussed to demonstrate that the controlled N-doping coupled with specific phase allows tuning the electronic properties of WO_xN_y films.

FP8 Enhanced Exchange Bias and Mechanical Properties of Al Incorporated Ni–Mn–Sb Ferromagnetic Shape Memory Alloy Thin Flms, ***R. Barman***, *D. Kaur (dkaurfph@iitr.ernet.in)*, Indian Institute of Technology Roorkee, India

Aluminium (Al) co-sputtered $Ni_{49.7}Mn_{37.1}Sb_{13.2}$ ferromagnetic shape memory alloy thin films deposited by magnetron sputtering onto Si (100) substrates at 823K were investigated. X-ray diffraction spectra revealed the formation of highly (220)-oriented pure $Ni_{49.7}Mn_{37.1}Sb_{13.2}$ austenite phase with significant decrease in grain size and crystallites with increasing Al power. Lattice parameters (a, b, c), Unit cell volume, grain size, characteristic temperatures (M_s, M_f , A_s, A_f, T_M), hysteresis loop width, exchange bias (H_{EB}) and Coercivity (H_C) of the films were evaluated using various techniques. A significant improvement of exchange bias field is observed in NiMnSbAl thin films compare to pure $Ni_{49.7}Mn_{37.1}Sb_{13.2}$ thin film. This enhancement of exchange bias is attributed to the increase of AFM-FM interactions that results from the existence of Antiferromagnetic phase in the martensite phase of NiMnSbAl at low temperature. Temperature dependence of resistivity (RT) curves showed a decrease in martensitic transformation temperatures with increasing Al content upto a certain extent after that it increases again and the shape memory behavior is lost in $Ni_{46.5}Mn_{33.2}Sb_{5.2}$ $Al_{15.1}$ thin films. A significant improvement in the hardness, elastic modulus and toughness H^3/E^2_r was observed in the NiMnSbAl nanocomposite films as compared to pure $Ni_{49.7}Mn_{37.1}Sb_{13.2}$ film.

FP9 Synthesis and Water Splitting Characterization of Ordered (Cu, Zn) Oxide Nanowire Arrays by PAM Template Assisted Method During Electrochemical Deposition, *Y.M. Shen*, National Cheng Kung University, Taiwan, *S.C. Wang*, Southern Taiwan University, Taiwan, *J.L. Huang (jlh888@mail.ncku.edu.tw)*, ***Y.H. Chen***, National Cheng Kung University, Taiwan

In this work, the (Cu, Zn) metal and (Cu, Zn) oxide nanowire arrays were fabricated through template-assisted electrochemical deposition method, which was controlled the pulse duration. The pulse potentials of (Cu-Zn) nanowire were -0.18 and -1.26 V/SCE, respectively. The microstructure and chemical composition of (Cu, Zn) nanowire arrays were characterized by field emission scanning electron microscopy (FE-SEM) and high resolution transmission electron microscopy (HR-TEM) equipped energy dispersive x-ray spectrometer (EDS). The SEM results indicated that the Cu-Zn nanowire arrays were assembled into the nanochannel of porous alumina template with diameter of 90-100 nm. SEM results shown the bamboo-like (Cu, Zn) multilayer structure was observed at 40 (Cu) and 20 (Zn) seconds pulse deposition. With the increasing of pulse potential duration, segments with homogeneous shape of Cu-Zn nanowires were disappeared to form the continuous shape. Growth mechanism of structural nanowire during electrochemical deposition was assumed to base on the reduction potential. During the various annealing time of segmented Cu-Zn nanowire process, the (Cu, Zn) oxide nanowire structures were exhibited segmented nanowire and continuous nanowire. In texture formation of (Cu, Zn) oxide nanowire was proposed on the Zn diffused into Cu oxide of heating process. The crystallinity of (Cu, Zn) oxide nanowire was characterized as single crystal. The application on water splitting characterization was obtained maximum photocurrent density of (Cu,Zn) oxide and Cu_2O-ZnO bamboo-like structure were 0.07 mA/cm^2 and 0.11 mA/cm^2, and the conversion efficiency were 0.1 % and 0.13 %, respectively.

Keywords: Porous alumina membrane, electrochemical deposition, pulse potential deposition, segmented nanowire, (Cu, Zn) metal and (Cu, Zn) oxide nanowire arrays, water splitting.

FP11 Evaluation of the Nanomechanical Properties of Vanadium Thin Films Prepared by RF Magnetron Sputtering, *M.A. Mamun, K. Zhang, H. Baumgart, A.A. Elmustafa (aelmusta@odu.edu)*, ***D. Nminibapiel***, Old Dominion University, US

Vanadium is a transition metal that finds primarily applications as steel additive to increase the strength in vanadium high-carbon steel alloys and high speed tool steels (vanadium steels) for surgical instruments and dental implants. It is also used for titanium alloys in jet engines. In comparison with other metals vanadium is harder than most metals, but oxidizes even in ambient air. Various vanadium suboxides exist, which stabilize the metal surface and protect it from further oxidation. The properties of bulk vanadium, which is a hard, silvery gray, ductile and malleable transition metal with body-centered cubic crystal structure, have been well documented in the literature. In contrast, very little work has been reported on vanadium thin films. In particular nanoindentation analysis investigating the nanomechanical properties of vanadium ultrathin films has hardly been covered in the literature. In this study we investigate vanadium thin films, which were deposited by magnetron sputtering of a vanadium metal target of 2 inch diameter with 99.9% purity on Si substrates. The base pressure of magnetron sputtering was less than 10^{-6} Torr, while sputtering deposition was conducted under Argon gas with a pressure of 3 mTorr. The growth temperature of vanadium on Si substrate was controlled at 450ºC to obtain

high crystallinity and uniformity. The crystal structure and phase purity of vanadium thin films was characterized by X-ray diffraction (XRD). Film surface morphology was inspected using a field emission scanning electron microscopy (FE-SEM) and atomic force microscopy (AFM). The nanomechanical properties were measured by nanoindentation to evaluate the hardness and modulus of vanadium thin films. The scanning electron microscopy (SEM) imaging on the 500 nm indents depicted a gradual progression of pile up as the film thickness increased from 75 nm to 100 nm. Radial cracks were observed in all indents from different films. It is noticed that as the film thickness increases the vanadium films experience softening effect and the hardness values depict the hardness of the Si substrate at deep indents.

FP12 Oriented Lanthanum Silicate Thin Film Electrolytes for IT-SOFCS, ***J.C. Oliveira*** *(joao.oliveira@dem.uc.pt), M. Macatrão, A. Cavaleiro*, SEG-CEMUC, University of Coimbra, Portugal

The major trend in the current research activity on SOFCs focuses on decreasing the operating temperature to the range 500-700ºC to reduce system and material costs and improve lifetime. Currently, Yttrium Stabilized Zirconia (YSZ) with 8 or 10% yttria is the most common electrolyte. To ensure sufficient ionic conduction operating temperatures ranging from 800 to 1000 ºC must be used. These high temperatures place stringent requirements on the cell components, such as chemical stability in oxidizing and reducing environments, chemical stability of contacting materials and thermomechanical compatibilities. Exotic and costly materials have to be used, such as lanthanum chromite for current collectors. As a result, actual SOFCs concepts often fail to meet the expected durability requirements and their costs per W are still several times higher than economically feasible values.

The development of Intermediate Temperature SOFCs (IT-SOFCs) may be achieved by different strategies, including the development of new electrolyte materials, with better performance at intermediate temperatures, and reducing the electrolyte thickness to decrease the ohmic drop at the electrolyte. Silicate-based materials have attracted considerable interest as potential low cost electrolyte materials. Their ionic conductivity is higher than the conventional YSZ electrolyte at low temperatures (e.g. 0.01 S/cm at 700 ºC) and comparable to CGO at 600 ºC. Despite silicon oxide volatilization from the surface layers under reducing conditions, which results in conductivity degradation with time at temperatures above 1100 K, the silicate-based solid electrolytes possess a promising combination of transport properties, thermal expansion and stability, enabling their use for IT SOFCs operating at 500–700 ºC. Lanthanum silicate has a hexagonal structure with oxygen channels aligned with the c axis of the cell which are preferential conduction paths for the ions. As a result the ionic conductivity of lanthanum silicate is 10 times higher along the c axis than in perpendicular directions. In this work lanthanum silicate electrolyte films deposited by magnetron sputtering with preferentially oriented grains in such a way that the c axis of the crystals is aligned with the conduction direction.

FP13 Microstructure and Electronic Properties of Intrinsic and W-Doped Gallium Oxide Thin Films Made by Sputter-Deposition, *C. Ramana (rvchintalapalle@utep.edu)*, University of Texas at El Paso, ***E. Rubio***, *A. Miranda-Gallardo*, University of Texas at El Paso, US

Wide band gap oxides have been widely investigated in recent years due to their many practical applications. Gallium oxide (Ga_2O_3) exhibits a band gap of ~5 eV with a wide range of applications in luminescent phosphors, high temperature sensors, antireflection coatings, and solar cells. This material has been recognized as a deep ultraviolet transparent conducting oxide, which makes interesting for electrode applications in UV optoelectronics. The focus of the present work was to study the effect of tungsten (W) incorporation on the crystal structure, chemical composition, surface morphology and optical properties of Ga_2O_3 films. For the purpose, intrinsic and W-doped Ga_2O_3 films were grown by co-sputtering keeping the sputtering power to Ga_2O_3-target constant (100 W) while varying the sputtering-power (P_W) to W-target in a wide range (50-100 W) in order to vary W-concentration in the films. The samples were deposited on to Si (100) and sapphire substrates in a growth temperature range of 500-800ºC. Structural analysis indicates the β-phase of Ga_2O_3 in all the films. The structural data coupled with compositional analyses confirm the substitutional nature of W-incorporation into Ga_2O_3. Combined optical and electrical property evaluation indicates that the W-incorporation induced effects are significant on the electronic properties of Ga_2O_3 films. A correlation between growth conditions, composition and electronic properties in W-doped Ga_2O_3 films is established.

FP14 Purification of Commercial CNT Sheet Material for Composite Fabrication, ***A.R. Hopkins*** *(alan.r.hopkins@aero.org), H.A. Katzman*, The Aerospace Corporation, US

Satellite structures demand high strength and stiffness for dimensional stability and survival of both launch and orbital environments. The use of carbon nanotube-based sheets for composite laminates is currently being evaluated to replace carbon fiber composites in high strength / high modulus applications such as the skeletal support of next generation spacecraft. In this study, improvements in the purification of commercial, continuous carbon nanotube (CNT) reinforcement were made and their effects on the resulting composite laminate were investigated. CNT sheet purification was performed with a series of oxidative thermal treatments with concomitant purity assessment using thermal, elemental, and electron imaging techniques. Purification of the CNT fabric purification shows encouraging results in terms of reducing the amount of metal catalyst while minimizing oxidation of the CNT sidewalls as evidenced in X-ray photoelectron spectroscopy. Moreover, this treatment decreases the CNT fabric density by ~8%, and increases the thermal oxidation temperature by 40°C. We were successful in isolating and imaging individual multiwalled tubes of the purified sheet material which confirmed that the purification process was not deleterious to the surface morphology. Post-treatment steps (i.e. chemical sizing and plasma treatment) of the purified sheet were employed as noninvasive techniques which successfully enhanced the wetting and bonding properties without structural degradation of CNT material. This purification route is efficient and can be used to improve and maximize surface wetting and bonding of resin to carbon nanotube sheets in order to improve processability and mechanical properties.

FP15 Growth of Boron Nitride at High Temperature Chemical Vapor Deposition (Htcvd) Reactor Using Bcl3 and Nh3 as Precursors, *N. Coudurier, R. Boichot, F. Mercier,* ***E. Blanquet*** *(elisabeth.blanquet@simap.grenoble-inp.fr)*, SIMaP CNRS/Grenoble INP/UJF, France, *A. Henry*, Linköping University, IFM, Thin Film Physics Division, Sweden

Boron Nitride (BN) is a potential material for optoelectronic, piezoelectric sensors and high power electronic applications. However, BN is especially difficult to synthesize by thermal CVD in other phase than the poorly crystallized turbostratic phase (t-BN), between amorphous and hexagonal phases (h or r-BN). Recent attempts to obtain epitaxial layers of hexagonal BN phase with triethyl boron [1] and diborane [2] as boron source and NH3 as nitrogen source have succeeded. The growth rates allowing epitaxial growth of BN was below 200 nm/h.

Based on the results obtained in aluminum nitride layer at high temperature using AlCl3 has aluminum source [3], the epitaxial growth of BN is recently investigated via the same chemical pathway. Growth of BN at high temperature (1000-1700°C) on various substrates (lab-made AlN templates on c-saphire, W and Cr) has been studied using NH3, BCl3 and H2. The experiment set-up consists of a vertical water-cooled quartz reactor with an induction-heated graphite susceptor covered with AlN. Influence of the substrate temperature and N/B ratio in the gas phase on the quality of the grown BN layer have been investigated. As-grown BN layers have been characterized by Field Emission Scanning Electron Microscopy (FE-SEM) and X-ray diffraction (XRD) and Raman spectroscopy.

The study shows that the t-BN phase is predominately obtained with BCl3 as boron precursor, whatever the temperature and the B/N ratio in the range studied, for a growth rate in the order of 1 µm/h. To stabilize the h-BN growth on hetero substrate, a very low supersaturation (consequently growth rate) of BCl3 must be used.

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FP16 Effect of Anodization Parameters on Ca-P Incorporated Nanotubes Properties, ***P. Soares*** *(pa.soares@pucpr.br)*, Pontificia Universidade Católica do Paraná, Brazil, *V. Leszczak, K. Popat*, Colorado State University, US

The influence of different anodization conditions on Ca- and P-incorporated titania nanotubes properties was evaluated. TiO_2 nanotubes

were produced by potentiostatic anodization of Ti-cp in a viscous electrolyte containing HF and Ca and P ions, at different voltages (15 to 120 V) for different times (2 to 24 h), and annealed at 530 ℃ for 10 h. Characterization of the nanostructured oxide layer was conducted using scanning electron microscopy, glancing-angle X-ray diffraction, X-ray photoelectron spectroscopy, and contact angle measurements. During the anodization treatment, Ca and P ions were incorporated into the oxide layer. The results showed that the applied voltage and anodic oxidation duration have a large effect on the change in the characteristics of the nanotubes layer. The amount of anatase phase and morphology of the oxide layer were dependent on the voltage applied during the oxidation treatment. The size of the nanotubes was increased with increasing voltage of anodic oxidation. In addition, the resulting nanostructured layer have a superhydrophilic characteristic.

Keywords: TiO_2, nanotubes, anodization, wettability

FP17 Current-Voltage Characteristics During High Power Impulse Magnetron Sputter Deposition of TiO_2, *P.-H. Li,* MingDao University, Taiwan, *C. Liu*, Fujian University of Technology, Fuzhou, China, *J.-Y. Jian, C.-M. Yeh, C.L. Chang,* ***W.-Y. Wu*** *(wanyu@mdu.edu.tw),* MingDao University, Taiwan

Recently, high power impulse magnetron sputter (HiPIMS) process attracts attentions due to its ability for providing a highly ionized flux of sputtered species. The advantages of HiPIMS include low process temperature, well-adherent coating, better quality of the films, and droplet-free coating process. The deposition a uniform layer on substrate with complex shapes and trenches can also be achieved by HiPIMS. High density of peak current and peak power are the typical characteristics of HiPIMS. A low duty cycle (typically <5%) and the pulse duration approximately in a range between 10 and 1000 μs are commonly used in HiPIMS.

