Technical Sessions
Key to Session/Paper Numbers

UNASSIGNED Unassigned Topic

A Coatings for Use at High Temperature

B Hard Coatings and Vapor Deposition Technology

C Fundamentals and Technology of Multifunctional Thin Films: Towards Optoelectronic Device Applications

D Coatings for Biomedical and Healthcare Applications

E Tribology & Mechanical Behavior of Coatings and Engineered Surfaces

Ex Exhibition

F New Horizons in Coatings and Thin Films

G Applications, Manufacturing, and Equipment

PD Post Deadline Discoveries and Innovations

PL Plenary Talk

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 a.m. except for Monday where the sessions begin at 10:00 a.m. following the 8:00 a.m. Plenary Session
- Monday and Thursday afternoon sessions start at 1:30 p.m. Tuesday and Wednesday afternoon sessions begin at 2:10 p.m. All lunch breaks start at 12:00 p.m.
- 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 will be 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 p.m.and also Monday – Thursday 8:00 a.m–5:30 p.m.

If you are making a poster presentation:

Boards will be available for posting materials at approximately noon on Thursday, May 2. Prior to entering the Grand Hall, those presenting a poster will check in at a table located in the 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 number, title, and presenting author will aid each presenter in locating the correct board where your poster is to be displayed. The board which is provided is approximately four feet by four feet. All poster materials MUST be posted by 4:50 p.m. All presenters are required to be at their presentation during the entire session; this is in order 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 p.m. Thursday evening.

Plenary Lecture
8:00-9:45
Room: Town & Country

8:00 am

Plenary Lecture Session

8:20 am

Professor
Tobin Marks

Professor of Chemistry and Materials Science and Engineering
Northwestern University

8:40 am

"Designer Materials for Unconventional Electronics"

9:00 am

Please see full abstract on the
Plenary Session Page

9:20 am

8:00-9:45 a.m.
Town and Country

9:40 am

Monday Morning, April 29, 2013

	Coatings for Use at High Temperature Room: San Diego - Session A1-1 Coatings to Resist High Temperature Oxidation, Corrosion and Fouling Moderators: L.G. Johansson, Chalmers University of Technology, Sweden, F. Perez Trujillo, Universidad Compultense de Madrid, Spain, M. Weaver, University of Alabama, US	Hard Coatings and Vapor Deposition Technology Room: Royal Palm 4-6 - Session B1-1 PVD Coatings and Technologies Moderators: J.H. Huang, Department of Engineering and System Science National Tsing Hua University, Taiwan, S. Weiβmantel, University of Applied Sciences Mittweida, Germany
10:00 am	A1-1-1 Invited Oxidation and Coatings for High Temperature Mo-Si-B Alloys, J. PEREPEZKO, University of Wisconsin-Madison, US, R. SAKIDJA, The University of Alabama, US	B1-1-1 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-Institut für Werkstoff- und Strahltechnik, IWS Dresden, Germany
10:20 am	Invited talk continued.	Invited talk continued.
10:40 am	A1-1-3 Oxidation Performance Evaluation of Niobium Silicide Coatings for Aeronautical Gas Turbines, S. MATHIEU, L. PORTEBOIS, M. VILASI, Universite de Lorraine, France	B1-1-3 Hard DLC Coatings Developed by Using HIPIMS Technology, H. GERDES, R. BANDORF, M. EBERT, M. PETERSEN, G. BRÄUER, Fraunhofer Institute for Surface Engineering and Thin Films IST, Germany
11:00 am	A1-1-4 Effect of Water Vapor on Thermally-Grown Alumina Scales on Pt-Modified and Simple Aluminide Bond Coatings, M.J. LANCE, K.A. UNOCIC, J.A. HAYNES, B.A. PINT, Oak Ridge National Laboratory, US	B1-1-4 Tribological Properties of Tetrahedral amorphous Carbon layers on HSS- steel Drillers, K. GUENTHER, S. SCHOLZE, S. WEIBMANTEL, University of Applied Sciences Mittweida, Germany
11:20 am	A1-1-5 Invited NiAl-Based Metallic Coatings for Advanced Single Crystal Superalloys, H.B. GUO, Beihang University, China	B1-1-5 Preparation of Sharp Cutting Edges by Coating Processes in Nanostructured AlCrN Based Films, F. KAULFUSS, O. ZIMMER, Fraunhofer IWS, Germany
11:40 am	Invited talk continued.	B1-1-6 Pulsed Laser Deposition of Fe-SiC Multilayers for Spintronic Applications, M. KUMAR, R. CHANDRA, Indian Institute of Technology Roorkee, India, R. MISHRA, R. TIWARI, A. SAXENA, Division, Defence Materials & Stores Research & Development Establishment (DMSRDE) Kanpur, India
12:00 pm		
12:20 pm	**CSM Instruments: Focused Topic Session** **"High Temperature Nanoindentation Testing and Other Latest Developments at CSM Instruments"** **12:15-1:15 p.m.** **California Room**	

Monday Morning, April 29, 2013

	Hard Coatings and Vapor Deposition Technology Room: Royal Palm 1-3 - Session B5-1 Hard and Multifunctional Nanostructured Coatings Moderators: J. Paulitsch, Vienna University of Technology, Austria, J. Houska, University of West Bohemia – NTIS, Czech Republic	Fundamentals and Technology of Multifunctional Thin Films: Towards Optoelectronic Device Applications Room: Sunset - Session C1-1 Recent Advances in Optical Thin Films Moderator: J.H. Hsieh, Ming Chi University of Technology, Taiwan
10:00 am	B5-1-1 Invited Complexity in Characterization of Self Organized Structures in Nitride Nanocomposites, N. GHAFOOR, M. ODÉN, Linköping University, Sweden	C1-1-1 Invited Recent Progress in Plasmonics Applied to Optoelectronic Devices, K. OKAMOTO, Kyushu University, Japan
10:20 am	Invited talk continued.	Invited talk continued.
10:40 am	B5-1-3 High Speed Machining of Hardened Steel Using AIP Deposited Nano-multilayer Coating, K. YAMAMOTO, Kobe Steel Ltd., Japan, G. FOX-RABONOVICH, McMaster University, Canada, B BEAKE, Micro Materials Ltd., UK	C1-1-3 Influence of Sputtering Pressure on the Structural, Optical and Hydrophobic Properties of Sputtered Deposited HfO_2 Coatings, V. DAVE, H. GUPTA, R. CHANDRA, Indian Institute of Technology Roorkee, India
11:00 am	B5-1-4 Understanding the Structure of Metastable Multicomponent Nitride Thin Films by First Principles Calculations - Possibilities and Limitations, B. ALLING, Thin Film Physics Division, IFM, Linköping University, Sweden, I. ABRIKOSOV, Theoretical Physics Division, IFM, Linköping University, Sweden, L. HULTMAN, Thin Film Physics Division, IFM, Linköping University, Sweden	C1-1-4 Influence of the Parameters the Fabrication in Optical Properties of $Bi_xTi_yO_z$ Thin Films, J. ALFONSO, J. OLAYA, M. PINZON, National University of Colombia, Colombia
11:20 am	B5-1-5 High Temperature Wear Resistance of TiCrAlCN/TiAlN Multilayer PVD Coatings on M2 High Speed Steel, I. EFEOGLU, E. DEMIRCI, Atatürk University, Turkey, O. BARAN, Erzincan University, Turkey, Y. TOTIK, Atatürk University, Turkey	
11:40 am	B5-1-6 Wear Characteristics of Nitrogen-doped Al-Ti-Ni Nanocomposite Coatings Deposited on Austenitic Stainless Steel, J. LAWAL, M. AUDRONIS, A. MATTHEWS, A. LEYLAND, University of Sheffield, UK	
12:00 pm		
12:20 pm	**CSM Instruments: Focused Topic Session** **"High Temperature Nanoindentation Testing and Other Latest Developments at CSM Instruments"** **12:15-1:15 p.m.** **California Room**	

Monday Morning, April 29, 2013

	Coatings for Biomedical and Healthcare Applications Room: Sunrise - Session D2-1 Coatings for Bio-corrosion, Tribo-corrosion, and Bio-tribology Moderators: M. Stack, University of Strathclyde, UK, M. Mathew, Rush University Medical Center, US, J. Geringer, École Nationale Superieure des Mines, France	Tribology & Mechanical Behavior of Coatings and Engineered Surfaces Room: Golden West - Session E2-1 Mechanical Properties and Adhesion Moderators: M.T. Lin, National Chung Hsing University, Taiwan, R. Chromik, McGill University, Canada D. Bahr, Washington State University, US
10:00 am	D2-1-1 Why Does Titanium Alloy Wear Cobalt Chrome Alloy Despite Lower Bulk Hardness: a Nanoindentation Study?, S BULL, Newcastle University, UK, O. SAYGINER, Newcastle University, UK, Turkey, N. MOHARRAMI, Newcastle University, UK	E2-1-1 Time Resolved Synchrotron X-ray Strain Measurement in Biaxially Loaded Au Thin Films, D. FAURIE, LSPM-CNRS, Université Paris 13, Sorbonne Paris-Cité, France, P.O. RENAULT, Institut P' - Universite de Poitiers, France, G. GEANDIER, Institut Jean Lamour, France, E. LE BOURHIS, Institut P' - Universite de Poitiers, France, C. MOCUTA, D. THIAUDIÈRE, Soleil Synchrotron, France
10:20 am	D2-1-2 Invited Metal - Metal Oxide Thin Film-Biological Interfaces and the Role of Bio-mechano-electro-chemical Processes, J.L. GILBERT, V. SWAMINATHAN, M. HAERI, S. MALI, Syracuse University, US	E2-1-2 Grain Growth in Nanocrystalline Copper During Indentation at Very Low Temperatures, C.C. BATTAILE, B.L. BOYCE, S.M. FOILES, K.M. HATTAR, Sandia National Laboratories, US, E.A. HOLM, Carnegie Mellon University, US, E.R. HOMER, Brigham Young University, US, H. PADILLA, G.J. TUCKER, Sandia National Laboratories, US
10:40 am	Invited talk continued.	E2-1-3 Invited Inhomogeneous Stresses, Texture Transformations and Anomalous Grain Growth in Thin Metal Films, S. BAKER, Cornell University, US
11:00 am	D2-1-4 Dominant Role of Molybdenum in the Electrochemical Deposition of Biological Macromolecules on Metallic Surfaces, E. MARTIN, Northwestern University, US, R. POURZAL, M. MATHEW, Rush University Medical Center, US, K. SHULL, Northwestern University, US	Invited talk continued.
11:20 am	D2-1-5 Engineering Nanostructured Cubic Zirconia Coating for Enhanced Biointegration of Orthopaedic Implants, F. NAMAVAR, University of Nebraska Medical Center, US, R. SABIRIANOV, University of Nebraska at Omaha, US, A. RUBENSTEIN, R. MIRALAMI, G.M. THIELE, J.G. SHARP, K.L. GARVIN, University of Nebraska Medical Center, US	E2-1-5 Microstructure and Mechanical Properties of Nanodiamond Enhanced Diamond-like Carbon Thin Films on Ti Alloys, C. ZHANG, H. NIAKAN, L. YANG, Y. LI, Q. YANG, University of Saskatchewan, Canada
11:40 am		E2-1-6 Residual Stress Analysis in Thin Films using Focused Ion Beam and Digital Image Correlation - Stress Analysis by Raman Spectroscopy on Diamond Films, F. AHMED, M. KROTTENTHALER, C. SCHMID, K. DURST, University Erlangen-Nuremberg, Germany
12:00 pm		
12:20 pm	**CSM Instruments: Focused Topic Session** **"High Temperature Nanoindentation Testing and Other Latest Developments at CSM Instruments"** **12:15-1:15 p.m.** **California Room**	

Applications, Manufacturing, and Equipment
Room: California - Session G4-1+E

Coatings for Machining Advanced Materials and for use in Advanced Manufacturing Methods
Moderators: M. Arndt, OC Oerlikon Balzers AG, Liechtenstein, X. Nie, University of Windsor, Canada

10:00 am	G4-1+E-1 Invited Advanced Coatings and Tool Materials for Hobbing - a Major Step Forward in Productivity, P. IMMICH, KRETZSCHMANN, M. ROMMEL, T. FALK, R. FISCHER, LMT Fette Werkzeugtechnik GmbH & Co. KG, Germany	
10:20 am	Invited talk continued.	
10:40 am	G4-1+E-3 Physicochemical, Mechanical and Tribological Properties of Si_3N_4-MoS_2 Thin Films Deposited by Magnetron Sputtering, R. TRENTIN, A. BANDEIRA, C. AGUZZOLI, I. BAUMVOL, M. MORÉ FARIAS, C.A. FIGUEROA, UCS - Caxias do Sul University, Brazil	
11:00 am	G4-1+E-4 Effect of Silicon Content on Pvd Nitride Film Mechanical Properties and Cutting Performance of Coated Cemented Carbide Inserts, K.D. BOUZAKIS, Aristoteles University of Thessaloniki, Greece, E. BOUZAKIS, Fraunhofer Project Center for Coatings in Manufacturing (PCCM), Greece, S. KOMBOGIANNIS, G. SKORDARIS, S. MAKRIMALLAKIS, M. BATSIOLAS, Aristoteles University of Thessaloniki, Greece, R. M'SAOUBI, J. ANDERSSON, Seco Tools AB, Sweden	
11:20 am	G4-1+E-5 A Study on Friction and Wear Properties of Carbide Cutting Tools with MoS_2 Coating Deposited by Electrostatic Spray Coating, U. PATURI, S. NARALA, BITS-Pilani, India	
11:40 am	G4-1+E-6 Enhanced Cutting Performance of Tools Coated with Al2O3 –Based Coatings, M. JILEK, M. SIMA, SHM, Czech Republic, V. MAIXNER, Pramet Tools, Czech Republic	
12:00 pm		
12:20 pm	**CSM Instruments: Focused Topic Session** **"High Temperature Nanoindentation Testing and Other Latest Developments at CSM Instruments"** **12:15-1:15 p.m.** **California Room**	

Monday Afternoon, April 29, 2013

	Coatings for Use at High Temperature Room: San Diego - Session A1-2 Coatings to Resist High Temperature Oxidation, Corrosion and Fouling Moderators: L.G. Johansson, Chalmers University of Technology, Sweden, M. Weaver, University of Alabama, US, F. Perez Trujillo, Universidad Compultense de Madrid, Spain	Hard Coatings and Vapor Deposition Technology Room: Royal Palm 4-6 - Session B1-2 PVD Coatings and Technologies Moderators: J.H. Huang, Department of Engineering and System Science National Tsing Hua University, Taiwan, S. Weiβmantel, University of Applied Sciences Mittweida, Germany
1:30 pm	A1-2-1 Oxidation Behavior of Co-Doped NiCrAl Alloys in Dry and Wet Air, K.A. UNOCIC, B.A. PINT, Oak Ridge National Laboratory, US	B1-2-1 Invited Design and Metallurgy of High-performance Sputtering Target Materials, P. POLCIK, PLANSEE Composite Materials GmbH, Germany
1:50 pm	A1-2-2 Platinium Diffusion in Pure Nickel, M. ZAGULA-YAVORSKA, J. ROMANOWSKA, J. SIENIAWSKI, Rzeszów University of Technology, Poland	Invited talk continued.
2:10 pm	A1-2-3 Microstructure Degradation of EB-PVD TBCs on Pt and Pd/Pt-modified Aluminide Coatings under Cyclic Oxidation Conditions, R. SWADZBA, Institute for Ferrous Metallurgy, Poland	B1-2-3 Synthesis of Very Thick, Sputter-Deposited, Iron and Tantalum Film-Based Targets for Laser Experiments to Understand High Pressure Behavior in Materials, P. MIRKARIMI, K. BETTENCOURT, N. TESLICH, Lawrence Livermore National Laboratory, US
2:30 pm	A1-2-4 Ferritic-Martensitic Steels: Improvement of the Oxidation Behavior in Steam Environments via Diffusion Coatings, D. SCHMIDT, M. GALETZ, M. SCHÜTZE, DECHEMA-Forschungsinstitut, Germany	B1-2-4 Characterization of Al Sputter Process in Multiple Frequency Capacitively Coupled Plasmas (MFCCP), S. BIENHOLZ, N. BIBINOV, P. AWAKOWICZ, Ruhr University Bochum, Germany
2:50 pm	A1-2-5 Invited Oxidation under Pure Steam: Protective Oxides and Coatings, A. AGÜERO, V. GONZÁLEZ, M. GUTIÉRREZ, Instituto Nacional de Técnica Aeroespacial, Spain, R. MUELAS, Ingeniería y Servicios Aeroespaciales, Spain	B1-2-5 Influence of Magnetron Sputtering Conditions on WTi Thin Films, A. LE PRIOL, E. LE BOURHIS, P.O. RENAULT, Institut P' - Universite de Poitiers, France, H. SIK, P. MULLER, SAGEM Défense Sécurité, France
3:10 pm	Invited talk continued.	B1-2-6 Architectural Design of Al-rich Cubic Coating Materials within the AlN-CrN System, C. SABITZER, Christian Doppler Laboratory for Application Oriented Coating Development at Montanuniversitat Leoben and Vienna University of Technology, Austria, J. PAULITSCH, Vienna University of Technology and Montanuniversität Leoben, Austria, P. POLCIK, PLANSEE Composite Materials GmbH, Germany, M. ARNDT, R. RACHBAUER, OC Oerlikon Balzers AG, Liechtenstein, P.H. MAYRHOFER, Vienna University of Technology, Austria
3:30 pm	A1-2-7 Investigation of the Anti-adhesion Effect of Nano- and Micro-structured Surfaces, M. JUEZ LORENZO, V. KOLARIK, R. ROUSSEL, V. KUCHENREUTHER, Fraunhofer ICT, Germany, F. VELASCO, Universidad Carlos III-Madrid, Spain, S. GUZMAN, Universidad Carlos III- Madrid, Spain, F. PEDRAZA, Université de la Rochelle, France	B1-2-7 Influence of Argon Flow on Growth Rates in Reactive Magnetron Sputtering of Oxides and Production of an Esthetic Coating for Dental Implants, D. MUFF, C. PECNIK, R. SPOLENAK, ETH Zurich, Laboratory for Nanometallurgy, Switzerland
3:50 pm	A1-2-8 Chloride Induced High Temperature Corrosion in Waste and Biomass Fired Boilers – Degradation Mechanisms and Mitigation Measures, T. JONSSON, J. LISKE, J.E. SVENSSON, L.G. JOHANSSON, Chalmers University of Technology, Sweden	B1-2-8 Investigations of Arc-evaporated $(Al_{0.7}Cr_{0.3})_2O_3$ Coatings from Al-Cr-Si and Al-Cr-Fe Targets, J. PAULITSCH, Christian Doppler Laboratory for Application Oriented Coating Development at Montanuniversitat Leoben and Vienna University of Technology, Austria, R. RACHBAUER, J. RAMM, OC Oerlikon Balzers AG, Liechtenstein, P. POLCIK, PLANSEE Composite Materials GmbH, Germany, P.H. MAYRHOFER, Vienna University of Technology, Austria
4:10 pm	A1-2-9 Properties and Performance of Al/Al_2O_3 Coatings on 304 Steel in Metal Dusting Environments, E. URIBE, EGIC, Mexico, O. SALAS, J. OSEGUERA, D. MELO-MAXIMO, ITESM-CEM, Mexico, C. LEPIENSKI, UFPR, Brazil, R. TORRES, PUCPR, Brazil, R. DE SOUZA, Usp, Brazil	B1-2-9 Synthesis of Al-Ti-O-N Thin Flms by Reactive Magnetron Sputtering, J.F.T. SIMONET FOTSO, R. DANIEL, C. MITTERER, Montanuniversität Leoben, Austria
4:30 pm	A1-2-10 Microstructural Evolution of Cr/Cr_2O_3 coatings during exposure to Metal Dusting conditions, L. MELO-MAXIMO, Instituto Politécnico Nacional, Mexico, O. SALAS, ITESM-CEM, Mexico, V.M. LOPEZ-HIRATA, Instituto Politécnico Nacional, Mexico, D. MELO-MAXIMO, J. OSEGUERA, ITESM-CEM, Mexico, R. TORRES, PUCPR, Brazil, R. DE SOUZA, Usp, Brazil	B1-2-10 The Optimization of the Deposition Parameters to Prepare the $ZnSnO_3$ and Cd_2SnO_4 by RF Magnetron Sputtering from Powder Targets, Y.W. ZHOU, P.F. ZHU, S.L. LI, University of Science and Technology Liaoning, China
4:50 pm	A1-2-11 High-temperature Oxidation Corrosion of Boiler Steel with Al Coating under Co-firing of Biomass Charcoal / Coal Deposits, C.Y. TUNG, National Taiwan University of Science and Technology, Taiwan, Republic of China, C.J. WANG, S.P. WEN, National Taiwan University of Science and Technology, Taiwan, Republic of China	B1-2-11 Structural and Mechanical Properties of Cr-Al-O-N Thin Films Grown by Cathodic Arc Deposition, A. KHATIBI, Linköping University, Sweden, J. SJÖLEN, Seco tools AB, Sweden, G. GRECZYNSKI, J. JENSEN, P. EKLUND, L. HULTMAN, Linköping University, Sweden
5:10 pm		
5:30 pm	**Elsevier: Focused Topic Session "How to Get Published" California Room 5:30-6:00 p.m.**	**Welcome Mixer 6:00 - 7:30 p.m. Atlas Foyer Sponsored by Oerlikon Balzers**

Monday Afternoon, April 29, 2013

	Hard Coatings and Vapor Deposition Technology Room: Royal Palm 1-3 - Session B5-2 Hard and Multifunctional Nanostructured Coatings Moderators: J. Paulitsch, Vienna University of Technology, Austria, J. Houska, University of West Bohemia – NTIS, Czech Republic	Coatings for Biomedical and Healthcare Applications Room: Sunrise - Session D2-2 Coatings for Bio-corrosion, Tribo-corrosion, and Bio-tribology Moderators: M. Stack, University of Strathclyde, UK, J. Geringer, Ecole Nationale Superieure des Mines, France, M. Mathew, Rush University Medical Center, US
1:30 pm	B5-2-1 Texture Dependent Elastic Constants of Polycrystalline Zr—Al—N Predicted by *Ab Initio* Calculations, D. HOLEC, J. KECKES, P. WAGNER, Montanuniversität Leoben, Austria, F. TASNÁDI, Linköping University, Sweden, M. FRIÁK, Max-Planck-Institut für Eisenforschung, Germany, P.H. MAYRHOFER, Vienna University of Technology, Austria	D2-2-1 Evaluation of the Bio-tribocorrosion Processes of Colonized Ti6Al4V Implants in Presence of Organic and Cellular Material, M. RUNA, University of Minho, Portugal, M. MATHEW, Rush University Medical Center, US, M. FERNANDES, University of Porto, Portugal, L. ROCHA, University of Minho, Portugal
1:50 pm	B5-2-2 Influence of Zr on Structure and Properties of Ti-Al-N Coatings, Y. XU, Central South University, China, L. CHEN, Zhuzhou Cemented Carbide Cutting Tools Co., Ltd., China, B. YANG, Y. PENG, Y. DU, Central South University, China	D2-2-2 Tribocorrosion Evaluation of nc-TiN/a-Si_3N_4 Deposited on Ti6Al4V in Sliding Contact in Physiological Saline Solution, J. GARCIA, M. FLORES, Universidad de Guadalajara, Mexico, O. JIMENEZ, Universidad de Guadadalajara, Mexico, E. ANDRADE, Universidad Nacional Autónoma de México, Mexico
2:10 pm	B5-2-3 Invited Understanding Stress Development in Nanoscale Sputtered Thin Films from Real-Time Diagnostics, G. ABADIAS, A. MICHEL, A. FILLON, J. COLIN, C. JAOUEN, Institut P' - Universite de Poitiers, France	D2-2-3 Invited Nanotube Surface Modifications For Biomedical Applications, T. SHOKUHFAR, Michigan Technological University, US
2:30 pm	Invited talk continued.	Invited talk continued.
2:50 pm	B5-2-5 Hard Zr-Al-O Films with Enhanced Resistance to Cracking in Bending, J. SKLENKA, J. MUSIL, R. CERSTVY, R. JILEK, University of West Bohemia, Czech Republic	D2-2-5 Predicting Thickness of Passive Films in Order to Prevent Degradations of Implants, J. GERINGER, Ecole Nationale Superieure des Mines, France, M. TAYLOR, D. MACDONALD, Penn State University, US
3:10 pm	B5-2-6 AlN-based Optically Transparent Hard Nanocomposite Coatings: Going from Si to Sn, E. LEWIN, J. PATSCHEIDER, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland	D2-2-6 Electrochemical Behavior of Esthetic Dental Coatings Tested in Sodium Chloride Solution and Artificial Saliva, C. PECNIK, D. MUFF, R. SPOLENAK, ETH Zurich, Laboratory for Nanometallurgy, Switzerland
3:30 pm	B5-2-7 Invited Nanostructure of Plasma CVD Films Containing Nanoparticles, M. SHIRATANI, K. KOGA, G. UCHIDA, N. ITAGAKI, H. SEO, K. KAMATAKI, Kyushu University, Japan	D2-2-7 Submicroporous Ta_2O_5 Coating Enhanced the Initial Biological Responses to Ti Surface, Y.S. SUN, H.H. HUANG, National Yang-Ming University, Taiwan
3:50 pm	Invited talk continued.	D2-2-8 Scanning Electrochemical Microscopy (SECM) Investigation of Tribolayer Formation on a MoM Hip Implant, J. MEYER, Chicago State University, US, C. NAGELLI, M. MATHEW, M. WIMMER, J. JACOBS, Rush University Medical Center, US, R. LESUER, Chicago State University, US
4:10 pm	B5-2-9 Structure and Properties of TiAlSiN Nanocomposite Coatings Deposited by Deep Oscillation Magnetron Sputtering, Y. OU, Dalian University of Technology, China, J. LIN, Colorado School of Mines, US, W. SPROUL, Reactive Sputtering, Inc., US, J. MOORE, Colorado School of Mines, US, M. LEI, Dalian University of Technology, China	D2-2-9 Enhancements in Corrosion Resistance and Biocompatibility of Biomedical Ti-25Nb-25Zr Alloy Using Electrochemical Anodization Treatment, H.H. HUANG, C.P. WU, National Yang-Ming University, Taiwan, T.H. LEE, Chung Shan Medical University, Taiwan
4:30 pm	B5-2-10 Multifunctional Amorphous and Nanocomposite Nb-Si-C Coatings Deposited by dc-magnetron Sputtering, N. NEDFORS, Uppsala University, Sweden, O. TENGSTRAND, P. EKLUND, L. HULTMAN, Linköping University, Sweden, U. JANSSON, Uppsala University, Sweden	D2-2-10 Anti-fish Bacterial Pathogen Effect of Immobilized TiO_2/Fe_3O_4 Powder on Glass, T.C. CHENG, National Pingtung University of Science and Technology, Taiwan, Taiwan, Republic of China, Y.C. LEE, National Pingtung Univeristy of Science and Technology, Taiwan, Republic of China, H.C. HSU, National Pingtung University of Science and Technology, Taiwan, Republic of China
4:50 pm	B5-2-11 Nanocomposite Coatings as Protection Layer for PcBN Tools in Hard Machining, E. UHLMANN, J.A. OYANEDEL FUENTES, R. GERSTENBERGER, Technical University Berlin, Germany, H. FRANK, GFE Schmalkalden e.V., Germany	D2-2-11 Novel Functionalization of Anodized Ti6Al4V Nanotubes through Thermal Oxidation Approach, S. PATEL, C. TAKOUDIS, University of Illinois at Chicago, US
5:10 pm		D2-2-12 A Tribocorrosive Investigation of Commonly Used Implant Alloys, D. ROYHMAN, Rush University Medical Center, USA, M. MATHEW, Rush University Medical Center, US, J. YUAN, University of Illinois at Chicago, College of Dentistry, US, M. WIMMER, Rush University Medical Center, US, C. SUKOTJO, University of Illinois at Chicago, College of Dentistry, US
5:30 pm	**Elsevier: Focused Topic Session "How to Get Published" California Room 5:30-6:00 p.m.**	**Welcome Mixer 6:00 - 7:30 p.m. Atlas Foyer Sponsored by Oerlikon Balzers**