In this study, a HiPIMS system was used to deposit TiO_2 thin films. The used target is TiO_2 with a purity of 99.99% and a size of Φ150 x 5mm. Before the deposition, the I-V characteristics of the discharge are first measured to determine the duty cycle and the pulse duration. Duty cycles in the range of 1-5% and the pulse duration in the range of 25 to 200μs are used to investigate the I-V of the discharge. Besides, the optical emission spectroscopy (OES) is also used to diagnose the composition of the plasma. The voltage and the peak current in the range of 50 ~ 300 A were found increasing with decreasing the duty cycles and with increasing the pulse duration. The TiO_2 films was then deposited to discuss their crystalline structure, morphological features, and optical properties.

Keywords: TiO_2, HiPIMS, duty cycle, pulse duration

Submit to Poster Presentaion in Symposium F2. High Power Impulse Magnetron Sputtering (HIPIMS)

FP18 Thickness Dependent Magnetic Properties of Co-sputter Deposited Ni-Mn-Al Heusler Alloy Hard Nanostructured Thin Films, *A. Mishra, R. Chandra (ramesfic@gmail.com), S. Srivastava, A. Gehlot, P. Dubey, D. Kaur,* ***S. Chauhan***, Indian Institute of Technology Roorkee, India

Ni-Mn-Al thin films have been deposited using DC/RF magnetron sputtering from three different targets of Ni, Mn and Al. The off-stoichiometric films have been deposited for 2 min, 5 min, 10 min and 15 min. The elemental composition analysis of Ni-Mn-Al thin films has been carried out using an energy dispersive X-ray analysis. T he XRD patterns of the films reveal cubic B2 structure. The observation of cubic structure shows that the films exhibit high temperature austenite phase at room temperature. To further confirm the phase present in the films, the crystal structure of the films has been examined by transmission electron microscopy. Magnetization versus temperature curves reveal martensitic transition from austenite phase to martensite phase below room temperature which is further confirmed by resistivity versus temperature measurements. A splitting between ZFC and FC curves is observed at low temperatures which have been further studied by ac susceptibility measurements. A spin glass behaviour is observed in the system which may be responsible for complex magnetic behaviour at low temperatures. A large exchange bias has been observed at low temperature (5 K) associated with the coexisting spin glass and antiferromagnetic exchange interactions. The exchange bias is found to be dependent on the thickness of the film. Nanoindention of thin films reveals high hardness of magnetically ordered films.

Applications, Manufacturing, and Equipment
Room: Town & Country and San Diego - Session GP

Symposium G Poster Session

GP1 Fabrication and Characteristics of Ceramic/Ni-Cr-Mo Steel Coatings by Centrifugal Casting Process, *H. Kim,* Sejong University, Korea, *K. Oh, K. Yi, S. Kim,* S.M. Metal, Korea, ***K. Park*** *(kspark@sejong.ac.kr),* Sejong University, Korea

In this study, ceramic/Ni-Cr-Mo steel coatings were fabricated by centrifugal casting process. The microstructure and characteristics of the ceramic/Ni-Cr-Mo steel coatings prepared by the centrifugal casting process were discussed, depending on the rotation velocity of mold and the pouring temperature of Ni-Cr-Mo steel. The specimen with a size of $10\times10\times10mm^3$ was sectioned, mounted, ground, and polished with a diamond paste for characterization by X-ray diffraction and scanning electron microscopy. We investigated the microstructure of ceramic/Ni-Cr-Mo steel coatings, reaction products between the ceramic and Ni-Cr-Mo steel in the coatings, and microstructural stability of the coatings at high temperatures. The Ni-Cr-Mo steel matrix provided a good toughness supporting ceramics. Liquid infiltration using centrifugal force was highly effective to fabricate ceramic/Ni-Cr-Mo steel coatings. The centrifugal force was sufficient to obtain a full infiltration. Based on the present study, we believe that ceramic/Ni-Cr-Mo steel coatings can be applied in a wide range of industries, such as non-ferrous metal production (e.g., Mg), waste incinerators, boilers, gasification, etc.

GP2 Oxidation-induced Cu Coating on Steel Surface, *N. Li*, University of Science and Technology Liaoning, China, ***W. Sha*** *(w.sha@qub.ac.uk)*, Queen's University Belfast, UK

Copper is accumulated in recycled steels and is difficult to be removed during steelmaking processes when steel scrap is used as steel sources. Meanwhile, copper characteristic properties are of importance both to human beings and to animals and plants. In this paper, integrated copper coating was observed on the surface of copper-containing steels when the steels were heated at around 1150°C. However, the copper was separately scattered after heating at 1000°C. The forming mechanisms of copper coating will be discussed in detail. By choosing proper descaling reagent, self-generated oxidation-induced copper coating appeared on the steel surface. The method proposed in this work is environmentally friendly for nontoxic chemicals being used. In addition, this provides a new concept for producing protective composite by oxidizing from the substrate directly and there is no binding problem.

GP3 Desk-top RF-DC Plasma Nitriding System for Automotive Steel Parts, ***Y. Sugita*** *(y_sugita@ysel.jp),* YS-Eletric Industry, Co. Ltd., Japan, *T. Aizawa,* Shibaura Intitute of Technology, Japan, *K. Tsukui, E. Nakayama*, Yamanashi University, Japan

Most of commercial plasma nitriding system was driven by DC- and DC-pulse plasmas. In case of automotive parts such as piston rings or valves, thousands of parts were once installed into a chamber and then subjected to plasma treatment. Being constrained to this nitriding process in batch, a plasma nitriding has less means to be flexible to changing demand for surface treatment. In the present paper, a desk-top plasma nitriding system is proposed as a unit for distributed surface treatment.

The chamber has a diameter of 180 mm and a height of 180 mm. It is composed of a dipole electrode for RF-plasma generation, an IH-device for thermal control and a sample holder with DC-bias. In the present treatment, a product is set-up in this chamber, heated to the specified temperature by IH- device , and, then subjected to plasma nitriding. First, SKD61 is employed as a common work material to investigate the nitriding behavior via SEM observation, XRD and micro-hardness testing and to optimize the nitriding conditions. Next, an engine valve is selected as a typical automotive part for this desk-top plasma nitriding. Homogeneous nitriding takes place under optimum alignment of RF-electrode and IH- device in this system.

GP4 MicroporousN-doped Carbon Films Produced by Cold Atmospheric Plasma Jet and Compatibility with MC3T3-E1 Preosteoblasts, ***L.M. Li***, *X.M. Zhang, M. Zhang, P.H. Li, P.K. Chu (paul.chu@cityu.edu.hk)*, City University of Hong Kong, Hong Kong Special Administrative Region of China

Microporous nitrogen-doped carbon layers are deposited on silicon wafer using an atmospheric-pressure plasma jet at room temperature and thecytocompatibility is investigated by monitoring the proliferation and adhesion of MC3T3-E1 preosteoblasts. Improved cell proliferation and adhesion are observed from the microporous N-doped carbon layers. The *in vitro* enhancements can be attributed to the altered surface morphology and

new functional groups. The results suggest that a cold atmospheric plasma jet is a simple and practical tool to improve the cytocompatibility and suitable for biomedical applications.

Topical Symposia
Room: Town & Country and San Diego - Session TSP

Symposium TS Poster Session

TSP-1 Characterization of 4H-SiC Grown by Thermal Evaporation System Using Single Boat, *K. Mahmood (khalid_mahmood856@yahoo.com)*, ***M. Asghar***, The Islamia University of Bahawalpur, Pakistan, *I. Ferguson, R. Tsu*, University of North Carolina, US

SiC layer was grown on p-type Si (100) substrate by simple evaporation method. The chamber was evacuated using mechanical and diffusion pump with base pressure of $5x10^{-7}$ torr. A mixture of Si and C_{60} powder of high purity (99.99%) with weight ratio of 1:1 was used as source material and was evaporated by Mo boat. The XRD spectra of grown film consist of five peaks and related to 4H-SiC (003), Si (111), 4H-SiC (100), (004) and (110) respectively. The PL measurements consist of a strong band to band emission peak of 4H-SiC at 3.22 eV. A peak at 618 cm^{-1} in FTIR spectra shows the presence of Si-C bonding. Raman spectrum of grown film consists of TO and LO mode of 4H-SiC.

TSP-2 Dye Sensitized Solar Cells of TiO_2 Nanotubes by Anodization with $TiCl_4$-ZnO Treatment, *J.H. Yang, K.H. Kim,* ***H.W. Choi*** *(chw@gachon.ac.kr)*, Gachon University, Republic of Korea

Dye-sensitized solar cells have been intensively studied since the discovery of them in 1991. however, a number of problems remain to be solved in order to enhance their efficiency. In particular, one of the main limiting factors is the electron recombination that occurs due to contact between the transparent conductive oxide and the redox electrolyte.

In this work, we report an improvement in the photovoltaic characteristics of dye-sensitized solar cells by using a $TiCl_4$ and ZnO treated TiO_2 Nanotube. The introduction of one-dimensional structure with TiO_2 nanotube, with a much more open structure, allows the polymer electrolyte to penetrate easily inside the film, increasing the interfacial contact between the nanotube/dye and the electrolyte.

In addition, a suitable amount of $TiCl_4$ and ZnO in the film could provide a large surface area for dye adsorption. Therefore, It is well known that the photocurrent of DSSC is correlated directly with the number of dye molecules, with more dye molecules adsorbed leading to more incident light being harvested, as well as a larger photocurrent. It is expected that the photoelectrical performance of the DSSC can be improved.

TSP-3 Thermal Expansion and Elasticity of Metastable Cubic B1-AlN, ***M. Bartosik*** *(matthias.bartosik@tuwien.ac.at)*, Vienna University of Technology, Austria, *D. Holec*, Montanuniversität Leoben, Austria, *M. Todt*, Vienna University of Technology, Austria, *J. Todt*, Montanuniversität Leoben, Austria, *F.G. Rammerstorfer, P.H. Mayrhofer*, Vienna University of Technology, Austria

Aluminum nitride is an important material for various applications due to its specific properties. Whereas the stable wurtzite structure is well characterized, only little is known for the metastable high-pressure phase face centered cubic (B1, rock-salt type) AlN. By coherency strains to lattice matched materials, like B1-CrN, AlN can be stabilized in the metastable B1 crystal structure even under ambient conditions. However, the maximum thickness of fully stabilized B1-AlN is limited to a few nm because the high chemical driving force for transformation into its stable wurtzite allotrope prevents the existence of bulk free-standing pieces of this phase.

The experimental characterization of phases in such small dimensions is a challenging task. Here, an approach is proposed that combines in-situ wafer curvature experiments with continuum mechanics modeling to determine the in-plane coefficient of thermal expansion (CTE) and elastic properties of B1-AlN. In the experiments CrN/AlN superlattice films on Si (100) are investigated with 1 nm thick AlN layers stabilized in the B1 structure as confirmed by high-resolution transmission electron microscopy. The continuum mechanics approach is formulated as inverse problem solved by means of finite element methods.

To cross-validate the results, the temperature dependent CTE is calculated using *ab initio* methods. The elastic properties of B1-AlN are reproduced from previous studies, emphasizing the significant difference of B1-AlN compared to other nitride materials used as hard protective coating materials.

TSP-4 The Synthesis of Ag/Pt Bimetallic Nanoparticles Supported on Carbon with Enhanced Electocatalytic Activity by Solution Plasma Process, ***S.-M. Kim***, Korea Aerospace University, Republic of Korea, *J.W. Kim*, University of Incheon, Republic of Korea, *S.-Y. Lee (sylee@kau.ac.kr)*, Korea Aerospace University, Republic of Korea, *J.J. Lee*, Seoul National University, Republic of Korea, *W.Y. Jeung*, Korean Institute of Science and Technology, Republic of Korea

For the application of direct liquid fuel cell (DLFC), the Ag/Pt bimetallic nanoparticles were synthesized using an electrical discharge process in a liquid environment, namely solution plasma process (SPP). A SPP facilitated the concurrent synthesis of Ag/Pt bimetallic nanoparticles supported on carbon via the reduction of $AgNO_3$ and Pt (II) acetylacetonate, and the decomposition of ethylene glycol for carbon formation. It is shown from transmission electron microscopy (TEM) that the structure of Ag/Pt bimetallic nanoparticles exhibited dendritic nanocomposites consisting of faceted Pt nanocrystals on Ag branches. The activities of Ag/Pt bimetallic nanoparticles supported on carbon for the electrochemical oxidation of methanol were compared with Pt nanoparticles supported on carbon in acid solution by cyclic voltammetry. The Ag/Pt bimetallic nanoparticles supported on carbons exhibits much better methanol oxidation activity than the Pt nanoparticles supported carbons. This significant improvement in catalytic performance may be attributed to inhibition of CO oxidation. Detailed experimental results will be presented.

Acknowledgement

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIP) (No. 2013M2A8A1042684).

TSP-5 Completely Topographically Corrected Scratch Test – Examples and How it has Been Done, ***N. Schwarzer***, *N. Bierwisch (n.bierwisch@siomec.de)*, Saxonian Institute of Surface Mechanics, Germany

Roughness plays an important role in scratch testing. This is not only due to the fact that roughness influences the friction conditions and splits the otherwise single global contact into a jumble of smaller contacts, but simply also leads to a great variety of loads and moments contributing to the final displacement field. So, apart from the external normal and lateral (scratch) load one locally has to deal with lateral loads in the direction perpendicular to the scratch axis plus tilting and twisting moments only being caused by the surface topography or roughness.

This work will show which additional information are needed for this new approach and how the scratch measurements have to be performed. Examples will be used to show the differences between a corrected scratch test with complete topography information and a standard analysis using only the measured forces and pre scan information in scratch direction.

TSP-7 Optical Properties of Multi layers MnO/Sb/MnO Thin Films Prepared by Electron-beam Evaporation Technique, ***M. Alzamil*** *(alzamilm@hotmail.com)*, King Saud University, Saudi Arabia

Films of MnO/Sb/MnOwere deposited onto microscopic glass substrates by electron beam evaporation technique. The effect of annealing temperature on transmission, reflection and other optical properties were studied. The transmission and reflection spectra were measured in the wavelength range from 200-2500 nm. The film morphology was examined by scanning electron microscope (SEM). The obtained results from scanning electron microscope showed that the grain size of MnO/Sb/MnOfilms increased with increasing annealing temperature. The as-deposited films and the films annealed at low temperature showed very low transmission in the visible region and high reflection in the ultraviolet region. At annealing temperature of 550 ^oC the prepared films showed optical transmission about 85% in the visible region and their reflection exceeded 50% in ultraviolet region. Furthermore, it was found that the other optical parameters such as energy gap, extinction coefficient, refractive index and dielectric constants were strongly dependent on the annealing temperature process.

TSP-9 Reactor of Dielectric Barrier Discharge with Incidence in Liquid: One Efficient Tool for Extraction of Lignin, ***F.S. Miranda***, *F.L.C. Lucas, E.D. Santos*, University of Paraiba Valley (UNIVAP), Brazil, *R.J. Silva*, Technological Institute of Aeronautics (ITA), Brazil, *C. Carli, S. Rabelo, C. Rossel, J. Pradella*, Brazilian Bioethanol Science and Technology Laboratory, Brazil, *H.S. Maciel, R.S. Pessoa, L.V. Santos (lvs.lucia@gmail.com)*, University of Paraiba Valley (UNIVAP), Brazil

The worldwide need to obtain new sources of energy has motivated many types of research to supply the imminent scarcity of fossil fuels, with this promising scenario lignocellulosic materials such as bagasse and sugarcane are showing great potential, because from them is possible to obtain the second generation ethanol.

However, a major difficulty to obtain an efficient production of second generation ethanol is the pretreatment of biomass, which should at the same time, extract elements that hinder sugars conversion to ethanol and still keep them intact for subsequent process of fermentation and ethanol production.

Due to it, this paper present the results of the use of a new technology for pretreatment of lignocellulosic biomass, held by a plasma reactor with discharge by dielectric barrier, discharge which occur in the surface of the liquid, that different of conventional plasma technique explored in the literature, allows treat whole biomass and not just its surface. This modification in the process makes the pretreated biomass become more susceptible to next step of process, which is the enzymatic hydrolysis. From the pre-treatment used was possible to achieve a high degree of lignin extraction, which is a major inhibitor sugar extraction during the enzymatic hydrolysis with a lower concentration of lignin in the biomass is possible to achieve a higher yield enzyme, which lowers production costs and increases ethanol yield of the process.

TSP-10 Characteristics of Anticorrosion Layer of Silicon Oxide Films on Magnesium Alloys by Atmospheric Pressure Plasma Jet, ***Y.L. Kuo*** *(ylkuo@mail.ntust.edu.tw), K.H. Chang, J.Y. Jian*, National Taiwan University of Science and Technology (NTUST), Taiwan

Silicon oxide (SiO_2) thin films were deposited as anti-corrosion layers on AZ31 magnesium alloy substrates by atmospheric pressure plasma jet (APPJ) from tetraethoxysilane (TEOS) as the precursor. The effect of varying carrier gas flow rates resulted in control of surface morphology, microstructure, and chemical composition has been investigated and characterized by contact angle goniometer, XRD, FE-SEM, FTIR, and XPS, respectively. The corrosion resistance of SiO_x film evaluated using potentiodynamic polarization measurements in 3.5 wt% NaCl solutions confirmed that the anticorrosion behavior of 50nm-thick SiO_2 films deposited at the O_2 flow rate of 1800 sccm on AZ31 reveals a higher anticorrosion resistance with a corrosion potential (E_{corr} = -1.39 V) and a corrosion current ($I_{corr.}$= 5.3×10^{-4} mA cm^{-2}) as compared to raw AZ31 materials (E_{corr} = -1.46 mV ; $I_{corr.}$= 2.4×10^{-1} mA cm^{-2}).

TSP-11 Emerging Concepts for Large Scale Graphene Synthesis Towards Enhanced Electrochemical Applications, *D. Brownson, C. Banks (c.banks@mmu.ac.uk),* ***P. Kelly***, Dalton Research Institute, Manchester Metropolitan University, UK

Graphene, a planar monolayer of carbon atoms that are densely packed into a 2D honeycomb lattice, has become one of the most intensively explored carbon allotropes in materials science due to its reported unique electronic and mechanical properties. One area that graphene has significantly impacted is in the field of electrochemistry where it is potentially the world's thinnest electrode material and has been applied in many areas, such as in sensing and energy storage/conversion.

We report the electrochemical properties of pristine monolayer, double layer and few-layer (termed *quasi*-) graphene grown *via* CVD and transferred using PMMA onto an insulating substrate (silicon dioxide wafers). The graphene response is compared to other available graphitic electrodes, namely that of basal- and edge- plane pyrolytic graphite electrodes constructed from Highly Ordered Pyrolytic Graphite (HOPG) and information on the respective heterogeneous electron transfer rate constant (k^o) is obtained. We observe, for the first time, a correlation in the structure of graphene, in terms of its 'number of layers' directly upon its macroscopic electrochemical performance, which in turn corresponds to the density of edge plane like-site/defects comprising its structure. Given that pristine monolayer graphene has a low degree of edge plane coverage compared to the multi-layered structures of *quasi*-graphene and HOPG, in comparison it possesses slow electrochemical properties and thus in scenarios when a large/favourable k^o is required, recourse to *quasi*-graphene and edge plane of HOPG is suggested.

It is evident that manipulation of the graphene structure, in terms of orientation (such as exposing more edge) or through the introduction of surface edge plane like-sites/defects, will result in beneficial alterations in the observed electrochemical properties, with the development of scalable production techniques also likely to further encourage graphene exploitation.

TSP-12 Fabrication of Core-shell Particles Having the Absorption-desorption Property for a Fluidized Bed Electrode, ***E.H. Kim****, Y. Jung (jungyg@changwon.ac.kr),* Changwon National University, Korea, *J.-G. Yeo, S.-C. Yang, J. Choi*, Korea Institute of Energy Research, Korea

A membrane-capacitive deionization (CDI), consisting of a fixed carbon electrode and membrane, has been applied to seawater desalination equipment because of the relatively low energy consumption compared with the reverse osmosis method. However, ion absorbability gradually decreases b ecause ion absorption mainly takes place at the interface area in contact with solution, reducing the absorption–adsorption efficiency of the electrode. Therefore, a fluidized bed electrode is applied to seawater desalination to overcome the limited absorbability of the fixed bed electrode and eliminate the recycle process. In this work, active carbon particles were coated with a cation-exchanged polymer for preparing the core–shell particles having a simultaneous absorption–desorption property, to be used as a fluidized bed electrode in seawater desalination. To adequately utilize the features of the core–shell particles, the polymer should be uniformly coated on the surface of independent active carbon particles. To do that, the active carbon particles prior to the polymer coating were modified with an acid for individual separation without agglomeration between particles, producing a more effective coating of polymer on the carbon particles. The modified carbon particles were well dispersed in an aqueous solution by the hydrophilic group in the cation-exchanged polymer, resulting in the homogeneous coating of polymer on the surface of individual carbon particles. This means that the core–shell particles prepared with heterogeneous materials could be applicable to a fluidized bed electrode in seawater desalination.

TSP-13 Improving Oxidation Resistance and Fracture Strength of MgO-C Refractory Through Precursor Coating, ***G.-H. Cho****, J. Li, E.H. Kim, Y. Jung (jungyg@changwon.ac.kr),* Changwon National University, Republic of Korea, *Y.-Ki Byeun*, Technical Research Laboratories Pohang Research Lab, Republic of Korea

Aluminum (Al) precursor was coated onto the surface of carbon to improve the oxidation resistance in a magnesium carbon (MgO-C) refractory, and its effects on the fracture strength by controlling the amount of antioxidant and the coating thickness. To enhance the coating efficiency, the surface of graphite employed as a carbon source was treated by an acid. The Al-coated graphite showed a less weight loss than the pristine graphite in oxidation tests. The MgO-C refractory with the Al-coated graphite showed the similar fracture strength than that with the pristine refractory, even though the amount of antioxidant was reduced. The highest fracture strength was about 17 MPa, which was shown in the MgO-C refractory with the Al-coated graphite. The increase of fracture strength in the modified MgO-refractory was due to the homogeneous coating of Al precursor, showing the thickness of about 400 nm. The relationship between fracture strength and process parameters was discussed, based on the properties observed.

Coatings for Use at High Temperatures
Room: Sunrise - Session A2-2

Thermal and Environmental Barrier Coatings
Moderator: K.A. Unocic, Oak Ridge National Laboratory, V. Maurel, Mines-ParisTech, France, K. Lee, Rolls Royce, US

8:00am **A2-2-1 Deposition and Properties of a High Temperature Thermal Barrier Coating Using The Solution Precursor Plasma Spray Process**, ***M. Gell*** *(mgell@mail.ims.uconn.edu), E. Jordan, J. Roth, C. Jiang,* University of Connecticut, US, *J. Wang, B. Nair*, HiFunda LLC, US

Yttria Stabilized Zirconia (YSZ) thermal barrier coatings (TBCs) have been extensively used for over 40 years to insulate hot section gas turbine components because of their favorable combination of properties. One of the key properties of YSZ is a very high thermal expansion coefficient, which reduces the thermal expansion mismatch between the TBC and the underlying metal. Many oxide ceramics with lower thermal expansion coefficients than YSZ have been evaluated as potential second generation TBCs and have been rejected because of poor thermal cyclic durability.

The starting point for this research was to select an oxide ceramic with a potentially higher use temperature and other favorable properties, but with higher thermal expansion mismatch than YSZ to determine whether the greater thermal expansion mismatch strains could be overcome using the strain-tolerant microstructure that is produced by the solution precursor plasma spray (SPPS) process.

The precursors used were yttrium and aluminum nitrates dissolved in water or ethanol. A wide range of precursor and plasma spray parameters was investigated and will be described. These experiments showed that 250 micron thick YAG TBCs could be deposited by the SPPS process. The microstructures could be varied over a wide range, from highly porous with a "feather-like" appearance to relatively dense with vertical cracks. Thermal cycle durability, hardness, erosion and thermal stability of the SPPS YAG TBCs are being conducted and will be reported.

8:20am **A2-2-2 Feasability of Multilayer Sol-Gel Thermal Barrier Coating Sensor for Through-thickness Temperature Sensing and Interface Delamination Early Diagnostic**, ***E. Copin*** *(etienne.copin@mines-albi.fr), T. Sentenac, Y. Le Maoult,* Ecole Nationale Superieure des Mines - Albi, France, *F. Ansart*, CIRIMAT, University of Toulouse, France, *P. Lours*, Ecole Nationale Superieure des Mines - Albi, France

The degradation during service of the current standard Yttria Stabilized Zirconia (YSZ) Thermal Barrier Coatings (TBCs) protecting critical components in gas turbine engines is mainly caused by the initiation and the propagation of microcracks at the interface with the bond coat, which makes its early detection difficult. The development of reliable predictive models for TBCs spallation is hindered by the difficulty of accessing to the effective interface temperature through conventional means without compromising the integrity of the coating. This results in strongly conservative margins being imposed to allow safe operation.

In this context there have been a growing interest in the application of phosphor thermometry methods for the diagnostic of TBCs. The partial transparency of YSZ in the visible range of the spectrum allows to collect local information conveyed by the phosphorescence emissions from optically excited luminescent layers integrated within the depth of the TBC. This functionalisation can be obtained by the introduction of optically active components such as trivalent lanthanide ions directly into the crystal structure of YSZ, thus without detrimental alterations of the coating properties. Reported here is the fabrication feasibility study of such *multilayer TBC structures* by a *sol-gel process alternative to standard electron beam physical vapour deposition and plasma spraying methods used for YSZ coatings* for future applications in *through thickness measure of temperature and early spallation monitoring.*

9.7at%-YSZ phosphors have been synthesised via a sol-gel route by small additions of luminescent centers including Eu^{3+}, Dy^{3+}, Er^{3+}, Sm^{3+} and Tm^{3+} ions. The microstructure as well as the room temperature spectral and temporal responses of these materials were investigated to optimise both their luminescence and microstructural properties.. Different multilayer prototypes integrating functionalised layers were successfully deposited by dip-coating on an industrial grade single crystal nickel superalloy. The optical performance of these designs were evaluated for future applications in punctual and 2D temperature measurements throughout the depth of the TBCs. In addition TBC samples containing pre-calibrated delaminated areas were produced and characterised as a first attempt to study the effects of interface decohesion on the luminescent emissions from doped YSZ sublayers. Preliminary results are promising for the use of fully integrated YSZ-type phosphor layers for monitoring temperature profiles and sensing damage evolution in TBCs systems exposed to cyclic oxidation conditions.

8:40am **A2-2-3 Analysis of Possible Microstructures in Suspension Plasma Sprayed Deposits**, ***L. Pawlowski*** *(lech.pawlowski@unilim.fr), P. Sokolowski,* University of Limoges, France, *S. Kozerski,* Wroclaw University of Technology, Poland, *A. Denoirjean*, University of Limoges, France **INVITED**

Two commercially available zirconia stabilized powders, namely Metco 204NS, ZrO_2+ 8 wt. % Y_2O_3 and Metco, 205NS, ZrO2 + 24 wt.% CeO_2 + 2.5 wt.% Y_2O_3 were attritor milled to obtain the particles sizes smaller than ten micrometers. The fine solids were formulated in a suspension composed of 20 wt.% powder, 40 wt.% water, and 40 wt.% ethanol. The suspensions were used for plasma spraying using two torches and SG-100 of Praxair and Triplex of Sulzer Metco. The suspension was injected into plasma jet through a continuous stream injector installed inside (SG-100) or outside of plasma torch (Triplex). The spray processes were carried out by varying the spray distance, the torch scan velocity, the electric power input and, finally, the stainless steel substrates roughness. The latter was achieved by the sand blasting using alumina grit. The temperature of the coatings during deposition was monitored using a pyrometer. The coatings were prepared metallographically and their microstructure was characterized using field emission scanning electron microscope and transmission electron microscope. The microstructure was correlated to the operational spray parameters. Finally, thermal diffusivity of obtained coatings was tested using two different set ups in low (up to 300°C) and high temperatures (up to 800°C). Moreover, the some mechanical properties of the coatings were tested using scratch and indentation tests.

9:20am **A2-2-5 Slurry Based Thermal Barrier Coatings with Quasi-foam Structures from Sintered Micro-sized Hollow Alumina Spheres**, ***V. Kolarik*** *(vladislav.kolarik@ict.fraunhofer.de), M. Juez Lorenzo, R. Roussel, V. Kuchenreuther*, Fraunhofer ICT, Germany

Spherical Al particles in the range of 1 to 20 µm are deposited as slurry on the surface of a Ni- or Fe-based alloy according to the PARTICOAT concept (www.particoat.eu). During the heat treatment they oxidize to a topcoat from sintered hollow alumina spheres while forming an aluminized diffusion zone in the substrate. The topcoat effectuates as a thermal barrier by gas phase insulation and the diffusion zone forms a protective alumina layer.

Sheets of austenitic steels such as Alloy 321 were coated by spraying or tape casting using slurries with Al particles in a size range of 1 to 20 µm. Boron was added to the slurry to achieve a higher sintering degree and better adhesion to the substrate. To investigate the thermal barrier effect and the behaviour under exposure to temperature with the thermal gradient between the exposed side and the cooled backside, an experimental set-up was designed, which allows to heat the sample from one side while being cooled by airflow on the backside. The temperature is measured by thermocouples on both sides as a function of the time. An electric radiation heater or a Bunsen burner is used as heat source.

The coating provides a notable thermal barrier effect due to gas phase insulation by the hollow alumina sphere structure. A topcoat with a thickness of 300 µm for example, reduces the temperature at the backside by 350°C without and by 550°C with backside cooling when exposing the surface to 800°C. The temperature reduction by gas phase insulation remains stable over the investigated times of up to 100 h. The metastable alumina phases γ-Al_2O_3 and θ-Al_2O_3 are observed at the interface to the aluminium-rich diffusion zone confirming the reduction of temperature at the metal surface.