Monday Afternoon, April 29, 2013

	Tribology & Mechanical Behavior of Coatings and Engineered Surfaces Room: Golden West - Session E1-1 Friction, Wear, and Lubrication; Effects & Modeling Moderators: V. Fridrici, Ecole Centrale de lyon, France, O. Eryilmaz, Argonne National Laboratory, US, S.M. Aouadi, University of North Texas, US	Applications, Manufacturing, and Equipment Room: California - Session G4-2+E Coatings for Machining Advanced Materials and for use in Advanced Manufacturing Methods Moderators: M. Arndt, OC Oerlikon Balzers AG, X. Nie, University of Windsor
1:30 pm	E1-1-1 Tribological Comparison Between a Commercial DLC and an Experimental TaSiN Thin Films, M. FIGUEROA, E. GARCÍA, SEPI, ESIME-Zacatenco, Instituto Politécnico Nacional, Mexico, G. RAMÍREZ, Instituto de Investigaciones en Materiales,, S. MUHL, S. RODIL, Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de Mexico, A. CAVALEIRO, A. RAMALHO, Univ. of Coimbra, Portugal	G4-2+E-1 Invited Facing Challenge of Stamping Advanced High Strength Steels, B.J. JANOSS, Ionbond, US
1:50 pm	E1-1-2 Tribological Behavior of DLC Films with Various sp^3/sp^2 Ratios Deposited by Pulsed Laser Ablation and Lubricated by Base Oils, C. CHOUMAD-OULD, HEF, LaHC, LTDS, France, C. HÉAU, HEF, France, T. TITTE, A.S. LOIR, C. DONNET, F. GARRELIE, LAHC, France	Invited talk continued.
2:10 pm	E1-1-3 Invited In-situ Synthesis of DLC Boundary Films From Base Lubricating Oils at Sliding Tribological Interfaces, A. ERDEMIR, O. ERYILMAZ, Argonne National Laboratory, US	G4-2+E-3 Substrate Effects on Failure Behavior of Hard Coatings Under Inclined Cyclical Loading Conditions, J.F. SU, X. NIE, H. HU, University of Windsor, Canada, D. YOUNG, FORD Motor Company, US, D. ADAMSKI, General Motors, US, D.J. ZHOU, Chrysler Corporation, US, E. MCCARTY, Materials Technology Consulting, US
2:30 pm	Invited talk continued.	G4-2+E-4 Invited Manufacturing of Metal-based Microparts: Fabrication Strategies and Application of Coatings to Engineering of Tool Surfaces, Y. MU, K. CHEN, B. LU, W.J. MENG, Louisiana State University, US, G.L. DOLL, University of Akron, US
2:50 pm	E1-1-5 Critical Role of Tribofilm in the Performance of Electrical Contacts Involving Cu-DLC Nanocomposite Coating, R. HOMBO, Denso Corporation, Japan, T. TAKENO, Tohoku University, Japan, J. FONTAINE, LTDS, France, H. MIKI, Tohoku University, Japan, N. KATO, T. NOZU, N. INAYOSHI, Denso Corporation, Japan, M. BELIN, Ecole Centrale de Lyon, France	Invited talk continued.
3:10 pm	E1-1-6 Influence of the Coating Structure of a-C:H-W Coatings on their Wear-performance: a Theoretical Approach and its Practical Confirmation, A. GIES, OC Oerlikon Balzers AG, Liechtenstein, T. CHUDOBA, ASMEC GmbH, Germany, N. SCHWARZER, Saxonian Institute of Surface Mechancis, Germany, J. BECKER, Oerlikon Balzers Coating Germany GmbH, Germany	G4-2+E-6 Effects of Thin Film Metallic Glass Coating on Sharpness Improvements of Cutting Tools, C.L. LI, T.Y. LIU, J.P. CHU, National Taiwan Univ. of Science and Technology (NTUST), Taiwan, Republic of China, J.-W. LEE, Ming Chi Univ. of Technology, Taiwan, Republic of China, J.S.C. JANG, National Central University, Taiwan, Republic of China, M.J. CHEN, S.H. CHANG, Mackay Memorial Hospital, Taiwan, Republic of China
3:30 pm	E1-1-7 From Predictive Modelling via Optimized Testing to Applied Coating Development: DLC Coatings Durability under Nano-fretting Conditions, T. LISKIEWICZ, Leeds University, UK, B BEAKE, Micro Materials Ltd., UK, N. SCHWARZER, Saxonian Institute of Surface Mechanics, Germany, M. DAVIES, Micro Materials Ltd, UK	G4-2+E-7 Decomposition of Ti-Cr-Al-N/Ti-Cr-N Multilayer Coatings, R. FORSÉN, Linköping University, IFM, Thin Film Physics Division, Sweden, M. JOHANSSON, Seco Tools AB, Sweden, N. GHAFOOR, Linköping University, Sweden, M. ODÉN, Linköping University, IFM, Nanostructured Materials, Sweden
3:50 pm	E1-1-8 Microwear Investigations of DLC Coatings with Nanometer Resolution in Normal and Lateral Direction, T. CHUDOBA, K. MAYEKAR, ASMEC Advanced Surface Mechanics GmbH, Radeberg, Germany	G4-2+E-8 The Characteristics of Titanium Nitride Thin Films deposited by Reactive Plasma Deposition System and their Dependence on the Output Power of Plasma Gun, K. TANAKA, M. TAKAHASHI, Y. TANAKA, A. OSADA, Mitsubishi Materials Corporation, Japan
4:10 pm	E1-1-9 Failure Mechanisms of DLC and TiN Biomedical Coatings on SS316L and M2 Substrates under Cyclic Impact-sliding Loads, Y. CHEN, X. NIE, University of Windsor, Canada, J. HOUSDEN, Tecvac, Ltd., UK, A. MATTHEWS, University of Sheffield, UK	G4-2+E-9 Influence of PVD (Cr,Al)N Coatings and Surface Topography on Adhesion Behaviour towards PMMA, K. BOBZIN, N. BAGCIVAN, R.H. BRUGNARA, T. MÜNSTERMANN, Surface Engineering Institute - RWTH Aachen University, Germany
4:30 pm	E1-1-10 Tribological Behavior of the Superhard Coatings of Ta-N-Si and Nb-N-Si, G. RAMIREZ, Argonne National Laboratory, US, S. RODIL, Universidad Nacional Autónoma de México - Instituto de Investigaciones en Materiales, Mexico, A. ERDEMIR, O. ERYILMAZ, Argonne National Laboratory, US, S. MUHL, Universidad Nacional Autónoma de México - Instituto de Investigaciones en Materiales, Mexico	**Welcome Mixer 6:00 - 7:30 p.m. Atlas Foyer Sponsored by Oerlikon Balzers**
4:50 pm	E1-1-11 Friction Reduction by Thermal Post-deposition Treatment of Arc Evaporated TiAlTaN Coatings in Methane, N. SCHALK, Materials Center Leoben Forschung GmbH, Austria, C. MITTERER, Montanuniversität Leoben, Austria, C. CZETTL, CERATIZIT Austria GmbH, Austria, B. SARTORY, Materials Center Leoben Forschung GmbH, Austria, M. PENOY, C. MICHOTTE, CERATIZIT Luxembourg S.àr.l., Luxembourg	
5:10 pm	E1-1-12 Dangling Bonds Induced Cross-linking Model in Nanoscratched Graphene Layers, Q. ZHANG, Key Laboratory of Education Ministry for Modern Design and Rotor-Bearing System, School of Mechanical Engineering, Xi'an Jiaotong University, China, D.F. DIAO, Shenzhen University and Key Lab. Of Ed. Ministry for Modern Design and Rotor-Bearing Sys., Xi'an Jiaotong Univ., China, L. YANG, Key Laboratory of Education Ministry for Modern Design and Rotor-Bearing System, School of Mechanical Engineering, Xi'an Jiaotong University, China	**Elsevier: Focused Topic Session "How to Get Published" California Room 5:30-6:00 p.m**
5:30 pm		

Monday Afternoon, April 29, 2013

Topical Symposia
Room: Sunset - Session TS4-1

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

1:30 pm	TS4-1-1 Invited Self-Assembly of Two-Dimensional Nanosheets Induced by Interfacial Polyionic Complexation, F. KIM, J. ZOU, Kyoto University, Japan	
1:50 pm	Invited talk continued.	
2:10 pm	TS4-1-3 Synthesis of Mono- to Few-layer Graphene on Cu-Ni Alloy for Transparent Conducting Electrodes, L.Z. HUANG, P.K. NAYAK, National Cheng Kung University, Taiwan, Republic of China, S.C. WANG, Southern Taiwan University of Science and Technology, Taiwan, Republic of China, J.L. HUANG, National Cheng Kung University, Taiwan, Republic of China	
2:30 pm	TS4-1-4 Invited Soft Materials with Hard Skin: Synthesis, Assembly and Applications, F. CAVALLO, M. LAGALLY, University of Wisconsin-Madison, US	
2:50 pm	Invited talk continued.	
3:10 pm	TS4-1-6 The Effects of Electron Irradiation Conditions on the Formation of Embedded Graphene Sheets During Carbon Film Deposition in ECR Plasma, C. WANG, D.F. DIAO, Shenzhen University, Xi'an Jiaotong University, China	
3:30 pm	TS4-1-7 Invited Intrinsic Wettability of Graphene, H. LIU, University of Pittsburgh, US	
3:50 pm	Invited talk continued.	
4:10 pm	TS4-1-9 AFM Based Investigation of Organic Semiconductor Nanostructures Grown on Graphene Electrodes, M. KRATZER, Institute of Physics, Montanuniversitaet Leoben, Austria, B. VASIĆ, A. MATKOVIĆ, U. RALEVIĆ, R. GAJIĆ, Institute of Physics, University of Belgrade, Serbia, C. TEICHERT, Montanuniversität Leoben, Austria	
4:30 pm	TS4-1-10 Large-Scale Synthesis of Graphene Films by Pulsed Laser Deposition, T. TITE, A.S. LOIR, C. DONNET, F. BOURQUARD, S. REYNAUD, J.-Y. MICHALON, Laboratoire Hubert Curien, UMR 5516, Université de Lyon, Université Jean Monnet, France, J.P. CHATELON, Laboratoire Télécom Claude Chappe, EA 3523, France, F. GARRELIE, Laboratoire Hubert Curien, UMR 5516, Université de Lyon, Université Jean Monnet, France	
4:50 pm		
5:10 pm		
5:30 pm	**Elsevier: Focused Topic Session "How to Get Published" California Room 5:30-6:00 p.m**	**Welcome Mixer 6:00 - 7:30 p.m. Atlas Foyer Sponsored by Oerlikon Balzers**