The topcoat from sintered hollow alumina particles is capable to protect materials against temperature at low costs. The results with coated Alloy 321 confirm the thermal barrier effect of this novel coating system obtained by a heat treatment of slurry deposited spherical Al particles.

9:40am **A2-2-6 Characterization of Plasma Electrolytic Oxidized Coatings on Hot-dip Aluminized Carbon Steel**, ***F. Chang***, National Taiwan University of Science and Technology (NTUST), Taiwan, *J.W. Lee (jefflee@mail.mcut.edu.tw),* Ming Chi University of Technology, Taiwan, *C.J. Wang*, National Taiwan University of Science and Technology (NTUST), Taiwan

Recently, the plasma electrolytic oxidation (PEO), or the so-called micro-arc oxidation (MAO) process has been widely studied and applied in industries due to its ability to create functional oxide layers on light metals.

In this work, the hybrid method of PEO and hot-dipped aluminizing (HDA) was employed to deposit composite ceramic coatings on the surface of carbon steel plate. The HDA of carbon steel plate was executed at 700°C for 5 mins. The duty cycle and frequency of PEO were adjusted to fabricate six different HDA-PEO coatings. The chemical composition and microstructure of coatings were determined by a field emission electron probe microanalyzer (FE-EPMA), X-ray diffractometer (XRD) and scanning electron microscopy (SEM), respectively. The hardness and adhesion of coatings were determined by the micro hardness tester and scratch tester. The corrosion resistance of coatings was evaluated by the potentiodynamic polarization test in 3.5 wt.% NaCl aqueous solution. Effects of duty cycle and frequency on the microstructure, mechanical property and corrosion resistance of HDA-PEO coatings were discussed in this work.

Keywords: plasma electrolytic oxidation, hot-dipped aluminizing, duty cycle, frequency, scratch tester, corrosion test

10:00am **A2-2-7 The Influence of Temperature Gradients on the Interaction of Molten Silicates with Thermal Barrier Coatings**, ***R.W. Jackson*** *(rwesleyjackson@engineering.ucsb.edu), E. Zaleski, M.R. Begley, C.G. Levi*, University of California, Santa Barbara, US

As the operating temperature of turbine engines has increased, so has the prevalence of molten calcium magnesium alumino-silicate (CMAS) deposits infiltrating thermal barrier coatings (TBCs). The molten CMAS fills the pores in the TBC, which stiffens the coating, magnifying the stresses generated from the thermal strains, which increases the tendency for cracking. The aim of this presentation is to examine the effect that temperature gradients have on the interaction between silicate deposits and TBC systems. A thermal gradient test, in which a CO_2 laser is employed to impose a controllable thermal gradient, is used to investigate the interaction between CMAS and 7YSZ and GZO EB-PVD TBCs. The experimental results are then used to guide the development of expressions that describe the nature of silicate infiltration into the TBC, the evolution of coating elastic modulus, and the generation and release of stresses.

10:20am **A2-2-8 The Effect of Cycle Frequency, H_2O and CO_2 on TBC Lifetime with NiCoCrAlYHfSi Bond Coatings**, ***M. Lance*** *(lancem@ornl.gov), K.A. Unocic, J. Haynes, B.A. Pint*, Oak Ridge National Laboratory, US

Innovative turbine concepts to assist in carbon capture are being considered that may result in higher H_2O and/or CO_2 concentrations than typical experience with natural gas fired land based turbines. Furnace cyclic testing has been used to assess thermal barrier coating (TBC) lifetime with superalloy 1483 and X4 substrates and high velocity oxygen fuel (HVOF)-NiCoCrAlYHfSi bond coatings at 1100°C. Average air plasma sprayed (APS) yttria-stabilized zirconia (YSZ) top coating lifetimes were 5-6 times longer and interdiffusion was higher when 100h cycles were used to simulate base-load operation, rather than the 1h standard of aeroengines. With 100h cycles in air with 10%H_2O the average lifetime with X4 substrates increased 60% compared to 1483 substrates, while the difference was 40% in 1h cycles. Additions of 10-50%H_2O or 90%CO_2 did not strongly affect TBC lifetime on the 1483 substrates. Photo-stimulated luminescence spectroscopy (PSLS) and 3D microscopy were used to measure residual stress in the alumina scale and surface roughness, respectively, on specimens without a YSZ top coating. The average compressive stress in the scale was lowest in the 10%H_2O/airenvironment, however this difference did not correlate to changes in the TBC lifetime.

Research sponsored by the U. S. Department of Energy, Office of Fossil Energy, Coal and Power R&D.

10:40am **A2-2-9 Failure Characteristics And Mechanisms Of Eb-Pvd Tbcs With Pt-Modified Nial Bond Coat**, *L. Zhou, S. Mukherjee*, ***Y.H. Sohn*** *(Yongho.Sohn@ucf.edu)*, University of Central Florida, US

Failure characteristics of EB-PVD YSZ TBCs with Pt-modified NiAl bond coat were examined with furnace cycling at 1100°C with dwell time of 1 hour using photo-stimulated luminescence spectroscopy, X-ray diffraction, scanning electron microscopy, and transmission electron microscopy. To examine the influence of EB-PVD topcoat during thermal cycling, the other side of the button specimen was only coated with (Ni,Pt)Al. Rumpling occurred on both sides but the amplitude of interface roughness increased more rapidly when the ceramic topcoat was absent. However, the TGO grew faster for the YSZ-coated (Ni,Pt)Al bondcoat. The compressive residual stress of the TGO scale initially increased, then gradually decreased on both sides. While the magnitude of peak compressive stress was similar (3 to 4 GPa), the decrease in the magnitude as a function of thermal cycling was faster for the bare (Ni,Pt)Al side, especially for the TGO developed on ridges. Interfacial and strain energy of the TGO scale were also estimated. Evolutions in phase constituents and microstructure examined by electron microscopy and relevant selected electron area diffraction analyses. Results from luminescence, microscopy and ensuing analyses were correlated with the failure characteristics of the TBCs to elucidate failure mechanisms.

11:00am **A2-2-10 Time and Temperature Dependent Mechanical Properties of Superalloy Bond Coat at Nanometer Length Scale**, ***K. Rzepiejewska-Malyska*** *(karolina@hysitron.com), J. Vieregge, O.L. Warren, S.A.S. Syed*, Hysitron, Inc., US

Instrumented nanoindentation enables examination of materials' surface mechanical properties with greater resolution and accuracy than ever before. Many applications not only require testing materials at small scale but also at high temperatures before component reliability in the working conditions can be confirmed. Nanomechanical characterization at high temperatures has been limited due to a number of challenges related to the instrumentation.

We have recently developed a unique method that allows for complex characterization of a material's surface at elevated temperatures. A newly-designed, radically-different, low-drift heating stage for precise control of temperature up to 600 °C, combined with an improved nanoscale dynamic mechanical testing capability and *in-situ* scanning probe microscopy-based imaging, resulted in drift-free nanomechanical properties measurements over extended time.

Such experiments are particularly beneficial for investigation of materials such as superalloys and bond coats which were designed and optimized to serve in extreme atmospheric conditions. Based on the example of an intermetallic PtNiAl bond coat, we will demonstrate how our recently developed methodology for improved dynamic mechanical testing at elevated temperatures has been utilized for dynamic nanoscale creep characterization. Mechanical property mapping, for directly imaging mechanical response and properties with submicron spatial resolution, can further advance the understanding of material behavior.

11:20am **A2-2-11 Development and Performance Evaluations of HfO2-Si Based Bond Coat Systems for Advanced Environmental Barrier Coatings**, ***D. Zhu*** *(Dongming.Zhu@nasa.gov)*, NASA Glenn Research Center, US

Ceramic environmental barrier coatings (EBC) and SiC/SiC ceramic matrix composites (CMCs) will play a crucial role in future aircraft propulsion systems because of their ability to significantly increase engine operating temperatures, improve component durability, reduce engine weight and cooling requirements. Advanced EBC systems for SiC/SiC CMC turbine and combustor hot section components are currently being developed to meet future turbine engine emission and performance goals. One of the significant material development challenges for the high temperature CMC components is to develop prime-reliant, high strength and high temperature capable environmental barrier coating bond coat systems, since the current silicon bond coat cannot meet the advanced EBC-CMC temperature and stability requirements. In this paper, advanced NASA HfO2-Si based EBC bond coat systems for SiC/SiC CMC combustor and turbine airfoil applications are investigated. The coating design approach and stability requirements are specifically emphasized, with the development and implementation focusing on Plasma Sprayed (PS) and Electron Beam-Physic Vapor Deposited (EB-PVD) coating systems and the composition optimizations. High temperature properties of the HfO2-Si based bond coat systems, including the strength, fracture toughness, creep resistance, and oxidation resistance were evaluated in the temperature range of 1200 to 1500 ° C. Thermal gradient heat flux low cycle fatigue and furnace cyclic oxidation durability tests were also performed at temperatures up to 1500 ° C. The coating strength improvements, degradation and failure modes of the environmental barrier coating bond coat systems on SiC/SiC CMCs tested in simulated stress-environment interactions are briefly discussed and supported by modeling. The performance enhancements of the HfO2-Si bond coat systems with rare earth element dopants are also highlighted. The HfO2-Si based bond coat systems, when integrated with advanced EBC top coats, showed promise to achieve 1500 ° C temperature capability, helping enable next generation turbine engines with significantly improved engine component temperature capability and long-term durability.

11:40am **A2-2-12 Evaluation Of Hot Corrosion Resistance On Inconel 718 Superalloys Of Thermal Barrier Coatings**, ***K.M. Doleker*** *(mert.7@outlook.com), A.C. Karaoğlanlı*, Bartın University, Turkey

Hot corrosion of thermal barrier coatings (TBC) is one of the main failure mechanisms at gas turbines, which are used low quality fuels. This problem mainly associates with impurities such as Na and V in fuel contents. In this study, hot corrosion behavior of TBC on Inconel 718 substrates were investigated in molten salt mixture of (Na_2SO_4+V_2O_5) at 1000 °C . Microstructural analysis showed that spallation failure was resulted from infiltration of salts into yttria-stabilized zirconia (YSZ) layer by means of defects such as pores and microcracks. SEM and X-ray diffraction

techniques were used to determine corrosion products and phase contents in YSZ layer.

Keywords: Hot corrosion, Thermal barrier coatings, Molten salt, Spallation, Inconel 718

Hard Coatings and Vapor Deposition Technology
Room: Golden West - Session B3

Deposition Technologies for Diamond Like Coatings
Moderator: K. Böbel, Robert Bosch GmbH, C. Engdahl, Crystallume

8:00am **B3-1 The Chemical Functionalization of DLC to Create an Oleophobic and Hydrophobic Surface with High Thermal and Oxidative Stability**, ***D.A. Smith*** *(david.smith@silcotek.com)*, SilcoTek Corporation, US

Typical DLC depositions have reasonably high hydrophobicity, but are characteristically oleophilic, and exhibit poor thermal stability above 250°C. A unique functionalization process has been applied to enhance DLC and create a highly oleophobic and substantially more hydrophobic surface. The modified surface has excellent thermal resilience with the surface energy characteristics remaining stable even after extensive exposure to 300°C in an oxidative environment. These properties are achieved exclusively by chemical functionalization of the DLC surface, without alteration of the DLC thickness or physical modification of surface topography. A variety of characterization techniques have been used and will be presented, such as contact angle measurements, X-ray photoelectron spectroscopy, scanning electron microscopy, Raman spectroscopy, and tribological testing for wear and friction. The creation of a thermally stable, hydrophobic, oleophobic, DLC surface will expand the applicability and performance of these useful coatings when exposed to aqueous, hydrocarbon, and/or fouling environments.

8:20am **B3-2 Deposition of Diamond-like Carbon Films on Steel Surfaces by Enhanced Asymmetrical Bipolar Pulsed-DC PECVD Method and Acetylene as Precursor**, *G. Capote (gcapoter@unal.edu.co)*, National University of Colombia, Colombia, *E. Corat*, ***V. Trava-Airoldi***, Institute for Space Research, Brazil

Research and development of nanostructured materials with improved, tailor-designed properties is a fundamental need for the growth and advance of automotive, aerospace, chemical, biomedical and electronic industries among others. Diamond-like carbon (DLC) films have attracted significant attention recently due to their low friction, high hardness, high elastic modulus, chemical inertness, biocompatibility, and high wear resistance. These films are mostly obtained by plasma decomposition of a hydrocarbon-rich atmosphere. The major disadvantage of hard DLC coatings deposition and, therefore, their technical applications is that there is often a relatively low adhesion of these films on metallic substrates caused by very high total compressive stress on these coatings. In order to overcome the high residual stress and low adherence of DLC films on steel substrates, a thin amorphous silicon interlayer was deposited as an interface.

Amorphous silicon interlayer and DLC films were grown by employing an asymmetrical bipolar pulsed-DC PECVD system, using silane and acetylene atmospheres, respectively. DLC films were analyzed according to their microstructure, mechanical, and tribological properties as a function of self-bias voltage. The chemical composition and hydrogen content of the films were probed by means of Raman scattering spectroscopy. The total stress was evaluated through the measurement of the substrate curvature, using a profilometer, while nanoindentation experiments helped determine the films' hardness. The friction coefficient and critical load were determinated by using a tribometer. The corrosion resistance was evaluated by electrochemical potentiodynamic polarization techniques.

The use of an amorphous silicon interlayer improved the DLC films deposition onto steel substrates, producing good adhesion, low compressive stress, and a high hardness. The composition, microstructure, mechanical and tribological properties of the DLC films were strongly dependent on the self-bias voltages. All tests confirmed the importance of the intensity of ion bombardment during film growth on the mechanical and tribological properties of the films. Experimental results suggested that the surface roughness and hardness of the films are often closely related to the friction of the surface and to the wear resistance of the coatings. Also, they demonstrated that DLC coatings improve steel electrochemical corrosion resistances. The deposition rates combined with mechanical, tribological, and corrosion resistance properties of these films make them suitable candidates for specific industrial applications.

8:40am **B3-3 Developments of Amorphous Hydrogenated DLC Coatings for Automotive Applications**, ***M. Keunecke*** *(martin.keunecke@ist.fraunhofer.de), R. Wittorf, M. Weber, I. Bialuch, K. Bewilogua, G. Braeuer*, Fraunhofer Institute for Surface Engineering and Thin Films IST, Germany **INVITED**

Among other coatings and surface treatments DLC (diamond-like carbon) coatings play an important role due to a unique combination of excellent properties like high hardness, high wear resistance and low friction coefficients.

Diamond-like carbon (DLC) coatings, especially amorphous hydrogenated a-C:H and metal containing a-C:H:Me coatings are well established in the automotive industry as a solution to reduce or even eliminate wear problems of highly loaded components. With the actual strong focus on reducing fuel consumption and minimizing the CO2 emission the reduction of friction losses becomes a major intent. DLC coatings have a high potential for significant friction reduction both under dry and lubricated operation.

The term DLC describes a coating material class covering a broad range of physical and chemical properties. Well defined combinations of coating properties can be adjusted using different deposition processes and parameters. A brief overview about the variety of DLC coatings, the corresponding deposition techniques and the coating properties and application examples will be presented.

Some objectives of further development are adhesion improvement, increase of hardness and high coating quality on complex geometries. A promising technique to fulfill these requirements is the deposition of a-C:H coatings by reactive d.c. magnetron sputter deposition from a graphite target with acetylene as reactive gas. The a-C:H coating deposition was carried out working with varying parameters of substrate bias (d.c. and pulsed d.c.), acetylene flows and ion current densities. The hardness clearly depended on the hydrogen contents and the hardest coatings (up to 50 GPa) could be prepared at hydrogen contents of about 10 atom %.

In addition further results of recent developments of effective DLC-based coating solutions will be presented.

9:20am **B3-5 A MF-AC Enhanced PECVD Technology for High Rate Deposition of DLC**, *H. Tamagaki (tamagaki.hiroshi@kobelco.com), J. Haga, H. Ito*, ***A. Umeda***, Kobe Steel, Ltd., Japan

A new concept MF-AC enhanced PECVD system for high rate deposition of DLC(diamond like carbon) coating was developed. The feature of this new deposition system is the method to generate the plasma for deposition by applying mid-frequency AC voltage between the substrates divided into two groups connected two output of AC power supply. This new configuration results in high rate deposition of hydrogenated DLC coating at low contamination on the chamber wall and with long term stable operation, because the discharge plasma was held between two groups of substrates.

The depositions using this new technology were demonstrated at an industrial scale unbalanced magnetron sputtering equipment with 4 sputtering cathodes, 6-axes planetary rotary substrate table and with effective loading space of 450mm in diameter and 400mm in height. After etching and interlayer formation, depositions of 1-3micron thick DLC coatings were carried out under 1-3 Pa of C2H2 and by applying MF-AC power of a few kW range. The deposition rate of 1-5microns/Hr was demonstrated on substrates on 3-fold rotation fixtures under full load conditions. The hardness of DLC coating was measured as 20 to 28GPa and the tribological properties comparable to DLC coatings from the other deposition technologies were obtained.

9:40am **B3-6 Modifications of Closed Drift Ion Source for Various Surface Treatments from Etching to Coating**, ***S. Lee*** *(seunghun@kims.re.kr), K.-T. Kim, Y.-J. Kang, D.-G. Kim, J.-K. Kim*, Korea Institute of Materials Science, Korea

Linear plasma treatments have been applied to diverse web coater and batch type coater. And various linear ion sources have been required for noble vacuum coating processes from etching to coating. We have investigated closed drift linear ion sources for etching, pre-treatment, activation and deposition. 2D particle-in-cell and 3D electromagnetic calculations were conducted to predict electron trapping, ion extraction in the closed drift linear ion source, and plasma distribution in process region. Two types of ion sources were developed based on the theatrical calculation. High energy (>3 keV) and high flux (1 mA/cm^2) ion source using anode layer acceleration was developed for activation and etching processes of metal and polymer. Low energy (< 500 eV) high flux (>1 mA/cm^2) ion source were investigated for deposition process of diamond-like carbon film. In this presentation, the theoretical analysis of ion sources and the examples of the practical processes will be introduced.

10:00am **B3-7 Plasma Beam Deposition of Amorphous Carbon**, ***M.F. Weiler*** *(m.weiler@ccrtechnology.de)*, CCR TECHNOLOGY GmbH, Germany **INVITED**

Amorphous Carbon is used to describe a wide range of hydrogenated or none hydrogenated solids whereas its chemical structure mainly results out of the process parameter applied during thin film deposition. Beside common PVD methods like sputtering, laser ablation or cathodic arc deposition PECVD technologies are gaining more and more interest. PECVD has the advantage that the carbon precursor is a gas like acetylene or methane which for plasma excitation can be distributed over large areas and therefore allows one to control the amount and kinetic energies of ions as well as the chemical composition of ions and radicals in the film forming particle flux over large areas of several meters in dimensions. Beside a brief history of plasma beam deposition the focus in the present contribution will be a 13.56 MHz inductively coupled controlled plasma beam source called COPRA. Herein controlled plasma means that the amount of ions in the film forming particle flux as well as the chemical composition of the film forming particle flux can be adjusted independently to each other over a wide working pressure range from 1E-4mbar up to 1E-1mbar. These are ideal conditions to control the physical and chemical properties of the amorphous carbon in particular for plasma enhanced chemical vapor deposition of highly tetrahedral amorphous carbon with C-C sp^3 of more than 70 at %. On top of this control such an inductively coupled COPRA plasma excitation has a power coupling efficiency of more than 80% leading to high flux intensities and therefore to high deposition rates. Using for example C_2H_2 as precursor at a working pressure below 5E-4mbar it is possible to deposit highly tetrahedral amorphous hydrogenated carbon ta-C:H with deposition rates higher than 5nm/sec guaranteed by an ionization degree of nearly 90% in the film forming particle flux with $C_2H_2^+$ current densities of up 5mA/cm^2. On the other hand operating such an ICP-COPRA plasma beam source at a working pressure above 2E-2mbar it is possible to deposit polymers with rates of more than 20nm/sec resulting out of film forming particle flux containing nearly only C_xH_y radicals. In summary this contribution gives an overview of the current state of the art of using ICP – plasma beam deposition on a scientific as well as industrial level not only including known amorphous carbon modifications but also new approaches for amorphous and crystalline carbon compounds offered by the high dissociation degree of a COPRA plasma beam enabling to apply atomic plasma beams for example of protons (H^+) or atomic nitrogen (N^+) in combination with hydrocarbon precursors.

Hard Coatings and Vapor Deposition Technology
Room: Royal Palm 1-3 - Session B4-5

Properties and Characterization of Hard Coatings and Surfaces

Moderator: C. Mulligan, US Army ARDEC, Benet Laboratories, J. Lin, Southwest Research Institute, U. Beck, BAM Berlin

8:00am **B4-5-1 Bias Effect on Structure and Mechanical Properties of Magnetron Sputtered Nanocrystalline Zirconium Tungsten Nitride Thin Films**, ***P. Dubey***, *R. Chandra (ramesfic@gmail.com)*, Indian Institute of Technology Roorkee, India

Nano-crystalline zirconium tungsten nitride (Zr-W-N) thin films have been deposited on Si (100) substrates by magnetron sputtering at 200°C substrate temperature. The effect of substrate bias on structure and mechanical properties of deposited films has been studied in details using X-ray diffraction, field emission scanning electron microscopy, atomic force microscopy and nano-indentation. All Zr-W-N films exhibit a crystalline fcc phase with (111) and (200) preferred crystallographic orientations of grains. Increasing substrate bias decreases the crystallite size and increases the roughness of the Zr-W-N films. The lattice parameter and thickness of Zr-W-N films varies non-monotonically with increasing substrate bias. The Zr-W-N films have columnar structure which becomes finer at high substrate bias. Nano-indentation hardness and reduced elastic modulus of the films increases as the substrate bias goes up. Maximum wear resistance (H/E_r~0.22) and maximum resistance to fatigue fracture (H^3/E^2~1.1 GPa) have been achieved for the film deposited at -80 V bias voltage.

8:20am **B4-5-2 Structural, Mechanical and Electronic Properties of 3d Transition Metal Nitrides in Cubic Zincblende, Rocksalt and Cesium Chloride Structures: a First-Principles Investigation**, *Z. Liu, X. Zhou,* ***S. Khare*** *(sanjay.khare@utoledo.edu)*, University of Toledo, US, *D. Gall*, Rensselaer Polytechnic Institute, US

In the quest for super-hard materials widely used in cutting and coating industries, research attention has been drawn by transition metal nitrides. The existing literature is either limited to singular compounds or does not present the mechanical properties and their connection to electronic properties. We thus report systematic results from *ab initio* calculations with density functional theory on three cubic structures, zincblende (zb), rocksalt (rs) and cesium chloride (cc) of the ten 3d transition metal nitrides. We computed lattice constants, elastic constants, their derived moduli and ratios that characterize mechanical properties. Experimental measurements exist in the literature of lattice constants for rs-ScN, rs-TiN and rs-VN and of elastic constants for rs-TiN and rs-VN, all of which are in good agreement with our computational results. Similarly, computed Vicker's hardness values for rs-TiN and rs-VN are consistent with earlier experimental results. Several trends in our rich data set of 30 compounds were observed. All nitrides, except for zb-CrN, rs-MnN, rs-FeN, cc-ScN, cc-NiN and cc-ZnN, were found to be mechanically stable. A clear correlation in the atomic density with the bulk modulus (B) was observed with maximum values for B for FeN in zb, MnN in rs, and CrN in cc. The shear modulus, Young's modulus, Vicker's hardness (H_V) and indicators of brittleness showed similar trends and all showed maxima for cc-VN. The calculated value of H_V for cc-VN is above 30 GPa, while the next highest values are for rs-ScN and rs-TiN, above 24 GPa. A relation ($H_V \sim(\theta_D)^2$) between H_V and Debye's temperature (θ_D) was investigated and verified for each structure type. A tendency for anti-correlation of the elastic constant C_{44}, which strongly influences stability and hardness, with the number of electronic states around the Fermi energy, was observed.

8:40am **B4-5-3 Local Residual Stress Measurement on Amorphous Plasma-sprayed Single-splats**, ***M. Sebastiani*** *(seba@stm.uniroma3.it)*, University of Rome "Roma Tre", Italy, *G. Bolelli, L. Lusvarghi*, University of Modena and Reggio Emilia, Italy, *E. Bemporad*, University of Rome "Roma Tre", Italy

Residual stress was measured on plasma sprayed Nickel-Aluminum (Ni-Al), Alumina (Al_2O_3) and Alumina-Titania (Al_2O_3-TiO_2) single splats, by using the incremental focused ion beam micron-scale ring-core method (IμRCM). Results showed a tensile residual stress for polycrystalline Ni-Al, where the quenching stress is only partially relaxed by edge curling, through-thickness yielding and interfacial sliding. Conversely, a significant compressive stress for the amorphous Al_2O_3-TiO_2 splats and a relatively lower compressive stress for the large micro-cracked crystalline Al_2O_3 splats were measured.

The observed differences between the Al_2O_3 and Al_2O_3-TiO_2 splats suggest that, for these materials, a complex interaction exists between the stress component due to different thermal contraction and the quenching stress one, which is supposed to be reduced by different relaxation mechanisms, also correlated to the microstructural evolution and during splat formation.

The experimental methodology developed provided a unique way for the study of the residual stress build-up mechanisms in amorphous and crystalline single splats obtained by plasma spraying, and gave further insights into the actual micro-scale phenomena that give rise to adhesion and nano-mechanical behavior of thermally sprayed coatings.

9:00am **B4-5-4 Oxidation Behavior of $TiC_{0.81}N_{0.48}$ Coating and $TiC_{0.61}N_{0.44}O_{0.15}$ Coating Deposited by Chemical Vapor Deposition**, ***L. Zhu*** *(lhzhu@mail.shu.edu.cn), Y.M. Zhang, T. Hu*, Shanghai University, China, *P. Leicht, Y. Liu*, Kennametal Incorporated, US

This paper aims to investigate the effect of oxygen addition on the oxidation resistance of Ti(C,N) coating prepared by chemical vapor deposition (CVD). TiC0.81N0.48 coating and TiC0.61N0.44O0.15 coating were deposited by CVD, and their oxidation behavior at 600°C and 700°C was compared. At 600°C, the TiC0.61N0.44O0.15 coating oxidizes with a linear growth rate at the beginning of the oxidation. Nevertheless, the oxidation kinetics of TiC0.81N0.48 coating follows a linear law initially, and then changes to a parabolic law. The oxidation kinetics of TiC0.81N0.48 coating and TiC0.61N0.44O0.15 coating is similar and obeys a parabolic law at 700°C. The oxidation resistance of the TiC0.61N0.44O0.15 coating is inferior to that of the TiC0.81N0.48 coating. The reduced oxidation resistance of the TiC0.61N0.44O0.15 coating is ascribed to the formation of more gas holes, fissures and cracks.

9:20am **B4-5-5 Modulus and Compressive Stress Graded Ti-C Coating on Ti-6Al-4V Aerospace Alloy**, ***T.R. Kamalakshi Hemachandran*** *(ramantfb@iap.iisc.ernet.in), M. Rao Gowravaram*, Indian Institute of Science, India

In this study, to accommodate higher interfacial shear stress between Ti-C coating system and Ti64 substrate, coating modulus and compressive stresses are graded from interface to 4.5 µm thickness. The modulus gradient is achieved by varying Ti to C ratio by tuning the methane flow and compressive stress gradation from 0.1GPa to 3.5GPa by changing bias voltage during the reactive sputtering process. Micro tensile testing revealed that modulus and compressive stress graded coatings failed at 1.2% tensile strain, which is higher tensile load bearing capacity than the monolithic stoichiometric TiC coating. Hardness and modulus of the 4.5 µm thick film are 30GPa and 290 GPa respectively. At higher strain, coating started cracking and post-microscopy analysis shows variation of crack width at different zones of the tensile specimen. The gradation technique has shown that higher thickness films could be deposited without adhesion problems as compared to monolithic coatings.

9:40am **B4-5-6 Analysis of the Coating Interface Mechanics**, ***C.Y. Nie***, *L. Gu (gule@hit.edu.cn), D. Zheng, L. Wang*, Harbin Institute of Technology, China

The adhesive strength is the most important criterion to investigate a coating-substrate system. There is a lack of common standard in current methods of testing interface strength. Such as tearing test, indentation test and scratch test. In this paper, we used the method of images to solve the stress equations by complex variable function. According to the analytical solutions of stress and deformation in coating-substrate system, we could determine which place is susceptible to spall off in the interface. This analytical method will provide criterions to characterize or design a coating-substrate system.

Key words: coating-substrate system, interface mechanics, method of images

10:00am **B4-5-7 Corrosion and Tribological Behaviour of Laser Surface Alloyed Aisi 1016 Mild Steel**, ***O. Fatoba*** *(FatobaOS@tut.ac.za)*, Tshwane University of Technology, South Africa

Surface deterioration by wear and corrosion is one of the complications associated with ageing facilities and components especially under some service environments. In today's competitive global market, surface engineering offers industries improve performance of engineering components, longer component life and failure prevention. Laser Surface Alloying [LSA] offers a reliable and clean technique of depositing coatings unto the substrates to impart increased hardness, corrosion and wear resistance. This work is attempted to improve the mechanical and corrosion properties of mild steel, by developing highly corrosion resistant materials using binary combinations of metallic and ceramics materials as reinforcements. Mild steel laser alloyed surface was investigated for its hardness, wear and corrosion behaviour at different laser processing conditions. Zinc, aluminium and alumina powders were used in different compositions as ceramic and metallic reinforcement materials respectively. A 4.4KW continuous wave Rofin Sinar Nd:YAG laser was utilized for the fabrication process. The microstructures of the developed composites were characterized by optical (OM) and scanning electron microscope (SEM/EDS). Moreover, X-ray diffractometer (XRD) was used to identify the phases present. The addition of alloying elements increased the hardness, wear and corrosion resistances. The improvement of these properties was attributed to the formation of new phases and the microstructures.