Tuesday Morning, April 30, 2013

Exhibitors Keynote Lecture
11:00 a.m.-12:00 p.m.
Room: Town & Country

Coatings for Use at High Temperature
Room: San Diego - Session A2-1

Thermal and Environmental Barrier Coatings
Moderators: R. Trice, Purdue University, US, D. Litton, Pratt & Whitney, US, V. Maurel, Mines-ParisTech, France

8:00 am	**Exhibition Keynote Session**	A2-1-1 Invited Columnar Thermal Barrier Coatings (TBCs) by PS-PVD, R. VASSEN, G. MAUER, S. REZANKA, Forschungszentrum Jülich GmbH, Germany
8:20 am		Invited talk continued.
8:40 am	**Françoise Massines, CNRS, Perpignan, France**	A2-1-3 PS-PVD - Deposition of Thermal Barrier Coatings, M. GORAL, S. KOTOWSKI, J. SIENIAWSKI, Rzeszów University of Technology, Poland
9:00 am		A2-1-4 Development of Porous TBC Systems with Enhanced Durability using TriplexPro 210 Technology, R. DORFMAN, C. DAMBRA, J. MEDRANO, D. CHEN, M. NESTLER, Sulzer Metco (US) Inc.
9:20 am	**"Atmospheric Pressure Plasmas as a Solution for Inline Coatings: Status and Challenges"**	A2-1-5 Investigating CeO_2, TiO_2 Stabilized ZrO_2 for Application in Thermal Barrier Coatings (TBCs), C. MACAULEY, University of California, Santa Barbara, D. LIPKIN, General Electric (Global Research Center), US, C. LEVI, University of California, Santa Barbara, US
9:40 am		A2-1-6 Thermal Barrier Effect of Topcoats from Sintered Micro-sized Hollow Spherical Alumina Particles, R. ROUSSEL, V. KOLARIK, M. JUEZ-LORENZO, H. FIETZEK, Fraunhofer ICT, Germany
10:00 am		A2-1-7 Invited Multilayer Thermal Barrier Coatings: Interplay among coating design, processing and properties, S. SAMPATH, Stony Brook University, G. DWIVEDI, Stony Brook University, US, V. VISHWANATHAN, Stony Brook University, Y. CHEN, Stony Brook University, US
10:20 am		Invited talk continued.
10:40 am	**See Keynote Lecture page for abstract**	A2-1-9 Influence of Temperature on Phase Stability and Thermal Conductivity of Single- and Double-Ceramic-Layer EB-PVD TBC Top Coats consisting of 7YSZ, $Gd_2Zr_2O_7$ and $La_2Zr_2O_7$, K. BOBZIN, N. BAGCIVAN, T. BRÖGELMANN, B. YILDIRIM, Surface Engineering Institute - RWTH Aachen University, Germany
11:00 am	**11:00 am – 12:00 pm Town & Country**	A2-1-10 Invited Experimental Determination of Mode II Fracture Toughness of TBC's, B. ZHANG, S.J. LOCKYER-BRATTON, J. ELAWADY, K.J. HEMKER, Johns Hopkins University, US
11:20 am		Invited talk continued.
11:40 am		**Exhibition Opens-Grand Hall** **12:00-7:00 p.m.** **Enjoy lunch in the Exhibition Hall, compliments of Sulzer Metaplas**
12:00 pm		

Tuesday Morning, April 30, 2013

	Hard Coatings and Vapor Deposition Technology Room: Royal Palm 4-6 - Session B1-3 PVD Coatings and Technologies Moderators: J.H. Huang, Department of Engineering and System Science National Tsing Hua University, Taiwan, S. Weißmantel, University of Applied Sciences Mittweida, Germany	Hard Coatings and Vapor Deposition Technology Room: Royal Palm 1-3 - Session B6-1 Coating Design and Architectures Moderators: R. Daniel, Montanuniversität Leoben, Austria, M. Stüber, Karlsruhe Institute of Technology, Germany
8:00 am	B1-3-1 The Influence of Different Si-Contents of TiAlSiN PVD-Coatings on Mechanical and Tribological Properties at Elevated Temperatures, T. SPRUTE, W. TILLMANN, F. HOFFMANN, Technische Universität Dortmund, Germany, Y.Y. CHANG, National Formosa University, Taiwan, Republic of China, Y.Y. LIOU, Mingdao University, Taiwan, Republic of China	B6-1-1 Invited Flakey Stuff: Pushing the Limits of Engineering Coatings with Layered Atomic Structures, C. MURATORE, Air Force Research Laboratory, Materials and Manufacturing Directorate, Nanoelectronic Materials Branch, US, S.M. AOUADI, Southern Illinois University, US, J.J. HU, UDRI/Air Force Research Laboratory, Materials and Manufacturing Directorate, Nanoelectronic Materials Branch, US, A. VOEVODIN, Air Force Research Laboratory, Materials and Manufacturing Directorate, Nanoelectronic Materials Branch, US
8:20 am	B1-3-2 Compositional, Structural and Mechanical Evolution of Reactively and Non-reactively Sputtered Zr-Al-N Thin Films, P.H. MAYRHOFER, Vienna University of Technology, Austria, D. SONNLEITNER, Montanuniversität Leoben, Austria, J. PAULITSCH, Vienna University of Technology and and Montanuniversität Leoben, Austria,	Invited talk continued.
8:40 am	B1-3-3 Mechanical and Antimicrobial Characteristics in Zr-based Thin Film Metallic Glasses at Various Processing Temperature, J.H. CHU, H.W. CHEN, J.G. DUH, National Tsing Hua University, Taiwan, Republic of China, J.-W. LEE, Ming Chi University of Technology, Taiwan, Republic of China, J.S.C. JANG, National Central	B6-1-3 *Ab Initio* and Experimental Study on the Effect of Si Additives on the Phase Stability of γ - and α-Al_2O_3, F. NAHIF, D. MUSIC, S. MRÁZ, M. TO BABEN, J. SCHNEIDER, RWTH Aachen University, Germany
9:00 am	B1-3-4 Incorporation of Nano-crystalline TiB_2 Layers in Zr-Cu-Ni-Al Thin Film Metallic Glasses for Improved Anti-wear Characteristics, Y.C. CHAN, H.W. CHEN, J.G. DUH, National Tsing Hua University, Taiwan, Republic of China, J.-W. LEE, Ming Chi University of Technology, Taiwan, Republic of China	B6-1-4 A Combinatorial Approach to the Synthesis of Cr-Zr Oxynitride Thin Films by Reactive r.f. Magnetron Sputter Deposition, S. SPITZ, M. STÜBER, H. LEISTE, S. ULRICH, Karlsruhe Institute of Technology, Germany
9:20 am	B1-3-5 Corrosion Resistance of Amorphous, Nanocomposite, and Nanocrystalline Cr-C Films Deposited by Magnetron Sputtering, K. NYGREN, M. ANDERSSON, J. HÖGSTRÖM, W. FREDRIKSSON, K. EDSTRÖM, L. NYHOLM, U. JANSSON, Uppsala University, Sweden	B6-1-5 Invited Protective Coatings for Aerospace Applications: From Materials Architecture to Coating Removal, J.E. KLEMBERG-SAPIEHA, École Polytechnique de Montreal, Canada
9:40 am	B1-3-6 Corrosion Resistance and Tribological Properties of CrN, CrN/SiC, and CrN/DLC Coatings Grown by Cccelerated Plasma Arc Deposition, D. BELL, Phygen Coatings, Inc., US, C. MULLIGAN, M. SENICK, US Army ARDEC, Benet Laboratories, US, V. KHOMINICH, Z. GAY, Phygen Coatings, Inc., US	Invited talk continued.
10:00 am	B1-3-7 Invited Comparative Study of Transition Metal Boronitride Hard Coatings Fabricated by Reactive Magnetron Sputtering Process, J.-W. LEE, L.W. HO, Ming Chi University of Technology, Taiwan, Republic of China, W.S. LAI, C.J. WANG, National Taiwan University of Science and Technology, Taiwan, Republic of China	B6-1-7 Transformation Toughening as Applied to Coatings, C. WANG, Northwestern Polytechnical University, China, J. HAN, Northwestern University, US, J. PUREZA, Universidade do Estado de Santa Catarina, Brazil, Y.W. CHUNG, Northwestern University, US
10:20 am	Invited talk continued.	B6-1-8 Limits to the Preparation of Super- and Ultrahard Nanocomposites, S. VEPREK, M.G.J. VEPREK-HEIJMAN, Technical University Munich, Germany
10:40 am	B1-3-9 Using Filtered Vacuum-arc Plasma for PIII&D Process of Ti-Al-Y-N Coatings and their Abrasive and Cavitation Resistance, 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	B6-1-9 A Study of TiAl - powder Metallurgical Target Behaviour in Direct Current and High Power Impulse Magnetron Sputtering PVD Processes, S. KOLOZSVARI, P. POLCIK, PLANSEE Composite Materials GmbH, Germany
11:00 am	B1-3-10 Nanocomposite Mo-Ag-N Self-lubricating Hard Coatings Fabricated by Magnetron Sputtering, J.F. YANG, Institute of Solid State Physics, Chinese Academy of Sciences, China	B6-1-10 The Effect of Droplets in Arc Evaporated Hard Coatings on the Wear Behavior, M. TKADLETZ, Materials Center Leoben Forschung GmbH, Austria, C. MITTERER, Montanuniversität Leoben, Austria, B. SARTORY, Materials Center Leoben Forschung GmbH, Austria, C. MICHOTTE, CERATIZIT Luxembourg S.àr.l., Luxembourg
11:20 am		B6-1-11 In-situ Micro-fracture-test Investigations in the Influence of Structure and Phase Transformation of CrN/AlN Multilayer Coatings, M. SCHLOEGL, Montanuniversität Leoben and Vienna university of Technology, Austria, J. PAULITSCH, Vienna University of Technology, Austria, J. KECKES, C. KIRCHLECHNER, M.J. CHORDILL, Montanuniversität Leoben, Austria, P.H. MAYRHOFER, Vienna University of Technology, Austria STUDENT AWARD FINALIST
11:40 am		
12:00 pm	**Exhibition Opens-Grand Hall 12:00-7:00 p.m. Enjoy lunch in the Exhibition Hall, compliments of Sulzer Metaplas**	