Hard Coatings and Vapor Deposition Technology
Room: Royal Palm 4-6 - Session B7

Computational Design and Experimental Development of Functional Thin Films

Moderator: B. Alling, Linköping University, IFM, Thin Film Physics Division, D. Holec, Montanuniversität Leoben

8:00am **B7-1 Ab-initio Simulation of Vacancy Formation in $Ti_{0.5}Al_{0.5}N$ Alloy: From the Diverse Local Environments Towards Self-diffusion**, ***F. Tasnádi*** *(tasnadi@ifm.liu.se), I.A. Abrikosov*, Linköping University, IFM, Sweden, *M. Odén*, Linköping University, IFM, Nanostructured Materials, Sweden **INVITED**

Vacancies are common point defects in crystalline materials. Vacancy-mediated atomic transport, i.e. self-diffusion has fundamental importance in phase transformations, nucleations or even in the mechanical properties of hard coatings through spinodal decomposition, like in TiAlN alloys. Self-diffusion is determined by three major parameters: the (i) equilibrium vacancy concentration, the (ii) vacancy migration energy barrier and the (iii) vibrational entropy, what is connected to the jump-rate. Although self-diffusion is a fundamental physical phenomenon, it is purely studied for disordered alloys. Vacancy formation is believed to have a reasonably local, short-ranged environmental dependence. This fact has been used to develop a local cluster expansion technique [1] and applied recently in Al-Li, LixO2 alloys [1,2] and for hydrogen diffusion in Pd-Cu alloys [3].

Here we present how to perform a local environment analysis of metal (Ti, Al) and nitrogen (N) vacancy formations in Ti0.5Al0.5N using the Special Quasirandom Structure model [4] with the corresponding correction techniques. We underline the complexity of the problem and estimate the equilibrium vacancy formation energy and vacancy concentration in Ti0.5Al0.5N. Furthermore, we show that in non-equilibrium conditions – for example, during segregation, spinodal decomposition – vacancies are more favorable in some particular local environments, what can be selected by counting the number of first and second neighboring Al/Ti atoms around the vacant site, or by short-range order parameters.

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8:40am **B7-3 Room-Temperature Plasticity in ZrC: Role of Crystal Anisotropy**, *S. Kiani*, ***S. Kodambaka*** *(kodambaka@ucla.edu), C. Ratsch*, University of California, Los Angeles, US, *A. Minor*, University of California, Berkeley; National Center for Electron Microscopy, Lawrence Berkeley National Laboratory, US, *J.-M. Yang*, University of California, Los Angeles, US

NaCl structure Group IV and V transition-metal carbides are hard, stiff, and high-melting solids with excellent wear, abrasion, and corrosion resistances, and are commonly used in advanced high-temperature structural applications. In this presentation, we report results obtained from in situ transmission electron microscopy (TEM) studies and density functional theory calculations of uniaxial compression of ZrC(100) and ZrC(111) single crystals. In situ TEM observations show that dislocation motion and tangling lead to plastic deformation in ZrC(111), while slip along {110}<1-10> is dominant in ZrC(100). We find that the yield strengths of ZrC crystals increase with decreasing size. Interestingly, yield strengths of uniaxially compressed ZrC(111) crystals are lower than those of ZrC(100), unexpected for NaCl-structured compounds. Based upon the density-functional theory calculations, we attribute the orientation-dependent yield strengths to relatively lower energy barrier for shear along {110}<1-10> compared to {110}<1-10>. Our results provide important insights into the effects of crystal size and orientation on room-temperature plasticity. We expect that similar phenomena are likely to exist in other cubic-structured transition-metal carbides and nitrides.

9:00am **B7-4 Ab Initio Guided Design of Corundum Type $(Al_{1-x-y}Cr_xM_y)_2O_3$ Thin Films**, ***C.M. Koller*** *(christian.martin.koller@tuwien.ac.at)*, Vienna University of Technology, Austria, *J. Ramm*, Oerlikon Balzers Coating AG, Liechtenstein, *S. Kolozsvári*, Plansee Composite Materials GmbH, Germany, *D. Holec*, Montanuniversität Leoben, Austria, *J. Paulitsch, P.H. Mayrhofer*, Vienna University of Technology, Austria

Sophisticated alloying concepts are of utmost importance for application oriented coating development in order to obtain specifically tailored and optimised material properties allowing for extended application ranges. Recent studies on borides, nitrides, or oxides have proven the effectiveness of combining first principle calculations with experimental developments in obtaining an atomistic-to-macroscopic understanding of high performance materials. In this work we describe the impact of several selected alloying elements (M) on the quasi-binary system of $(Al_{1-x}Cr_x)_2O_3$ with focus on their capability to promote the desired corundum type α phase.

Based on *ab initio* calculated energies of formation for three different crystallographic structures (α, cubic B1-like, and cubic γ) it was investigated if elements such as B, Si, Hf, Ta, or Y promote the formation of metastable cubic phases instead of the desired α phase. The findings are compared with coatings synthesised by reactive cathodic arc evaporation. In the case of Fe alloying, for example, our predictions reveal no explicit impact on the phase stability sequence α, B1-like, and γ, whereas experiments suggest an increased amount of α phase fractions. Detailed analysis of the binding characteristics and structural defect sensibility provides an atomistic understanding of the sometimes observed discrepancy between calculations and experiments. This advanced approach allows for a knowledge-based development of high performance Al-Cr-based oxide coatings.

9:20am **B7-5 Accelerated Molecular Dynamics Simulation of Adatom Kinetics using SISYPHUS**, ***A. van de Walle*** *(avdw@brown.edu)*, Brown University, US, *P. Tiwary*, ETH Zurich, Switzerland **INVITED**

We present a method called SISYPHUS (Stochastic Iterations to Strengthen Yield of Path Hopping over Upper States) for extending accessible time scales in atomistic simulations. The method proceeds by separating phase space into basins and transition regions between the basins based on a general collective variable (CV) criterion. The transition regions are treated via traditional molecular dynamics (MD) while Monte Carlo (MC) methods are used to (i) estimate the expected time spent in each basin and (ii) thermalize the system between two MD episodes. In particular, an efficient adiabatic switching based scheme is used to estimate the time spent inside the basins. The method offers various advantages over existing approaches in terms of (i) providing an accurate real time scale, (ii) avoiding reliance on harmonic transition state theory, and (iii) avoiding the need to enumerate all possible transition events. Applications of SISYPHUS to adatom island ripening in fcc Al are presented.

10:00am **B7-7 Molecular Dynamics Study of the Growth of Various Crystalline Phases of Metal Oxides**, ***J. Houska*** *(jhouska@kfy.zcu.cz)*, University of West Bohemia, Czech Republic, *S. Mráz, J. Schneider*, RWTH Aachen University, Germany

Thin films of crystalline metal oxides are of high interest due to a wide range of functional properties. Because of different properties exhibited by individual phases, it is necessary to define pathways for preparation of desired phases. We study the growth of individual phases using atom-by-atom molecular dynamics (MD) simulations (>=3000 deposited atoms per simulation). We focus on the effect of intrinsic process parameters such as particle energy, ion fraction in the particle flux, growth temperature and growth template. We report a methodological progress: while most of the structures of various materials obtained (predicted) previously by classical MD are amorphous, we study the growth of multiple competing crystalline phases described by a single interaction potential. We identify which interaction potentials allow such simulations and which do not.

In the case of TiO_2, experiments indicate that the deposition of rutile requires higher temperatures and/or energies compared to anatase. However, MD simulations [1] allow us to disentangle crystal nucleation and crystal growth, and show that the growth of (previously nucleated) rutile can take place in a wider range of process parameters compared to anatase.

In the case of Al_2O_3, MD simulations [2] allow us to identify that an energy of 50-70 eV (at 300 K) or 30-40 eV (at 800 K) is ideal for the growth of (previously nucleated) alpha-Al_2O_3. We show that all atom impacts have to be considered separately, i.e. all arriving atoms have to have the correct energy (correct average energy per atom is insufficient).

In all cases, the crystal growth is supported (the amorphization is slowed down) if the crystal (column) is sufficiently wide compared to the thermal spike size. In such a case, the undamaged crystal cells support "healing" of the damaged neighboring cells.

Phenomena observed experimentally are in agreement with the MD results. Collectively, the results provide an insight into the complex relationships between process parameters and deposited film structures. Consequently, they allow one to tailor the synthesis pathways for the production of metal oxide thin films, considering conditions for nucleation and different conditions for growth.

Acknowledgment

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10:20am **B7-8 Lattice Ordering Effects on Toughness Enhancement in TiN and VN Thin Films Alloys**, *D. Edström, D. Sangiovanni*, ***V. Chirita*** *(vio@ifm.liu.se)*, *L. Hultman*, Linköping University, IFM, Thin Film Physics Division, Sweden

Enhanced toughness in hard and superhard thin films is a primary requirement for present day ceramic hard coatings, known to be prone to brittle failure during ***in-use*** conditions, in modern applications. In our previous Density Functional Theory (DFT) investigations, we predicted significant improvements in the hardness/ductility ratio of several pseudobinary B1 NaCl structure transition-metal nitride alloys, obtained by alloying TiN or VN with NbN, TaN, MoN and WN [1, 2]. The initial calculations, which were carried out on model, highly ordered configurations with Cu-Pt ordering on the cation sublattice, reveal that the electronic mechanism responsible for toughness enhancement stems from the high valence electron concentration (VEC) of these alloys, and ultimately allows a selective response to tetragonal and trigonal deformations.

Recently, these results have been validated experimentally. Single-crystal $V_{0.5}Mo_{0.5}N$/MgO(001) [3] and $V_{0.6}W_{0.4}N$/MgO(001) [4] alloys, were grown by dual-target reactive magnetron sputtering, together with VN/MgO(001) and TiN/MgO(001) reference samples. The $V_{0.5}Mo_{0.5}N$ films exhibit hardness >50% higher than that of VN, and, in contrast to nanoindented VN and TiN reference samples, which suffer from severe cracking, the $V_{0.5}Mo_{0.5}N$ films do not crack. No ordering on the cation sublattice is observed in the $V_{0.5}Mo_{0.5}N$ films, however, the onset of W ordering on adjacent {111} planes of the metal sublattice, is observed in $V_{0.6}W_{0.4}N$ alloys.

Here we present new DFT results, which address the issue of lattice ordering effects on the mechanical properties of these pseudobinary alloys. Our investigations concentrate on $V_{0.5}Mo_{0.5}N$, $V_{0.5}W_{0.5}N$, $Ti_{0.5}Mo_{0.5}N$ and $Ti_{0.5}W_{0.5}N$ alloys obtained by alloying TiN and VN with WN and MoN. Our calculations, carried out for structures with increasing levels of disorder, reveal that while the degree of electronic structure layering, i.e. the formation of alternating layers of high and low charge density upon shearing, becomes less pronounced in disordered configurations, the overall VEC effect is not affected. The essential feature in the disordered alloys, as initially predicted for highly ordered configurations, remains the increased occupancy of electronic d-t_{2g} metallic states, which allows the selective response to tensile/shearing stresses, and explains the enhanced toughness confirmed experimentally for $V_{0.5}Mo_{0.5}N$ films.

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10:40am **B7-9 A Computational Approach to Designing Boron Based Coatings**, ***H. Euchner*** *(holger.euchner@tuwien.ac.at)*, *J. Paulitsch, P.H. Mayrhofer*, Vienna University of Technology, Austria **INVITED**

Computational materials science has proven to be an extremely useful tool for developing high performance materials tailor made for specific applications. Recent studies show, that first principle calculations allow to reliably predict crystal structure, phase stability or elastic properties of ceramic-like hard coatings. However, while structure optimization and determination of elastic properties are nowadays rather standard calculations, hardness still remains a quantity that is difficult to access computationally. Here we present a detailed ab initio study on hardness and elastic properties of transition-metal (TM) diborides, which due to their intrinsically high hardness values are highly acknowledged for a wide range of industrial applications. Based on a semi-empirical approach, mainly using the concept of bond strength, the hardness values of several binary TM diborides, like TiB_2 or WB_2, as well as ternary TM diborides, e.g. $TiAlB_2$ and $WAlB_2$, were evaluated and compared with experimental data obtained by nanoindentation on sputter deposited coatings.

Our results may indicate possible pathways for further advances in the design of tailored functional materials, based on atomistic scale simulations.

11:20am **B7-11 Modeling the Thermo-Mechanical and Optical Properties of Solar Selective Coatings**, ***I. Heras*** *(irene.heras@research.abengoa.com)*, Abengoa, Spain

The design of solar selective coatings for photo-thermal conversion applications requires of a complex study of the coating materials layers and substrate. In particular, this type of coatings must have suitable optical properties (high solar absorptance in the solar spectrum and low thermal emittance in the infrared wavelength range) and should be stable at high temperatures and have good adhesion between layers as well.

To obtain the ideal configuration of the coatings deposited using physical vapor deposition approaches, both optical simulations and finite element analysis have been carried out.

The computer simulation program CODE has been used to calculate solar absorptance and thermal emittance of various multilayers coatings combinations. The optical properties of the heterogeneous composite material were simulated with a physical model proposed by Bruggeman which averages the dielectric function of the components of the composite. This allows the composite system to be treated as an effective medium.

To predict the mechanical behavior of the coating and prevent crack formation and delamination with cyclic thermal loads, residual stress generated after the deposition, a numerical model based on Finite Element solver has been employed.

This contribution compares simulated optical properties for different nanocomposite structural configurations. The calculated results are in the

range of 0.91-0.97 for solar absorptance and 0.02 - 0.07 for thermal emittance at high temperatures, with good thermo-mechanical compatibility of the materials.

Advanced Materials for Modern Device Applications
Room: Sunset - Session C2

Novel Aspects in Thin Film Characterization and Data Modeling

Moderator: J. Krueger, BAM Berlin, Germany, T. Hofmann, University of Nebraska–Lincoln

8:00am **C2-1 Spectroscopic Ellipsometry Characterization in the Photovoltaic Device Configuration**, ***N.J. Podraza*** *(nikolas.podraza@utoledo.edu)*, University of Toledo, US **INVITED**

Information on material characteristics such as chemical composition, order (crystal phase, grain size, or disorder), and sample structure (thin film thicknesses, interface formation, spatial non-uniformity, general morphology) are extracted from spectroscopic ellipsometry measurements of thin films in photovoltaic device configurations. Optical properties in the form of the complex dielectric function ($\varepsilon = \varepsilon_1 + i\varepsilon_2$) are extracted for semiconductor layers, transparent conducting oxides (TCOs), and metal contacts. Variations in *e* are compared with structure for amorphous and nanocrystalline hydrogenated silicon (Si:H), grain size and strain for cadmium telluride (CdTe), composition of copper indium gallium diselenide (CIGS), and electronic transport properties as reflected using Drude oscillator models for tin oxide and zinc oxide TCOs and molybdenum and silver metal contacts. All of these properties influence the behavior of the thin film in the device as well as the device's ultimate performance. In situ real time spectroscopic ellipsometry (RTSE) applied during thin film growth has been to track structural evolution in Si:H, compositional changes including phase segregation of copper selenide and CIGS, and interface filling on textured substrates used for amorphous and nanocrystalline Si:H and CdTe solar cells. In particular, growth evolution of complete Si:H devices (including the doped and undoped semiconductor layers, transparent conducting oxides, and metal back contacts) will be compared on specular and textured substrates. Ex situ mapping spectroscopic ellipsometry measurements are conducted for the same samples studied by RTSE to demonstrate that structural models developed by RTSE can be applied to assess spatial non-uniformity over large areas—in essence connecting fundamental material studies to manufacturing issues. The influence of layer structural characteristics (thicknesses) and intrinsic properties of each material are connected to device performance through mapping spectroscopic ellipsometry measurements collected over arrays of small area photovoltaic devices. Comparison of these mapping results enable a large amount of devices with slightly different properties, arising from spatial non-uniformity of each component layer, to be evaluated with only a few complete device fabrication processes. In this manner, principles guiding optimization of photovoltaic devices can be developed.

8:40am **C2-3 Broad Band Spectroscopic Ellipsometry Modelling of Metallic Structures using FDTD**, ***J.A. Zapien*** *(apjazs@cityu.edu.hk)*, *Y. Foo*, City University of Hong Kong, Hong Kong Special Administrative Region of China

Localized plasmon resonances (LPR) can be used to efficiently concentrate EM energy by several orders of magnitude. They can be tailored to enable single-molecule chemical detection arising from Surface Enhanced Raman Spectroscopy (SERS), alternatively they can be used to develop hybrid photonic/plasmonic nanostructures such as NW-based plasmonic lasers with small cross section area mode capable to bridge the size gap between electronic and optoelectronic devices. We will first present an overview of the current efforts to develop hybrid photonic/plasmonic devices for energy and sensing applications with special emphasis their optical modeling.

The optical characterization of such plasmonic devices is thus a current issue of scientific and technological interest. Spectroscopic ellipsometry (SE) is a mature thin film characterization technique that can provide quantitative information about thickness, surface roughness, and dielectric functions of thin films using regression analysis and a transfer matrix formalism using Fresnel coefficients. For periodic samples, such as 1D gratings, the use of numerical simulation techniques, such as rigorous coupled wave analysis, SE has been capable to provide exquisite subwavelength structural characterization which is widely used for critical dimension metrology in the semiconductor industry. However, and for a number of reasons that will be discussed in the presentation, it is desirable to develop additional numerical capabilities to assist in data interpretation of complex samples. We have recently demonstrated that Finite-Difference Time Domain (FDTD) can provide quantitative SE data analysis of thin films and non-planar samples with sensitivity approaching 1/2 monolayer in the case of an ideal dielectric film on c-Si substrate. In the second part of this presentation we will summarize our recent breakthroughs in the use of FDTD as a powerful tool capable to provide quantitative modeling of SE data for plasmonic structures.

9:00am **C2-4 Phase Stability and Intrinsic Growth Stresses in Ti/Nb Multilayered Thin Films**, ***L. Wan***, *X.X. Yu, G.B. Thompson (Gthompson@eng.ua.edu)*, The University of Alabama, US

Structural phase transformation in thin films has a significant influence on properties, including electrical conductivity, hardness, and optical appearance. This presentation will address the underlying driving forces that contribute structural transformations in these materials. Using an in-situ laser interferometer curvature measurement technique, the intrinsic growth stress evolution was monitored for a series of Ti/Nb multilayered films. Each multilayer had a different bilayer spacing but each individual layer thickness within the bilayer was equivalent. Upon the HCP Ti to BCC Ti transformation, the overall compressive stress, for a given thickness, increased. This resulted in a measurable change in the interfacial stress, with the Nb layer exhibiting a more compressive response as compared to the Ti layer. Electron microscopy and atom probe tomography characterized the films. Molecular dynamic simulations were used in conjunction with the experimental results to explain the phase transformation in relationship to interfacial stress and chemical intermixing.

9:20am **C2-5 Experimental and Simulation Studies of Compact Nitride Layers Growth During Plasma Nitriding of Pure Iron**, ***C. Jimenez***, *C. León, J. Oseguera (joseguer@itesm.mx), F. Castillo*, ITESM-CEM, Mexico

Different approaches have been developed concerning growth description of the compact nitride layers, especially those produced by ammonia. Nitriding by plasma uses a glow discharge technology to introduce nitrogen to the surface which in turn diffuses itself into the material. During this process, the ion bombardment causes sputtering of the specimen surface.

This paper presents a study of the kinetics of compound layer formation during plasma nitriding of pure iron. The study considers the erosion effect at the plasma-nitriding interface due to sputtering. Experimental data obtained by the authors as well as other sources are discussed. A mathematical model which simulates the process is introduced. The erosion effect is computer simulated and adjusted in order to consider its contribution to the study of layer growth kinetics. Finally, experimental and numerical results are compared in order to provide a better understanding of the process.

9:40am **C2-6 Metal-Dielectric Coatings and their Applications in Optical Instruments and Optical Microscopy - Optimizing Performance and New Developments**, ***H. Niederwald*** *(niederwald@zeiss.com)*, Carl-Zeiss Jena GmbH, Germany **INVITED**

Combined metal-dielectric coatings have their applications in optical instruments , optical and opto-electronic devices since many decades. There are broadband reflectors, neutral filters, line filters, beam splitters, phase retarders or absorbers, transparent conductors and induced transmittance filters - just to name some. Developments result from improvements in process control, new challenges as expectations for decrasing losses or growing precision demands but also in the effort to overcome the drawbacks of most metal based coatings , that is mainly the high sensitivity to environmental, chemical and mechanical hazards. This presentation will show examples of some developments for new applications or for higher value products. Elements like the choice of materials, process technology, the design and implementation involving very thin layers (nanofilms) or the gain in performance and environmental stability will be discussed. Particularly considered will be coating imperfections, which play a major role in the long term stability of metal-dielectric coatings.

Applications, Manufacturing, and Equipment
Room: Tiki - Session G6

Advances in Industrial PVD & CVD Deposition Equipment

Moderator: M. Schuisky, Sandvik Coromant, K. Bobzin, RWTH Aachen University, Germany

8:00am **G6-1 Comparison of Plasma Characteristics of DC and Pulsed Arc Evaporation**, ***T. Takahashi*** *(takahashi@kcs-europe.de), R. Cremer,* KCS Europe GmbH, Germany, *S. Hirota*, Kobe Steel Ltd., Japan

Among several types of PVD techniques, cathodic arc deposition, also referred to as arc ion plating, and magnetron sputter deposition are widely used in industry, especially for hard and tribological coating applications. The plasma properties of above technologies are linked to the coating properties and hence better understanding thereof is of great practical importance. It is however often the case that the resulting coating properties are dependent on a coating unit employed rather than basic experimental parameters. This dependency of coating unit appears be more pronounced in industrial equipments compared to small scale laboratory ones. This gives rise to a difficulty in comparing intrinsic plasma and/or coating properties.

Our goal is to correlate the fundamental plasma characteristics of each PVD technique to the coating properties for better process optimization and further development. Different types of PVD methods of pulsed cathodic arc, conventional dc cathodic arc, HIPIMS, and dc magnetron sputtering, respectively, are operated in a single industrial coating unit. The plasma characteristics thereof are studied using optical emission spectroscopy, and compared to each other under process conditions of typical transition metal nitride coatings such as TiAlN and CrN. The spectrum intensity ratio of metal ions to neutrals is used as an indicator of the degree of metal ionization. In cathodic arc deposition OES intensities associated with metal ions are clearly detected while in the case of dc magnetron sputtering metal ions are hardly seen. The degree of metal ionization in HIPIMS is variable. It is found to be increased as the peak power is increased, providing a wide range of plasma properties ranging from less ionized plasma like dc magnetron sputtering up to highly ionized plasma like cathodic arc. In analogy to the principle of HIPIMS, pulsed cathodic arc enables to deliver a higher arc current in a pulse form while the time-averaged arc current on the target is kept comparable to a conventional dc cathodic arc. The influence of pulse parameters on the plasma characteristics is systematically analyzed and compared to those of conventional dc cathodic arc. A correlation of the OES results to the basic properties of coatings deposited is also discussed.

8:20am **G6-2 Hybrid Coatings in Arc Systems: HI3 Process (HIPAC plus arc), Types of Nitriding Processes and DLC**, ***J. Vetter*** *(joerg.vetter@sulzer.com), J. Crummenauer, J. Mueller, O. Jarry*, Sulzer Metaplas GmbH, Germany

Advanced coating devices have to provide at least high productivity and flexibility, should be modular designed and render latest high performance coating solutions. The factors to success are innovative technologies and processes on one platform as well as most advanced coatings; one platform many choices, various opportunities and many solutions. Latest approaches to a new industrial PVD coating system resulted in a symbiosis of form and function to meet all these requirements by implementation of different hyprid processes. Three different hybrid processes will be described.

Arc + HIPAC

A new class of advanced PVD-coaters, the METAPLAS.DOMINO series , for dedicated coating applications comprise both improved vacuum arc evaporators (APA, Advanced Plasma Assisted) and high power impulse magnetron sputtering (HIPIMS) sources (HIPAC - High Ionized Plasma Assisted Coating). The ion cleaning is based on the (AEGD, Arc Enhanced Glow Discharge) process. This combination of the three highly ionized processes is named HI3 (High Ionization Triple). It's possible to run the processes in different modes, e.g. pure APA arc evaporation or pure HIPAC magnetron sputtering. However the combination of the two high ionized deposition processes to generate multilayer, nanomultilayers and nanocomposite layers opens new horizons in tailoring of coating architectures.

Nitriding before coating

Nitriding processes are used to improve the mechanical properties of substrates before the deposition of hard coatings. Three different nitriding methods are possible to carry out in PVD arc systems: traditional glow discharges at gas pressures in the range of several mbar, AEGD nitriding and LPAN (Low Pressure Anodic Nitriding).

DLC coatings

DLC coatings are of special interest for low friction coatings. Solutions to deposit various types of hydrogenated (a-C:H:Me, a-C:H:X) and hydrogen free DLC coatings (a-C, ta-C) in addition to the classical arc coatings are discussed.

Selected coating solutions from latest approaches to hybrid will be presented to underline the leading edge technology.

8:40am **G6-3 Recent Developments in ALD Equipment and Processes**, ***M. Ritala*** *(mikko.ritala@helsinki.fi)*, University of Helsinki, Finland **INVITED**

Atomic layer deposition is a unique method for highly controlled thin film deposition. ALD is based on saturative surface reactions between alternately dosed gaseous precursors. The film growth is self-limiting, thereby ensuring a number of advantageous characteristics, such as excellent conformality, large area uniformity, accurate and simple thickness and composition control, and reproducibility.

While ALD is currently in use already widely especially in semiconductor industry but also elsewhere, its still wider adoption has been limited by cost issues. In particular the throughput of ALD is modest as coatings are build up in a (sub)monolayer-by-(sub)monolayer manner. Expensive precursor chemicals are also sometimes needed. Another limiting factor has been the lack of proper ALD processes and precursors for many materials of an interest. During the past years substantial progress has been made, however, both in ALD equipment and chemistry. Batch tools are effective in increasing the throughput while spatial-ALD has developed rapidly as an alternative for high throughput ALD, though with limited selection of materials.

This presentation makes a survey of basic features of ALD equipment that are currently commercially available and under development. Also ALD processes will be discussed as the chemistry and precursors are strongly influencing the equipment design.

9:20am **G6-5 Integration of HiPIMS Equipment into an Industrial Coating Production for Cutting Tools**, *T. Leyendecker (christoph.schiffers@cemecon.de), O. Lemmer, W. Koelker,* ***C. Schiffers***, CemeCon AG, Germany

HiPIMS coatings are rapidly gaining ground for cutting tool applications due to advantages such as smooth, droplet free coatings with superb adhesion and perfect homogeneity all around the tool geometry. Hence, more and more cutting tool producers are in the process of integrating HiPIMS coating machines into their production.

This paper will discuss the full process chain of an industrial coating production – starting with jigging, surface and cutting edge preparing, cleaning, coating and finishing operation – with regard to the specific needs of the HiPIMS process. Advances of the HiPIMS deposition equipment will be presented as well as specific modifications of the auxiliary processes prior and after coating.

A novel AlTiSiN film deposited with HiPIMS will be presented as a model system for all the steps of a commercial coating production including a film characterisation and recent cutting test results.

9:40am **G6-6 Replacement of Electroplating Produced in a Flexible Inline Production Platform**, *D. Driesenaar (dDriesenaar@hauzer.nl),* ***J. Landsbergen***, *I. Kolev, J. Clabbers, R. Tietema, T. Krug*, IHI Hauzer Techno Coating BV, Netherlands

Nowadays plastics are a popular substrate choice for many products, sometimes because of their low weight, for example in the automotive industry, but also because of costs considerations or material characteristics such as lack of corrosion. In many cases, for aesthetic reasons, the plastics are made to look like metals. Chrome plating has long been seen as the only solution for decorative coatings on plastics, to ensure hardness and a bright color. In the meantime several processes have been developed involving lacquer and PVD coatings, sometimes with a lacquer top coat, sometimes without.

But whatever process will be chosen, mass production is a necessity in the production process, ensuring the costs will be kept to a minimum and the coating will be uniform and reproducible. In this presentation we will show the characteristics of a flexible, inline production platform needed for mass production of PVD coatings on decorative products. We will show how the platform can be integrated in a fully automated lacquer plant of different sizes. We will elaborate on the modular design, rack return, linear motion systems and the possibilities to shorten cycle times.

10:00am **G6-7 Mechanical and Tribological Property of Titanium Series Thick Coating Deposited by our Kobelco new PVD Machine, AIP-G60R**, ***S. Tanifuji*** *(fujii.hirofumi@kobelco.com), H. Fujii, H. Nomura*, Kobe Steel Ltd., Japan

Dry coating techniques such as PVD(Physical Vapor Deposition) or CVD(Chemical Vapor Deposition) is widely used in various fields. In industrial applications, in particular, these coating technology are used for applying to the surface of new features and characteristics different from the material properties of the substrate, so it make it possible to allow a high efficiency of production in the field and extend the life of the base material such as cutting tools, it has contributed significantly to the reduction of running cost in the each industrial fields.

AIP(Arc Ion Plating) is known such as a kind of PVD technique, and during the deposition, a vacuum arc discharge is used, then target materials are evaporated and ionized by using the Joule heat of the vacuum arc discharge, and it are deposited on the substrate surface that is applied to the negative bias. Coating film formed by AIP technique is high dense and high hardness, so it is widely used as a mass production technology of hard wear resistant coating around the cutting tool field in the 1990s.

Recently, needs of high-value-added and high-performance of the product is increasing, AIP technology is expanding automotive field, also aircraft field as well as the cutting tool field. On the other hand, new coating equipment, arc evaporation sources, or coating process have been developed to address the needs that have been advanced and diversified, resulting in the spread of technology has been accelerating.

So far, KOBELCO has commercialized batch coating equipment with AIP technology in 1986, and coating equipment, coating process and hard wear resistant coating for several industrial application also have been developing.

In this report, KOBELCO new PVD equipment "G60R" is going to be introduced, then mechanical and tribological properties of metal nitride coating deposited by G60R with new AIP cathode are going to be reported.