Tuesday Morning, April 30, 2013

	Fundamentals and Technology of Multifunctional Thin Films: Towards Optoelectronic Device Applications Room: Sunset - Session C2-1 Fundamentals of Thin Films towards Optoelectronics Devices Moderators: T. Terasako, Graduate School of Science and Engineering, Ehime University, Japan, J.A. Zapien, City University of Hong Kong, Hong Kong Special Administrative Region of China	Coatings for Biomedical and Healthcare Applications Room: Sunrise - Session D1-1 Surface Functionalization, Drug Delivery, and Anti-microbial Coatings Moderators: S. Rodil Posada, Universidad Nacional Autonoma de Mexico, Mexico, D. Shtansky, National University of Science and Technology "MISIS", Russian Federation
8:00 am	C2-1-1 Carrier Transport and Photoluminescence Properties of Ga-Doped ZnO Films Grown by Ion-Plating and by Atmospheric-Pressure CVD, T. TERASAKO, Y. OGURA, S. FUJIMOTO, Graduate School of Science and Engineering, Ehime University, Japan, H. SONG, H. MAKINO, Kochi University of Technology, Japan, M. YAGI, Kagawa National College of Technology, Japan, S. SHIRAKATA, Graduate School of Sci. and Eng., Ehime Univ., Japan, T. YAMAMOTO, Kochi University of Technology, Japan	D1-1-1 Fabrication and Characterizations of ZnO Nanorods/ Ag Nanoparticle Composite on the Electropolished Ti Substrate., H. CHEN, National Chi-Nan University, Taiwan, Republic of China, Y.M. YEH, S.M. LIU, WuFeng University, Taiwan, B.Y. HUANG, J.Z. CHEN, National Chi-Nan University, Taiwan, Republic of China
8:20 am	C2-1-2 Invited Materials Smart Design of Wide Bandgap ZnO: Function Core, T. YAMAMOTO, H. MAKINO, H. SONG, Kochi University of Technology, Japan	D1-1-2 Evaluations of Biocompatibility and Antibacterial Property: Effects of Various Coatings, T.Y. KAO, J.P. CHU, C.L. LI, National Taiwan University of Science and Technology (NTUST), Taiwan, Republic of China, Y.J. CHANG, National Taipei Municipal University of Education, Taiwan, Republic of China, J.-W. LEE, Ming Chi University of Technology, Taiwan, Republic of China, M.J. CHEN, S.H. CHANG, Mackay Memorial Hospital Tamsui Campus, Taiwan, Republic of China, J.C. LIN, Mackay Memorial Hospital Tamsui Campus, Taiwan, Republicof China
8:40 am	Invited talk continued	D1-1-3 Invited Diamond-like Carbon for Articulation in Joint Replacements - Remaining Issues, G. Thorwarth, DePuy Synthes Companies, Switzerland, K. Thorwarth, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland, D. Bernoulli, A. Wyss, ETH Zürich, Switzerland, U. Mueller, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland, R. Spolenak, ETH Zürich, Switzerland, R. Hauert, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland Invited talk continued.
9:00 am	C2-1-4 Electrical Properties of the ZnO Thin Films Grown on a-plane Sapphire Substrates using Catalytically Generated High-energy H_2O, N. YAMAGUCHI, T. TAKEUCHI, E. NAGATOMI, T. KATO, Nagaoka University of Technology, Japan, H. UMEMOTO, Shizuoka University, Japan, K. YASUI, Nagaoka University of Technology, Japan	
9:20 am	C2-1-5 PEDOT:PSS Film having High Catalytic Activity for use as a Counter Electrode in Dye-sensitized Solar Cell, C.C. CHANG, L.C. CHEN, D. MISHRA, J.M. TING, National Cheng Kung University, Taiwan	D1-1-5 Bacterial Adhesion and Corrosion Studies on TiO_2 and ZrO_2 Coatings, R. GALICIA, Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Mexico, P. SILVA-BERMUDEZ, Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de Mexico, México, A. ALMAGUER-FLORES, Universidad Nacional Autónoma de México, Mexico, S. RODIL, Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de Mexico, Mexico
9:40 am	C2-1-6 Formation and Characterization of CIS Thin Films by Co-sputtering Using $CuSe_2$ and $InSe_2$ Targets, E. BLEZA, J. JEON, W. LEE, N. KIM, Chosun University, Korea	D1-1-6 Invited Surface Properties of Biomaterials and Their Application in Endogenous Tissue Engineering, R. OLIVARES-NAVARRETE, Georgia Institute of Technology, US
10:00 am	C2-1-7 Optical Properties of Sputter-Deposited Germanium Oxide (GeO_2) Films, C. RAMANA, University of Texas at El Paso, US, N. MURPHY, L. SUN, J. JONES, R. JAKUBIAK, Air Force Research Laboratory, Materials and Manufacturing Directorate, US	Invited talk continued.
10:20 am	C2-1-8 Experimental and Theoretical Analysis of Solar Absorbing Mo-SiO_2 Cermet Coating, Z. TAN, J. ZHOU, Tsinghua University, China, D. HE, F. ZHOU, J. YI, Camda Institute of New Energy Technology, China	D1-1-8 Effect of Salivary Protein Adsorption in the Bacterial Adhesion on Microestructured Titanium Surfaces, M. MARTÍNEZ-HERNÁNDEZ, A. ALMAGUER-FLORES, Universidad Nacional Autónoma de México -Facultad de Odontología, Mexico
10:40 am	C2-1-9 Effect of Nitrogen Incorporation on the Optical, Structural and Electrical Properties of Indium Zinc Oxide., J. ORTEGA, Universidad Autónoma de San Luis Potosí, Mexico, M. AGUILAR-FRUTIS, Instituto Politécnico Nacional, Mexico, C. FALCONY, Instituto Politecnico Nacional, Mexico, V. MÉNDEZ-GARCÍA, Universidad Autónoma de San Luis Potosí, Mexico, J. ARAIZA, Universidad Autónoma de Zacatecas, Mexico	D1-1-9 Cell Response to Amorphous-Crystalline TiO_2 Thin Films, P. SILVA-BERMUDEZ, Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de Mexico, México, A. ALMAGUER-FLORES, Facultad de Odontología, Universidad Nacional Autónoma de México, Mexico, SL. HYZY, R. OLIVARES-NAVARRETE, Georgia Institute of Technology, US, S. RODIL, Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de Mexico, México
11:00 am		D1-1-10 Effect of Dielectric Properties of Ceramic Surface on its Binding with Protein in Solvent, R. SABIRIANOV, University of Nebraska at Omaha, US, A. RUBINSTEIN, F. NAMAVAR, University of Nebraska Medical Center, US
11:20 am 11:40 am 12:00 pm	**Exhibition Opens-Grand Hall 12:00-7:00 p.m. Enjoy lunch in the Exhibition Hall, compliments of Sulzer Metaplas**	

Tuesday Morning, April 30, 2013

	Tribology & Mechanical Behavior of Coatings and Engineered Surfaces Room: Golden West - Session E2-2 Mechanical Properties and Adhesion Moderators: M.T. Lin, National Chung Hsing University, Taiwan, R. Chromik, McGill University, CanadaD. Bahr, Washington State University, US	Applications, Manufacturing, and Equipment Room: California - Session G1-1 Innovations in Surface Coatings and Treatments Moderators: L. Bardos, Uppsala University,Sweden, R. Cremer, KCS Europe GmbH, Germany
8:00 am	E2-2-1 Effects of Copper on the Microstructural and Functional Properties of Sputter-Deposited Ni-Ti Thin Films, M. CALLISTI, B.G. MELLOR, T. POLCAR, University of Southampton, UK	G1-1-1 High Density Plasma Nitriding of Dualumn Alloys for Automotive Parts, T.A. ZHO, K.M. MATSUBARA, Shibaura Institute of Technology, Japan, Y.S. SUGITA, YS Electric Industry, Co. Ltd., Taiwan
8:20 am	E2-2-2 Invited Mechanical Response of Nanotwinned Metallic Coatings, X. ZHANG, D. BUFFORD, Y. LIU, H. WANG, Texas A&M University, US	G1-1-2 Indentation Recovery of Thin Film Metallic Glass: Effects of Annealing Conditions, A. TESFAYE, J.P. CHU, National Taiwan University of Science and Technology (NTUST), Taiwan, Republic of China
8:40 am	Invited talk continued.	G1-1-3 Invited Influence of Deposition Technology and Process Parameters on the Formation of Growth Defects in PVD Hard Coatings, P. PANJAN, Jožef Stefan Institute, Slovenia
9:00 am	E2-2-4 Structural and Mechanical Properties of Al-Cu-Fe Quasicrystalline Thin Films, S. OLSSON, F. ERIKSSON, E. BROITMAN, M. GARBRECHT, J. BIRCH, Thin Film Physics Division, IFM, Linköping University, Sweden, L. HULTMAN, Thin Film Physics Division, IFM, Linköping University, Sweden	Invited talk continued.
9:20 am	E2-2-5 The Microstructure and Mechanical Properties of Nitrogen and Boron Contained ZrCuAlNi Thin Film Metallic Glasses, T.P. HSIAO, National Taipei University of Technology, Taiwan, Republic of China, J.-W. LEE, Ming Chi University of Technology, Taiwan, Republic of China, Y.C. YANG, National Taipei University of Technology, Taiwan, Republic of China, C.L. LI, J.P. CHU, National Taiwan University of Science and Technology (NTUST), Taiwan, Republic of China	G1-1-5 Suppression of Intermetallic Compounds through Microstructural Tunability in DC-sputtered Ni under Bump Metallization, Y.H. WU, J.G. DUH, National Tsing Hua University, Taiwan, Republic of China
9:40 am	E2-2-6 Comparison of Nanoindentation and Micro-tensile Measurements on the Strain-hardening Ability of Nano-scale Metallic Multilayers, R. SCHOEPPNER, Washington State University, US, D. BAHR, Purdue University, US, H. ZBIB, Washington State University, US	G1-1-6 Influence of the Application Technology on the Corrosion Resistance of DLC-Coatings, J. ELLERMEIER, U. DEPNER, M. OECHSNER, TU Darmstadt, Germany
10:00 am	E2-2-7 High Temperature Instrumented Indentation System: Characterization and Optimization, M. FAJFROWSKI, V. JARDRET, Michalex, France	G1-1-7 Cold Shield Production for Optoelectronic Applications, G. DEMIRCI, Aselsan Inc., Turkey, İ. KARAKAYA, M. ERDOĞAN, MS. ARAS, B. ARSLAN, F. ULU, Middle East Technical University, Turkey
10:20 am	E2-2-8 High-temperature Mechanical Behaviour of TiAlN Coatings, C. CIUREA, V. BHAKHRI, Imperial College London - South Kensington Campus, UK, P.H. MAYRHOFER, Vienna University of Technology, Austria, F. GIULIANI, Imperial College London - South Kensington Campus, UK	G1-1-8 Silicides Coating for Fuel Cladding in Gen IV Nuclear Reactors, S. MATHIEU, N. CHAIA, Universite de Lorraine, France, F. ROUILLARD, CEA Saclay, France, M. VILASI, Universite de Lorraine, France, M. LEFLEM, CEA, France
10:40 am	E2-2-9 Magnetron Sputtered W-V-N Superhard Nanocomposite Coatings, H. SHARMA, D. KAUR, Indian Institute of Technology Roorkee, India	G1-1-9 Multiscale Characterization of Physico-chemical Properties of an AISI 304L Surface Melted with a Nanopulsed Laser: Application to the Enhancement of the Corrosion Resistance After Laser Surface Melting, W. PACQUENTIN, N. CARON, C. BLANC, M. TABARANT, F. MISERQUE, CEA, France, R. OLTRA, CNRS, France
11:00 am	E2-2-10 Microstructure and Mechanical Properties of Copper-tin Shape Memory Alloy Deposited from an Ionic Liquid Electrolyte, N. MOHARRAMI, S. GHOSH, S. ROY, S BULL, Newcastle University, UK	G1-1-10 Novel Preparation of Single-layer and Few-layer Mica Nanosheets, D.S. KWAK, Y.J. KWON, H.Y. CHO, T.V. KHAI, H.W. KIM, Hanyang University, Republic of Korea
11:20 am		
11:40 am 12:00 pm	**Exhibition Opens-Grand Hall 12:00-7:00 p.m. Enjoy lunch in the Exhibition Hall, compliments of Sulzer Metaplas**	

Tuesday Afternoon, April 30, 2013

	Coatings for Use at High Temperature Room: San Diego - Session A2-2 Thermal and Environmental Barrier Coating Moderators: D. Litton, Pratt & Whitney, US, R. Trice, Purdue University, US, V. Maurel, Mines-ParisTech, France	Hard Coatings and Vapor Deposition Technology Room: Royal Palm 4-6 - Session B4-1 Properties and Characterization of Hard Coatings and Surfaces Moderators: J. Lin, Colorado School of Mines, ACSEL, US, B. Zhao, Exxon Mobile, US
2:10 pm	A2-2-1 Thermal Barrier Coating Lifetimes for High Temperature, Low Density Superalloys, J. NESBITT, R. MACKAY, K. REAMY, NASA Glenn Research Center, US	B4-1-1 Invited Low-temperature Plasma Surface Hardening of Austenitic and Martensitic Stainless Steels, M. LEI, Dalian University of Technology, China, X.M. ZHU, Dalian Jiaotong University, China
2:30 pm	A2-2-2 Ultra-Low Thermal Conductivity Yttria Stabilized Zirconia Thermal Barrier Coatings Using the Solution Precursor Plasma Spray Process, M. GELL, E. JORDAN, J. ROTH, C. JIANG, University of Connecticut	Invited talk continued.
2:50 pm	A2-2-3 Invited Observations of Ferroelastic Switching by Raman Spectroscopy, M. GENTLEMAN, SUNY - Stony Brook, US	B4-1-3 Microstructural Origins of Stress Gradients in Nanocrystalline Thin Films: the Dominant Role of Grain Evolution Against Texture, R. DANIEL, J. KECKES, C. MITTERER, Montanuniversität Leoben, Austria
3:10 pm	Invited talk continued.	B4-1-4 Effect of Tetramethylsilane Gas on the Fabrication of CrZrSiN Coatings by Cathodic Arc Deposition System, T.C. TSENG, J.-W. LEE, Ming Chi University of Technology, Taiwan, Republic of China, S.H. HUANG, National Chiao Tung University, Taiwan, Republic of China
3:30 pm	A2-2-5 Impact of Superalloy Composition and Bond Coat Roughness on Plasma-Sprayed TBCs with HVOF NiCoCrAlX Bond Coatings, J.A. HAYNES, K.A. UNOCIC, B.A. PINT, Oak Ridge National Laboratory, US	B4-1-5 Toughness Measurement of Nanocomposite Coatings by a Micro Double Cantilever Beam Method, S. LIU, University of Cambridge, UK, X.Z. DING, X.T. ZENG, Singapore Institute of Manufacturing Technology, Singapore, W. CLEGG, University of Cambridge, UK
3:50 pm	A2-2-6 A New Approach to Protect Thermal Barrier Coatings Against CMAS Corrosion using Sol-gel Process, G. PUJOL, F. ANSART, J.P. BONINO, CIRIMAT, France, A. MALIÉ, S. HAMADI, Snecma, SAFRAN Group, France	B4-1-6 Microstructure and Characterization of TaN Protective Coatings, K.Y. LIU, F.B. WU, National United University, Taiwan, Republic of China
4:10 pm	A2-2-7 Interaction of CMAS with MOCVD Coatings in the System Y_2O_3-Al_2O_3, N.K. EILS, P. MECHNICH, W. BRAUE, German Aerospace Center (DLR), Germany	B4-1-7 Structure and Residual Stress Analysis of Titanium Nitride Coatings Produced by DC Magnetron Sputtering, G. MARTINEZ, C. RAMANA, University of Texas at El Paso, US
4:30 pm	A2-2-8 Examination of CMAS-induced TBC Failure in Typical Service Conditions, V.K. TOLPYGO, Honeywell Aerospace, US	B4-1-8 Surface Directed Spinodal Decomposition at TiAlN / TiN Interfaces, A. KNUTSSON, I. SCHRAMM, K. GRÖNHAGEN, Linköping University, IFM, Nanostructured Materials, Sweden, F. MUCKLICH, Saarland University, Functional Materials, Germany, M. ODÉN, Linköping University, IFM, Nanostructured Materials, Sweden
4:50 pm		
5:10 pm		
5:30 pm	**Exhibition Reception-Grand Hall 5:30-7:00 p.m. Reception drinks compliments of Plansee**	