Topical Symposia
Room: California - Session TS6

Atmospheric Plasma Applications
Moderator: H. Barankova, Uppsala University, D. Dowling, University College Dublin

8:00am **TS6-1 Superhydrophobic Coating Deposition with Atmospheric rf Plasma**, ***S. Kim*** *(shkim@engr.psu.edu), D. Marchand*, Pennsylvania State University, US **INVITED**

Superhydrophobicity has recently drawn a great deal of attention for both fundamental understandings and practical applications due to its potential applications in various technologies and consumer products such as weather-resistant or self-cleaning fabrics, windshields, display panels, microfluidic devices, etc. Superhydrophobicity requires both right surface chemistry (mostly hydrophobic) and proper surface roughness. In previous plasma-based superhydrophobic coatings, fluoro-hydrocarbons were often used as a process gas to deposit fluorinated coatings on textured surfaces. Recently, the direct superhydrophobic coating with atmospheric rf plasma on flat surfaces without pre-texturing was demonstrated. But, it still used fluoro-hydrocarbon which generates environmental hazard issues. This talk will discuss the direct deposition of hydrocarbon coatings with a static water contact angle higher than 150o using non-fluorinated precursor gases in helium plasma generated in ambient air without any pre-roughening of the silicon (100) substrate. Two types of precursor gases were investigated – pure hydrocarbons and organic-inorganic hybrids. Since the plasma is generated in air, all films show some degree of oxygen incorporation. These results imply that the incorporation of a small amount of oxygenated species in hydrocarbon films due to excitation of ambient air is not detrimental for superhydrophobicity, which allows the atmospheric rf plasma with the non-fluorinated precursor to produce rough surface topography needed for superhydrophobicity.

8:40am **TS6-3 Atmospheric Plasma Deposition of Thin Films for Aerospace Applications**, ***A.N. Ranade*** *(alpana.n.ranade@boeing.com)*, The Boeing Company, U.S.

Polymeric materials are usually less expensive and more convenient to manufacture than alternative materials. In addition, the lightweight nature of these materials makes them desirable for aerospace applications, where weight is a crucial factor. However, polymeric surfaces are susceptible to abrasion and erosion damage, resulting in increased haze and decreased clarity for transparent parts. For example, when materials such as polycarbonate or stretched acrylic are used in windows, windshields, and canopies, one of the drawbacks is the tendency to scratch and craze. Polymeric windows have been historically coated with polysiloxane or polyurethane based coatings to overcome this limitation by improving the surface resistance to scratches. Improvements to the coating processes can decrease manufacturing times, improve durability, and can offer long-term solutions in which additional functionalities can be incorporated.

Advanced thin films created using Atmospheric Pressure Plasma-Enhanced Chemical Vapor Deposition (AP-PECVD) can improve the durability or functionality of many components on aircraft. These technologies can be exploited to generate materials with high performance which are also environmentally friendly and produced with solvent-free processes. At Boeing, some areas of AP-PECVD research include transparent durable films for protection of polymeric substrates such as passenger windows and military canopies, adherent films for carbon fiber reinforced polymers (CFRPs), multilayer films with tailored conductivity and durability, and oxygen barrier films for CFRP substrates to prevent degradation of the polymer at high temperatures. In addition, multiple materials are under investigation in order to create films with specific electrical, thermal, or optical properties in order to meet certain requirements such as static dissipation or hydrophobicity.

9:00am **TS6-4 Atmospheric Pressure Plasma Polymerization on PE to Increase Bone Cement Adhesion**, ***P. Cools*** *(pieter.cools@ugent.be), N. De Geyter, S. Van Vrekhem*, Ghent University, Belgium, *A. Van Tongel*, Ghent University Hospital, Belgium, *P. Dubruel*, Ghent University, Belgium, *F. Barberis*, Universita' degli Studi di Genova, Italy, *R. Morent*, Ghent University, Belgium

Surface modification of polymers for biomedical applications is a thoroughly studied area. The goal of this paper is to show the use of atmospheric pressure plasma technology as a useful addition as a pre-treatment for polyethylene (PE) shoulder implants. Atmospheric pressure plasma polymerization of methyl methacrylate (MMA) will be performed on PE samples to increase the adhesion between the polymer and a PMMA bone cement. For the plasma polymerization, a dielectric barrier discharge (DBD) is used, operating in a helium atmosphere at ambient pressure. Parameters such as treatment time, monomer gas flow and discharge power are varied one at a time. Chemical and physical changes at the sample surface are studied making use of X-ray photon spectroscopy (XPS) and atomic force microscopy (AFM) measurements. Coating thicknesses are determined by making use of optical reflectance spectroscopy. After characterisation, the coated samples are incubated into a phosphate buffer solution (PBS) for a minimum of one week at 37°C, allowing to test the coating stability, when exposed to implant conditions. These simulations are done both for healthy and infected tissue. The results show that PMMA coatings can be deposited with a high degree of control concerning chemical composition and layer thickness. In a final stage, adhesion of the plasma coated samples to bone cement is tested through a pull-out test. All samples are cut to standard dimensions and immersed in bone cement in a reproducible way with a sample holder specially designed for this purpose. The results prove indirectly that the plasma modifications lead to a more reliable implant material, with a longer implant life-time.

9:20am **TS6-5 Disinfection, Decontamination, and Nano-particle Production using a Pulsed Submerged Arc**, *N. Parkansky (naump@eng.tau.ac.il)*, ***R.L. Boxman***, Tel Aviv University, Israel **INVITED**

Pulsed submerged arc (SA) treatment generates plasma within a vapor bubble submerged within a liquid. Most previous investigations of SA treatment used high voltage (~kV's) and very high currents, e.g. kA's. In contrast, we report on a low voltage technique, which is easier and less expensive to use. It was obtained that low energy repetitively pulsed submerged arcs are effective and efficient in inactivating E. coli bacteria, breaking down Sulfadimathoxine (SDM) antibiotic and Methylene Blue (MB) dye, and producing various nanoparticles (NPs).

Water was treated with a SA using C, Fe, Ti, and Cu electrodes, and their combinations, both without and with the addition of (0.01-0.5%) H_2O_2. It was found that MB was decomposed both during and after arc treatment. The treated solutions were examined by Raman and absorption spectroscopy. Particles produced during the arc treatment were studied by SEM, XPS and XRD.

It was found that the particles eroded from electrodes defined the character of removal and the level of the removal ratio after SA treatment. With C/C electrodes, the MB concentration exponentially decreased for the duration of the experiment, while with the other electrodes the MB concentration saturated. The saturation is explained by a decrease of the oxidative species concentration with SA treatment time for these electrodes. The aging of the SA treated solutions in the presence of H_2O_2 with all combinations of electrodes removed ~99 % of the MB contaminant. The effect of aging may be associated with accumulation of oxidative species, particularly

peroxides, on the surface of eroded particles which gradually oxidized MB. A high MB removal yield of $G_{99.6}$=90 g/kWhr was obtained using SA water treatment with Ti electrodes and 0.5% H_2O_2 addition.

Two SA modes were used to produced micro- and nano-particles: contact mode – in which the electrodes periodically contacted and separated; and breakdown mode – in which high voltage pulses broke down the inter-electrode gap maintained at a constant separation. Different metal, metal oxides, and metal carbides were produced as nano-particles. W-C alloy wastes were crushed and recycling as WC powder. Super-paramagnetic carbon nano-particles with critical temperature > 300 K were synthesized. Ni-C particles coated with a layer of carbon were also produced. These particles had a C-concentration in the Ni alloy ~3× greater than the maximum solid equilibrium solubility. These particles were almost insoluble in acids and had super-paramagnetic properties in a wide temperature interval $T>T_B$=8 K. The material had a very narrow hysteresis loop, i.e. H_c<8 Oe (i.e. it is a soft magnet) in the super-paramagnetic state.

10:00am **TS6-7 Plasma Reforming of Ethanol**, *H. Barankova (hana.barankova@angstrom.uu.se)*, ***L. Bardos***, Uppsala University, Sweden

The plasma source with a coaxial geometry was used for generation of plasma inside water and the ethanol-water mixtures. Atomic hydrogen and OH groups were observed by OES, indicating the hydrogen forming reactions. The hydrogen detector placed at the outlet from the hermetic reactor measures the hydrogen content up to 60% in the outlet gas flow. Various regimes of plasma generation were examined. The effects of the mixture composition and of the power delivered to the discharge on the hydrogen production and the reaction kinetics are investigated. An important role of the plasma source design is discussed.

10:20am **TS6-8 Growth of Multifunctional Nanocomposite Thin Films on Wood Substrates using Dielectric Barrier Discharges at Atmospheric-pressure**, *J. Profili,* LAPLACE and U. Montréal, Canada, *O. Levasseur*, ***L. Stafford*** *(luc.stafford@umontreal.ca),* Université de Montréal, Canada, *N. Gherardi*, CNRS-LAPLACE, Canada

We have recently extended the range of applications of cold, dielectric barrier discharges (DBD) at atmospheric pressure to the modification of wood surfaces with the objective of improving its durability following natural weathering. In the first set of experiments, wood samples were placed on the bottom electrode of a plane-to-plane DBD and the plasma was sustained in presence of hexamethyldisiloxane (HMDSO) with either He or N2 as the carrier gas. In both cases, water-repellent wood surfaces were achieved with water contact angles (WCA) in the 140 degrees range. Based on FTIR analysis, such feature was ascribed to the deposition of a homogeneous coating with hydrophobic organosilicon compounds. For relatively thick coatings (about 200 nm for a treatment of 4 minutes), WCA following natural aging under uncontrolled conditions remain constant for a minimum period of 8 months, which indicates a very good stability of the plasma-deposited layers. In order to achieve multifunctional properties, a new challenge is the plasma-assisted deposition of nanocomposite coatings. This contribution is focused on the growth on freshly-sanded wood samples of nanocomposites based on TiO_2 nanoparticles embedded in a silica-like matrix with the objective of synthesizing barrier layers with improved resistance to UV irradiation. Experiments were carried out with either N_2 or He as the carrier gas, a mixture of hexamethyldisiloxane, and either nitrous oxide (for experiments in N_2) or O_2 (for experiments in He) for the growth of the SiO_2 matrix, and TiO_2 nanoparticles which are introduced by nebulizing stable colloidal solutions. Preliminary results show that TiO_2 nanoparticles can successfully be incorporated in the film. In addition, as in low-pressure plasma conditions, electrostatic forces were found to play a very important role on the transport of nanoparticles in the discharge. As a result, an appropriate tuning of the applied voltage waveform (shape, amplitude and frequency) was found to directly impact the spatial distribution of nanoparticles in the film.

10:40am **TS6-9 Removal of Organic and Inorganic Coatings using Atmospheric Pressure Air Plasma**, ***P. Yancey*** *(peter.yancey@aplasmasolution.com),* Atmospheric Plasma Solutions, Inc., US **INVITED**

The removal of paint and other organic coatings from metal and composite surfaces represents a substantial cost burden and source of environmental concern across many industries. Most coating removal methods produce large quantities of potentially hazardous waste that must then be disposed of properly. An alternative, media free, coating removal process is needed to reduce the generation of these waste materials. A 2kW plasma torch operating at atmospheric pressure using compressed air as a working gas has been developed to safely remove such organic coatings. The atmospheric plasma coating removal (APCR) process uses the oxygen and nitrogen in air to produce activated chemical species which oxidize the organics in the coatings. The activated chemical species in the plasma plume convert much of the organic coating matrix into water vapor and carbon dioxide leaving behind only a fraction of the original mass of coating. No additional media, other than air, is used to perform the coating removal process. After APCR there is typically no need for any secondary cleaning before coating reapplication can begin.

Alternatively, the plasma torch can operate with other gas mixtures in order to change the chemistry of the plasma plume. When operated using hydrogen rich gas mixtures, a chemically-reducing plasma can be produced. The reducing plasma has been used to remove inorganic oxides from certain metal surfaces.

It will be shown that an APCR process can be used to effectively remove both organic and selected inorganic coatings from a wide range of metal and composite substrates.

11:20am **TS6-11 Facile Synthesis of Pt-Pd Bimetallic Nanoparticles by Plasma Discharge in Liquid and their Electrocatalytic Activity Toward Methanol Oxidation in Alkaline Media**, *S.-M. Kim, A.-R. Cho,* Korea Aerospace University, Korea, *J.W. Kim,* University of InCheon, Republic of Korea, ***S.-Y. Lee*** *(sylee@kau.ac.kr),* Korea Aerospace University, Korea

Plasma discharging in water, so-called solution plasma process (SPP), has been recently paid much attention for nanoparticles synthesis. SPP is faster (microseconds), simpler (one-step method) and more cost-effective (only requiring an ion source) than traditional colloid methods and SPP has been employed for the synthesis of various nanoparticles for many applications including biomedical, heat exchanger for improved efficiency, catalysts, etc.

In this approach, various electrocatalysts such as Pt and heterogeneous Pt/M (M=Ag, Pd, Ni, Cu) were successfully synthesized using SPP, in an attempt to enhance fuel cell efficiency with reduction of Pt amount. Nano-porous (or mesoporous) and dendritic Pt electrocatalysts showed better electrocatalytic performace than ultra-fine Pt because interconnected structures potentially could not only have high surface area, but also supply enough absorption sites for all absorbed molecules involved over a close range. In methanol environment, the Pt/Ag bimetallic electrocatalyst exhibited enhanced activity and much improved stability toward CO with respect to pure Pt. This could be attributed to the electronic interaction between individual components of bimetal catalysts and the geometric change (particle shape and dispersion state). In addition, various processing variable in SPP and their effects on electrochemical activities of Pt/M (M=Ag, Pd, Ni, Cu) bimetallic electrocatalysts will be presented in detail.

Acknowledgement

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11:40am **TS6-12 An Atmospheric Pressure Inductively Coupled Plasma (AP-ICP) Torch for Anti-corrosive Silicon Carbide Coating of the Consumables for a 450 mm Wafer Etching Equipment**, ***Y. Glukhoy*** *(glukhoy1@aol.com), A. Ryaboy, T. Kerzhner*, Nanocoating Plasma Systems, Inc., US

This technology and device with an atmospheric pressure inductively coupled plasma (AP-ICP) torch will replace a traditional thin film CVD technology used for anti-corrosive silicon carbide coating of the consumables for a 450 mm wafer processing equipment especially for gas distribution plates called “showerheads”. The showerhead distributes the etching gas through several thousand small holes into a process plasma .Being converted into etching plasma with the reactive radicals and ions such gas impacts the wafer surface. Drawback of the plasma etching technology is corrosion of the showerhead and its short lifetime. So a process side faced to the wafer as well as the gas holes should be protected from a plasma chemical corrosion. Such 3D protecting surface coating with a controlled sheet resistance provides also uniform distribution of the RF power on the process side of the showerhead. Due such control the originally non-uniform RF power should be deposited uniformly into the process plasma. Therefore, a monolithic SiC coating allows a total replacement of the expensive silicon monocrystal as material for showerheads by the much cost-effective graphite material. Precursors for such deposition are silane and methane injected in the different area of the torch. The AP-ICP torch is designed with three temperature zones distributed along axis of the reactor that provide a thermal decomposition of silane, plasma chemical reaction between the radicals of silane and methane and maintain a focused vapor flow of the product directed into the holes. Therefore , a mechanism of a gas focusing with a crossover commeasured with a size of hole is a key element of such technology. The AP-ICP SiC chemical deposition can be provides for the large showerheads used for a 450 mm wafer technology without requirement for high vacuum chambers or enclosures, which usually restrict their size as well as a commercial viability. In Phase I we will test such deposition and develop technology using our prototype with the AP-ICP torch and the RF, gas distributing and

process monitoring equipment. Taken together, these activities will add new insights on reaction mechanism and guide strategies for future development of the production lines for a corrosion protection of the large area 3D objects.

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