Tuesday Afternoon, April 30, 2013

	Hard Coatings and Vapor Deposition Technology Room: Royal Palm 1-3 - Session B6-2 Coating Design and Architectures Moderators: R. Daniel, Montanuniversität Leoben, Austria, M. Stüber, Karlsruhe Institute of Technology, Germany	Fundamentals and Technology of Multifunctional Thin Films: Towards Optoelectronic Device Applications Room: Sunset - Session C3-1 Optical Characterization Of Thin Films, Surfaces and Devices Moderators: J. Krueger, BAM Berlin, Germany, T. Hofmann, University of Nebraska–Lincoln, US
2:10 pm	B6-2-1 Invited Design of Novel Protective Coatings for High Temperature Applications, M. SCHÜTZE, DECHEMA-Forschungsinstitut, Germany	C3-1-1 Invited In Situ Observation of Sub-monolayer Films and Surface Reconstructions by Polarization Optical Spectroscopy, C. COBET, Johannes Kepler University, Austria
2:30 pm	Invited talk continued.	Invited talk continued.
2:50 pm	B6-2-3 Design of Diffusion Coatings Developed via Pack Cementation, A. NAJI, M. GALETZ, M. SCHÜTZE, DECHEMA-Forschungsinstitut, Germany	C3-1-3 The Surface Morphology and Optical Properties of Refining Glass Inorganic Nano-molecules, M. DRAJEWICZ, Rzeszow University of Technology, Poland, M. PYTEL, Rzeszów University of Technology, Poland
3:10 pm	B6-2-4 Invited Inhomogeneous Structural and Mechanical Properties of Thin Films and Coatings Revealed at the Micro- and Nano-Scale, J. KECKES, R. DANIEL, Montanuniversität Leoben, Austria, A. RIEDL, M. STEFENELLI, Materials Center Leoben Forschung GmbH, Austria, C. MITTERER, Montanuniversität Leoben, Austria	C3-1-4 Optical Constants of Uranium Trioxide Thin Films, 1.25 to 6 eV, W. BELL, D. ALLRED, Brigham Young University, US
3:30 pm	Invited talk continued.	C3-1-5 Invited Infrared Ellipsometry for Characterization of Thin Films, KH. HINRICHS, Leibniz-Institut für Analytische Wissenschaften - ISAS - e.V., Germany
3:50 pm	B6-2-6 The Effects of Bilayer Periods on the Mechanical Properties of Cr-B-N/Ti-B-N Multilayered Thin Films., W.T.. TSAI, J.-W. LEE, Ming Chi University of Technology, Taiwan, Republic of China	Invited talk continued.
4:10 pm	B6-2-7 Ion Energy Distributions in Cathodic Arc Plasma of AlCr Composite Cathodes in Inert and Reactive Atmosphere, R. FRANZ, Montanuniversität Leoben, Austria, P. POLCIK, PLANSEE Composite Materials GmbH, Germany, A. ANDERS, Lawrence Berkeley National Laboratory, US	C3-1-7 Thickness Optimization of OLED Encapsulation, J.A. ZAPIEN, C.H. TO, C.S. LEE, F.L. WONG, City University of Hong Kong, Hong Kong Special Administrative Region of China
4:30 pm		C3-1-8 Effect of Oxygen Gas Flow Rate on the Structure and Optical Properties of Sputter-deposited Gallium Oxide Thin Films, E. RUBIO, S. SAMALA, C. RAMANA, University of Texas at El Paso, US
4:50 pm		C3-1-9 Optical Emission Spectroscopic Determination of Most Suitable Region for Micro-arc Oxidation on Metal Titanium, H.J. CHU, C.H. CHEN, J.L. HE, Feng Chia University, Taiwan, Republic of China
5:10 pm		C3-1-10 Deposition of Nanocrystalline SnSe Thin Films by Spin Coating Technique for their Application in Fabrication and Characterization of n-$MoSe_2$/Nc p-SnSe Heterojunction Diode, K. HINGARAJIYA, G.K. SOLANKI, K. PATEL, N. GOSAI, Sardar Patel University, India
5:30 pm	**Exhibition Reception-Grand Hall 5:30-7:00 p.m. Reception drinks compliments of Plansee**	

Tuesday Afternoon, April 30, 2013

	Tribology & Mechanical Behavior of Coatings and Engineered Surfaces Room: Golden West - Session E1-2 Friction, Wear, and Lubrication; Effects & Modeling Moderators: V. Fridrici, Ecole Centrale de lyon, O. Eryilmaz, Argonne National Laboratory, US, S.M. Aouadi, University of North Texas	New Horizons in Coatings and Thin Films Room: Sunrise - Session F1-1 Nanomaterials, Nanofabrication, and Diagnostics Moderators: Y. Yamada-Takamura, Japan Advanced Institute of Science and Technology, Y. Gonzalvo, Hiden Analytical Ltd.
2:10 pm	E1-2-1 Invited Tribology of Hard Carbon Coatings under Ultra- und Super-low Friction Conditions, V. WEIHNACHT, S. MAKOWSKI, F. SCHALLER, A. LESON, Fraunhofer IWS, Germany	F1-1-1 The influence of Reaction Temperature and Volume of Oleic Acid to Synthesize SnS Nano Crystals by using Thermal Decomposition Method, B. LIANG, National Cheng Kung University, Taiwan, Republic of China, S.C. WANG, Southern Taiwan University of Science and Technology, Taiwan, Y.M. SHEN, J.L. HUANG, National Cheng Kung University, Taiwan, Republic of China
2:30 pm	Invited talk continued.	F1-1-2 Nanoparticles Deposition by Temporally Shaped Femtosecond Pulsed Laser: In Situ Plasma and Nanoparticles Diagnostic, F. BOURQUARD, J.P. COLOMBIER, A.S. LOIR, C. DONNET, R. STOIAN, F. GARRELIE, Laboratoire Hubert Curien, UMR 5516, Université de Lyon, Université Jean Monnet, France
2:50 pm	E1-2-3 Mechanical Properties and Tribological Behavior of a Silica and/or Alumina Coating Prepared by Sol- gel Route on Stainless Steel, A. MARSAL, F. ANSART, V. TURQ, J.P. BONINO, CIRIMAT, France, JM. SOBRINO, YM. CHEN, J. GARCIA, Cetim, France	F1-1-3 Invited Nanoparticle Synthesis via Laser-induced Plasma in Liquid Environment, T. ITO, Osaka University, Japan
3:10 pm	E1-2-4 Tribochemically Active Ti-C-S Nanocomposites - a New Concept for Self-lubricating Coatings, J. SUNDBERG, H. NYBERG, E. SÄRHAMMAR, K. KÁDAS, Uppsala University, Sweden, L. WANG, Lanzhou Institute of Chemical Physics, China, O. ERIKSSON, T. NYBERG, S. JACOBSON, U. JANSSON, Uppsala University, Sweden	Invited talk continued.
3:30 pm	E1-2-5 Lubricious Silver Tantalate Films For Extreme Temperature Applications, D. STONE, A. HARBIN, Southern Illinois University, US, H. MOHSENI, J.-E. MOGONYE, T. SCHARF, University of North Texas, US, C. MURATORE, Air Force Research Laboratory, Thermal Sciences and Materials Branch, US, A. VOEVODIN, Air Force Research Laboratory, Materials and Manufacturing Directorate, US, A. MARTINI, University of California Merced, US, S.M. AOUADI, Southern Illinois University, US STUDENT AWARD FINALIST	F1-1-5 Bonding of Metallic Nanoparticles, M. CHANDROSS, T. BOYLE, B. CLARK, P. LU, Sandia National Laboratories, US
3:50 pm	E1-2-6 Lubricious Zinc Titanate Films for High Temperature Applications, V. AGEH, H. MOHSENI, T. SCHARF, University of North Texas, US	F1-1-6 The Preparation of FeS_2 Pyrite Nanocrystal Inks for Photovoltaic Thin Film, S.C. HSIAO, K.W. WU, S.H. HUANG, S.H. CHIU, L.H. CHOU, National Tsing Hua University, Taiwan, Republic of China
4:10 pm	E1-2-7 Study of the Friction Coefficient and Wear of Boride Coating Film on Stainless Steel AISI 410 at Different Temperatures, E. GARCÍA, M. FIGUEROA, G RAMÍREZ-CASTRO, I. CAMPOS-SILVA, Instituto Politécnico Nacional, Mexico, S. MUHL, Universidad Nacional Autónoma de México - Instituto de Investigaciones en Materiales, Mexico, A. CAVALEIRO, University of Coimbra, Portugal, T. POLCAR, Czech Technical University in Prague, Czech Republic	F1-1-7 Morphological and Optical Properties of AlN Nano-islands Prepared by Plasma Enhanced Chemical Vapor Deposition, Z. BOUCHKOUR, Université de Limoges - CNRS, France, E. THUNE, ENSCI-CNRS, France, C. JAOUL, J.C. ORLIANGES, Université de Limoges - CNRS, France, R. GUINEBRETIÈRE, ENSCI-CNRS, France, P. TRISTANT, C. DUBLANCHE-TIXIER, Université de Limoges - CNRS, France
4:30 pm	E1-2-8 Plasma Diffusion Treatments to improve the Tribological Performance of Ti-4Al-4Mo-2Sn, G. CASSAR, B. ATTARD, University of Malta, Malta, A. MATTEWS, A. LEYLAND, University of Sheffield, UK	F1-1-8 Effect of Indium Concentration on Luminescence and Electrical Property of Indium Doped ZnO Nanowires, S.Y. LIM, National Cheng Kung University, Taiwan, Republic of China, R.C. WANG, National University of Kaohsiung, Taiwan, C.P. LIU, S. BRAHMA, J.L. HUANG, National Cheng Kung University, Taiwan, Republic of China
4:50 pm	E1-2-9 Tribological Behavior of Pvd Coated Cemented Carbide Against Superduplex Stainless Steel, J.M. PAIVA JR., Faculdade de Tecnologia SENAI Joinville, Brazil, R. TORRES, F.L. AMORIM, P.C. SOARES JR., Pontificia Universidade Católica do Paraná, Brazil	F1-1-9 Carbon Monoxide-induced Reduction and Healing of Graphene Oxide, B. NARAYANAN, S.L. WEEKS, Colorado School of Mines, US, B. MACCO, Eindhoven University of Technology, Netherlands, J.-W. WEBER, Eindhoven University of Technology, Netherlands, M.C.M. VAN DE SANDEN, Dutch Institute for Fundamental Energy Research, Netherlands, S. AGARWAL, C. CIOBANU, Colorado School of Mines, US
5:10 pm	E1-2-10 Influence of the Normal Force and Abrasive Slurry Concentration on the Coefficient of Friction of Thin Films in Micro-abrasive Wear Tests, B. GUERREIRO, R.C. COZZA, Centro Universitário da FEI – Fundação Educacional Inaciana "Padre Sabóia de Medeiros", Brazil	F1-1-10 Studies on the Optoelectronic Characteristics of the V_2O_5-PtO_2 Core-shell Nanowires, K.Y. PAN, National Tsing Hua University, Taiwan, Republic of China, K.C. CHEN, Chinese Culture University, Taiwan, Republic of China, H.C. SHIH, National Tsing Hua University, Taiwan, Republic of China
5:30 pm	**Exhibition Reception-Grand Hall 5:30-7:00 p.m. Reception drinks compliments of Plansee**	

Tuesday Afternoon, April 30, 2013

Applications, Manufacturing, and Equipment
Room: California - Session G3-1

Atmospheric and Hybrid Plasma Technologies
Moderators: H. Barankova, Uppsala University, Sweden, D. Pappas, EP Technologies, LLC, US

2:10 pm	G3-1-1 High Performance Thin Films for Aerospace Applications, A. RANADE, M.A. MATOS, The Boeing Company, US	
2:30 pm	G3-1-2 The Effect of Processing Parameters and Substrate Composition on the Corrosion Resistance of Plasma Electrolytic Oxidation (PEO) Coated Magnesium Alloys, R. HUSSEIN, D. NORTHWOOD, X. NIE, University of Windsor, Canada	
2:50 pm	G3-1-3 Invited PVD-Quality Coatings at Atmospheric Pressure, D.N. RUZIC, Y.L. WU, Z. OUYANG, P. RAMAN, T.S. CHO, University of Illinois at Urbana-Champaign, US	
3:10 pm	Invited talk continued.	
3:30 pm	G3-1-5 Atmospheric Plasma Treatment Inside Hollow Substrates, H. BARÁNKOVÁ, L. BARDOS, Uppsala University, Sweden	
3:50 pm	G3-1-6 ICP Dual Frequency Discharges: A Potential Tool for Large Area Plasma Processing, A. MISHRA, T.H. KIM, K.N. KIM, G.Y. YEOM, Sungkyunkwan University, South Korea	
4:10 pm	G3-1-7 Effects of Low Energy Plasma Immersion Ion Implantation of Nitrogen on Titanium, R. RAO, GITAM Institute of Technology, GITAM University, India	
4:30 pm		
4:50 pm		
5:10 pm		
5:30 pm	**Exhibition Reception-Grand Hall 5:30-7:00 p.m. Reception drinks compliments of Plansee**	

Wednesday Morning, May 1, 2013

	Coatings for Use at High Temperature Room: San Diego - Session A2-3 Thermal and Environmental Barrier Coatings Moderators: R. Trice, Purdue University, US, D. Litton, Pratt & Whitney, US, V. Maurel, Mines-ParisTech, France	Hard Coatings and Vapor Deposition Technology Room: California - Session B3-1 Deposition Technologies for Diamond Like Coatings Moderators: K Böbel, Bosch GmbH, Germany, C. Engdahl, Crystallume, US
8:00 am	A2-3-1 Invited Environmental Barrier Coatings for Turbine Engines: Current Status and Future Directions, D. ZHU, NASA Glenn Research Center, US	B3-1-1 Physical Vapor Partial Filtering for Chemical Composition Control in Hybrid PECVD / EB-PVD Process, C. JAOUL, Université de Limoges - CNRS, France, F. MEUNIER, Sulzer Sorevi, France, P. TRISTANT, J.P. LAVOUTE, C. DUBLANCHE-TIXIER, Université de Limoges - CNRS, France
8:20 am	Invited talk continued.	B3-1-2 A Multi Source PECVD Technology for Extremely Planar, Thick and Large-scale DLC Coatings, S. MEIER, S. SCHNAKENBERG, Fraunhofer Institute for Mechanics of Materials, IWM, Germany
8:40 am	A2-3-3 Y_2SiO_5 Coatings Fabricated by RF Magnetron Sputtering, P. MECHNICH, German Aerospace Center (DLR), Germany	B3-1-3 A Comparison on the Influence of Different Inert Gases for Reactive HiPIMS and DCMS CN_x Deposition Processes, S. SCHMIDT, Linköping University, IFM, Thin Film Physics Division, Sweden, ZS. CZIGÁNY, Hungarian Academy of Sciences, Research Centre for Natural Sciences, Hungary, G. GRECZYNSKI, J. JENSEN, L. HULTMAN, Linköping University, IFM, Thin Film Physics Division, Sweden
9:00 am	A2-3-4 Invited Optimum Design of High Temperature Thermal Radiation Energy Reflection Coatings for SiC/SiC Components, Y. KAGAWA, National Institute for Materials Science, Japan	B3-1-4 Deposition and Characterization of Advanced DLC Coatings Deposited by Low Frequency Plasma Enhanced Chemical Vapour Deposition (LF PECVD), C. CHOUQUET, DMX sas, France, C. DUCROS, CEA/Liten/DTNM/LTS, France, F. SCHUSTER, CEA Cross-Cutting Programme on Advanced Materials, France, A. BILLARD, LERMPS-IRTES, France, F. SANCHETTE, ICD-LASMIS, Nicci, UTT Antenne de Nogent, France
9:20 am	Invited talk continued.	B3-1-5 Invited State-of-the-Art of DLC Coatings: Industrial Deposition Methods and Tribological Applications 60 Years after the Discovery of DLC, J. VETTER, Sulzer Metaplas, Germany
9:40 am	A2-3-6 Tridimensional Analysis of Interfacial Defects Consequences on Delamination of Thermal Barrier Coatings, R. SOULIGNAC, Mines-ParisTech, France	Invited talk continued.
10:00 am	A2-3-7 Adsorption of Various REs Atoms on NiAl and Al2O3 Surface: An Implication for Grain Boundary Diffusion in Thermal Barrier Coatings, T. ZHANG, H.B. GUO, Beihang University, China	B3-1-7 Modification of Femtosecond-Pulsed Laser Deposited Diamond-Like Carbon films by Temporal Pulse Shaping, F. BOURQUARD, T. TITE, A.S. LOIR, C. DONNET, Laboratoire Hubert Curien, UMR 5516, Université de Lyon, Université Jean Monnet, France, H. FTOUNI, O. BOURGEOIS, Institut Néel, UPR 2940 CNRS, France, F. GARRELIE, Laboratoire Hubert Curien, UMR 5516, Université de Lyon, Université Jean Monnet, France
10:20 am	A2-3-8 Microstructure and Thermal Oxidation Behavior of Yttria-Stabilized Hafnia Coatings, E. RUBIO, M. NOOR-A-ALAM, S. STAFFORD, C. RAMANA, University of Texas at El Paso, US	B3-1-8 Thermal Stability of DLC-MoS_2 Thin Films in Different Environments, H. NIAKAN, C. ZHANG, J. SZPUNAR, Q. YANG, University of Saskatchewan, Canada
10:40 am	A2-3-9 Tribocorrosion Mechanisms in Laser Deposited Titanium-based Smart Tribological Composite Smart Coating, P. OLUBAMBI, M.L. LEPULE, B. OBADELE, Tshwane University of Technology, South Africa, J.O. BORODE, Federal University of Technology, Nigeria	B3-1-9 Advanced PECVD Process Control through the use of RF and Plasma Key Parameters for Transfer of Layer Properties, T. GROTJAHN, S. SCHNAKENBERG, Fraunhofer IWM, Germany, R. PLÖTZE, P.H.F. Beratung, Germany, R. ROTHE, Plasmetrex GmbH, Germany, S. MEIER, Fraunhofer IWM, Germany
11:00 am		B3-1-10 High-rate Deposition of Dense Hydrogenated Amorphous Carbon Thin Films using High Power Impulse Magnetron Sputtering Based Process, A. AIJAZ, K. SARAKINOS, M. RAZA, U. HELMERSSON, Linköping University, IFM, Plasma and Coatings Physics, Sweden
11:20 am		
11:40 am		
12:00 pm	**Exhibition Closes Today 2:00 p.m.**	

Wednesday Morning, May 1, 2013

	Hard Coatings and Vapor Deposition Technology Room: Royal Palm 4-6 - Session B4-2 Properties and Characterization of Hard Coatings and Surfaces Moderators: J. Lin, Colorado School of Mines, US, ACSEL, B. Zhao, Exxon Mobile, US	Hard Coatings and Vapor Deposition Technology Room: Royal Palm 1-3 - Session B7-1 Computational Design and Experimental Development of Functional Thin Films Moderators: B. Alling, Thin Film Physics Division, IFM, Linköping University, Sweden, D. Holec, Montanuniversität Leoben, Austria
8:00 am	B4-2-1 Invited Plasma Immersion Ion Deposition of Diamond-like Carbon Coatings on Inner Surface of Long Pipes for Industry Applications, K. COULTER, R.H. WEI, Southwest Research Institute	B7-1-1 Invited Nanoengineered Oxide and Nitride Thin Films with Unique Functionalities, H. WANG, J. LEE, A. CHEN, M. MYERS, C. TSAI, Q. SU, Y. ZHU, L. CHEN, L. JIAO, J. JIAN, W. ZHANG, F. KHATKATTY, C. JACOB, Texas A&M University, US, Q. JIA, Los Alamos National Laboratory, US, J. DRISCOLL, University of Cambridge, UK, J. GAN, J. COLE, Idaho National Lab, US
8:20 am	Invited talk continued.	Invited talk continued.
8:40 am	B4-2-3 Microstructural Investigation of Erosion Resistant TiN-TiAlN Laminated Coatings Deposited by Arc Ion Plating, T. TAKAHASHI, R. CREMER, P. JASCHINSKI, KCS Europe GmbH, Germany	B7-1-3 Invited Modeling Amorphous Materials from First Principles, E. HOLMSTROM, R. LIZARRAGA, Instituto de Fisica, Universidad Austral de Chile, Valdivia, Chile
9:00 am	B4-2-4 Shake-up Features in Titanium Nitride Bilayer Systems used to Model Ultra-hard TiN/ Si_3N_4 Nanocomposites, D. JAEGER, J. PATSCHEIDER, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland STUDENT AWARD FINALIST	Invited talk continued.
9:20 am	B4-2-5 Diamond Coatings' Adhesion and Residual Stresses Assessment by Inclined Impact Tests, K.D. BOUZAKIS, G. SKORDARIS, Aristoteles University of Thessaloniki, Greece, S. MAKRIMALLAKIS, Fraunhofer Project Center for Coatings in Manufacturing (PCCM), Germany, E. BOUZAKIS, Fraunhofer Project Center for Coatings in Manufacturing (PCCM), Greece, S. KOMBOGIANNIS, Aristoteles University of Thessaloniki, Greece, O. LEMMER, CemeCon AG, Germany	B7-1-5 Advanced Modelling of Amorphous Ceramics, J. HOUSKA, University of West Bohemia - NTIS, Czech Republic
9:40 am	B4-2-6 Study Of Structural and Mechanical Properties Of CrAlYN/CrY Multilayer Thin Film Deposited On M2 Steel, M.T. TAHMASEBIAN MYANDOAB, I. EFEOGLU, V. EZIRMIK, Y. TOTIK, E. DEMIRCI, Atatürk University, Turkey, O. BARAN, Erzincan University, Turkey	B7-1-6 Dynamics of Ti, N, and TiN_x (x = 1 - 3) Admolecule Transport on TiN(001) Islands and Surfaces, D. EDSTRÖM, D. SANGIOVANNI, V. CHIRITA, L. HULTMAN, Linköping University, IFM, Thin Film Physics Division, Sweden, I. PETROV, J. GREENE, University of Illinois at Urbana-Champaign, US
10:00 am	B4-2-7 Growth of ZrO_2 by Heat Treating ZrN Thin Film in Vacuum, J.H. HUANG, J.-W. HSIEH, G.P. YU, National Tsing Hua University, Taiwan, Republic of China	B7-1-7 *Ab Initio* Study of the Effect of Al Addition on Surface Kinetics of Ti, Hf and Zr Nitrides, C. THOLANDER, B. ALLING, F. TASNADI, Linköping University, Sweden, I. PETROV, J. GREENE, University of Illinois at Urbana-Champaign, US, L. HULTMAN, Linköping University, Sweden
10:20 am	B4-2-8 Structural and Elastic Properties of Ternary Metal Nitride $Zr_{1-x}Ta_xN$ Alloys Thin Films: Relationship with the Working Gas Pressure, P. DJEMIA, LSPM-CNRS, Université Paris 13, Sorbonne Paris-Cité, France, L. BELLIARD, UPMC-Institut des NanoSciences de Paris, France, G. ABADIAS, Institut P' - Universite de Poitiers, France	B7-1-8 First-principles Study of Electronic, Elastic and Thermodynamic Properties of CrN, L. ZHOU, Vienna University of Technology and Montanuniversität Leoben, Austria, D. HOLEC, Montanuniversität Leoben, Austria, P.H. MAYRHOFER, Vienna University of Technology, Austria
10:40 am	B4-2-9 High Temperature Tribological Properties of CrAlTiN Coating, T. POLCAR, University of Southampton, UK, A. CAVALEIRO, University of Coimbra, Portugal	B7-1-9 Invited Importance of Finite Temperature Effects in *AB INITIO* Simulations of Materials for Hard Coating Applications, I. ABRIKOSOV, P. STENETEG, O. HELLMAN, L. HULTBERG, F. TASNADI, N. SHULUMBA, O. VEKILOVA, B. ALLING, Linköping University, Sweden
11:00 am	B4-2-10 On Hardness and its Benefit to the Characterization and Optimization of Coatings, M. FUCHS, Chemnitz University of Technology, Germany, N. SCHWARZER, Saxonian Institute of Surface Mechancis, Germany	Invited talk continued.
11:20 am	B4-2-11 Microstructure, Properties and Microtribological Performance of Magnetron-sputtered V-C Coatings, M. STÜBER, Karlsruhe Institute of Technology, Germany, P. STOYANOV, Karlsruhe Institute of Technology, and Fraunhofer-Institute for Mechanics of Materials IWM, Germany, E. NOLD, Fraunhofer-Institute for Mechanics of Materials IWM, Germany, M. DIENWIEBEL, Karlsruhe Institute of Technology, and Fraunhofer-Institute for Mechanics of Materials IWM, Germany, S. ULRICH, Karlsruhe Institute of Technology, Germany	
11:40 am	B4-2-12 Adherent Amorphous Hydrogenated Carbon Coatings on Steel Surfaces Deposited by Enhanced Asymmetrical Bipolar Pulsed-DC PECVD Method and Hexane as Precursor, G. CAPOTE, J. OLAYA, National University of Colombia, Colombia, G. FARIA, G. MARTINS, E. CORAT, V. TRAVA-AIROLDI, Institute for Space Research, Brazil	
12:00 pm	**Exhibition Closes Today 2:00 p.m.**	

Wednesday Morning, May 1, 2013

	Fundamentals and Technology of Multifunctional Thin Films: Towards Optoelectronic Device Applications Room: Sunset - Session C4-1 Thin Film Growth and Characterization for Optoelectronic Devices Moderators: K. Yu, Lawrence Berkeley National Laboratory, US, A. Ranade, The Boeing Company, US	Tribology & Mechanical Behavior of Coatings and Engineered Surfaces Room: Golden West - Session E2-3 Mechanical Properties and Adhesion Moderators: R. Chromik, McGill University, Canada, D. Bahr, Washington State University, US, M.T. Lin, National Chung Hsing University, Taiwan
8:00 am	C4-1-1 Fabrication and Characterizations of CIGS Films Using One-step Electrochemical Co-deposition Methods, Y.M. YEH, WuFeng University, Taiwan, H. CHEN, National Chi-Nan University, Taiwan, Republic of China, S.M. LIU, WuFeng Univ., Taiwan, S.T. HUANG, Y.J. CHEN, National Chi-Nan Univ., Taiwan, Republic of China	E2-3-1 Deformation and Fracture of Wear-Resistant Laser Oxide Coatings on Metallic Substrates, S. LAWRENCE, Washington State University, US, D. ADAMS, Sandia National Laboratories, US, H. ZBIB, D. BAHR, Washington State University, US, N. MOODY, Sandia National Laboratories, US
8:20 am	C4-1-2 Preparation of CdMnS Thin Film: Applications in Photoelectrochemical Cell, J.S. DARGAD, Dayanand Science College, Latur, Swami Ramanand Teerth Marathwada University, Nanded, Maharashtra, India	E2-3-2 Influence of Film Thickness on Fragmentation and Contact Damage of Diamond-Like Carbon (DLC) Coated Titanium Substrates, D. BERNOULLI, A. WYSS, K. HÄFLIGER, ETH Zurich, Laboratory for Nanometallurgy, Switzerland, K. THORWARTH, R. HAUERT, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland, G. THORWARTH, DePuy Synthes Companies, Switzerland, R. SPOLENAK, ETH Zurich, Laboratory for Nanometallurgy, Switzerland
8:40 am	C4-1-3 Invited Fabrication and Characterization of High-efficiency CdTe-based Thin-Film Solar Cells, Y. YAN, N. PAUDEL, The University of Toledo, US	E2-3-3 Influence of Application Technology on the Erosion Resistance of DLC-Coatings, U. DEPNER-MILLER, H. SCHEERER, J. ELLERMEIER, M. OECHSNER, Technische Universitat Darmstadt, Germany, K. BOBZIN, N. BAGCIVAN, T. BRÖGELMANN, R. WEIß, RWTH Aachen University, Germany, K. DURST, C. SCHMID, Friedrich-Alexander-University Erlangen-Nuernberg, Germany
9:00 am	Invited talk continued.	E2-3-4 Elevated Temperature Nanoindentation of Multilayered Coatings, G. MOHANTY, J. WHEELER, R. RAGHAVAN, EMPA Swiss Federal Laboratories for Materials Science and Technology, Switzerland, B. BELLATON, P. KEMPE, CSM Instruments SA, Switzerland, J. MICHLER, EMPA Swiss Federal Laboratories for Materials Science and Technology, Switzerland
9:20 am	C4-1-5 The Optimization of Indium Codoping Concentration in 100-nm-thick GZO Films for Low Resistivity and High Humidity Resistance Properties, H. SONG, H. MAKINO, N. YAMAMOTO, Kochi University of Technology, Japan, S. KISHIMOTO, Kochi National College of Technology, Japan, T. YAMAMOTO, Kochi University of Technology, Japan	E2-3-5 Energy Loss and Internal Frictions Study of Nanocrystalline Metal Thin Films, M.T. LIN, C-J. TONG, Y-T. WANG, National Chung Hsing University, Taiwan, Republic of China
9:40 am	C4-1-6 Effects of Native Defects on the Electrical and Optical Properties of Cadmium Oxide, K. YU, Lawrence Berkeley National Laboratory, US, L. REICHERTZ, RoseStreet Laboratories, US, S. GRANKOWSKA, Warsaw University, Poland, D. DETERT, O. DUBON, University of California, Berkeley; Lawrence Berkeley National Laboratory, USA, A. ANDERS, W. WALUKIEWICZ, Lawrence Berkeley National Laboratory, US	E2-3-6 Effect of the Anisotropic Growth on the Fracture Toughness Measurements Obtained in the Fe_2B Layer, E. HERNANDEZ-SANCHEZ, G. RODRIGUEZ-CASTRO, Instituto Politecnico Nacional, Mexico, M. ROMERO-ROMO, UAM-A, Mexico, I. ARZATE-VAZQUEZ, I. CAMPOS-SILVA, Instituto Politecnico Nacional, Mexico
10:00 am	C4-1-7 Study of the Instability of Amorphous InGaZnO Thin Film Transistor under the DC and AC Drain-bias Stress, L.W. LIN, T.C. CHANG, S.Y. HUANG, M.C. YANG, National Sun Yat-Sen University, Taiwan, Republic of China, K.H. YANG, University of Toronto, Canada, M.H. WU, M.C. CHEN, K. MAI, Y.J. CHIU, National Sun Yat-Sen University, Taiwan, Republic of China, B.L. YEH, Advanced Display Technology Research Center, AU Optronics, Taiwan	E2-3-7 Invited Characterising Micromechanical Deformation of Commercially Pure Zirconium, T.B. BRITTON, University of Oxford and Imperial College London, UK, J. GONG, D. LLOYD, A. WILKINSON, S. ROBERTS, University of Oxford, UK
10:20 am	C4-1-8 Microwave-assisted Hydrothermal Synthesized Nitrogen-doped TiO_2 Photocatalysts for Enhanced Visible Light Response, W.C. HUANG, J.M. TING, National Cheng Kung University, Taiwan	Invited talk continued.
10:40 am	C4-1-9 Effect of Thermal Annealing on Nickel Oxide Doped AZO Transparent Conducting Thin Films Prepared by DC Magnetron Sputtering System, Y.D. JO, Pusan National University, Republic of Korea	E2-3-9 Super-hard or Super-tough? - Nanomechanics for Improving the Toughness and Durability of Hard Nanocomposite Films, B BEAKE, Micro Materials Ltd., UK, V. VISHYNAKOV, Manchester Metropolitan University, UK, A.J. HARRIS, Micro Materials Ltd, UK, J.S. COLLIGON, Manchester Metropolitan University, UK, J. SMITH, M. DAVIES, Micro Materials Ltd, UK
11:00 am	C4-1-10 Characteristics of Plasma Generated by ICP-CVD with Various H2/SiH4 Ratios and the Resultant Properties of nc-Si-H Thin Films, J.H. HSIEH, Y.L. LAI, Ming Chi University of Technology, Taiwan, Republic of China, C. LI, National Central University, Taiwan, Republic of China, J. SETSUHARA, Osaka University, Japan	E2-3-10 Fatigue Property Improvements of Ti Alloys by Metallic Glass and TiN Thin Films, C.M. LEE, Department of Materials Science and Engineering and Graduate Institute of Applied Science and Technology, National Taiwan University of Science and Technology, Taipei 10607, Taiwan, Taiwan, Republic of China, J.P. CHU, National Taiwan University of Science and Technology, Taiwan, Republic of China, J.-W. LEE, Ming Chi University of Technology, Taiwan, Taiwan, Republic of China
11:20 am	C4-1-11 Optoelectronic Characterization of *p*-type NiO_x and *n*-type TiO_2 Thin Films Deposited by Laser Ablation, A. HIRATA, CNyN-UNAM, US	E2-3-11 Microstructure and Properties Characterization of WC-Co HVOF Coatings Obtained From Standard, Superfine and Modified by Nanocarbides Feedstock Powders, G. MOSKAL, K. SZYMAŃSKI, H. MYALSKA, Silesian University of Technology, Poland
11:40 am	**Exhibition Closes Today**	
12:00 pm	**2:00 p.m.**	

Wednesday Morning, May 1, 2013

New Horizons in Coatings and Thin Films
Room: Sunrise - Session F2-1

High Power Impulse Magnetron Sputtering
Moderators: D. Lundin, Université Paris-Sud 11, France, J. Sapieha, Ecole Polytechnique de Montreal, Canada

8:00 am	F2-1-1 Invited Applications of HIPIMS Metal Oxides, V. SITTINGER, O. LENCK, S.K. GURRAM, D. NIEWERTH, G. BRÄUER, Fraunhofer IST, Germany	
8:20 am	Invited talk continued.	
8:40 am	F2-1-3 Optical Coatings Prepared by HiPIMS – Does this Technology Meet our Expectations?, M. HALA, R. VERNHES, O. ZABEIDA, J.E. KLEMBERG-SAPIEHA, L. MARTINU, Polytechnique Montreal, Canada	
9:00 am	F2-1-4 Epitaxial (001) Oriented Mo/V Superlattice Grown on MgO(100) by HiPIMS, S. SHAYESTEHAMINZADEH, H.P. GÍSLASON, S. ÓLAFSSON, University of Iceland	
9:20 am	F2-1-5 High Power Impulse Magnetron Sputtering of Compound Targets, A. ANDERS, Lawrence Berkeley National Laboratory, US, E. OKS, High Current Electronics Institute, Russian Federation, R. FRANZ, C. CLAVERO, R. MENDELSBERG, Lawrence Berkeley National Laboratory, US	
9:40 am	F2-1-6 TiO_2 Coatings Deposited by Arc Free Deep Oscillation Magnetron Sputtering, J. LIN, Colorado School of Mines, ACSEL, US, B. WANG, Colorado School of Mines, US, W. SPROUL, Reactive Sputtering, Inc., US, Y. OU, Colorado School of Mines, US, I. DAHAN, Nuclear Research Center, Beer-Sheva, Israel	
10:00 am	F2-1-7 Deposition Rate Enhancement in HiPIMS at Preserved Ionized Fraction of the Deposition Flux, J. CAPEK, University of West Bohemia, Czech Republic, M. HALA, O. ZABEIDA, Ecole Polytechnique de Montreal, Canada, J.E. KLEMBERG-SAPIEHA, Ecole Polytechnique de Montréal, Canada, L. MARTINU, École Polytechnique de Montréal, Canada	
10:20 am	F2-1-8 Optimization of the Substrate Conditions by Monte Carlo Modeling of Sputtered Particle Transport, D. LUNDIN, C. VITELARU, Université Paris-Sud 11, France, N. BRENNING, Royal Institute of Technology, Sweden, T. MINEA, Université Paris-Sud 11, France	
10:40 am	F2-1-9 Temporal Characterization of Ion Dynamics in High Power Impulse Magnetron Plasma by Means of Plasma Monitor, Ridded Retarding Field Energy Analyzer and Modified Katsumata Probe, M. CADA, P. ADAMEK, J. OLEJNICEK, Z. HUBICKA, Institute of Physics of the ASCR, v.v.i., Czech Republic	
11:00 am	F2-1-10 Mechanism of the Instabilities in HiPIMS Discharge and Correlation with Deposition Conditions, A. HECIMOVIC, T. DE LOS ARCOS, V. SCHULZ VON DER GATHEN, J. WINTER, Institute for Experimental physics 2, Ruhr University Bochum, Germany	
11:20 am	F2-1-11 Influence of High Power Impulse Magnetron Sputtering (HIPIMS) Pulse Shape Regarding Voltage and Current Time Evolution on Plasma Characteristics, Deposition Rate and Ionization for Titanium Aluminum, F. PAPA, Hauzer Techno Coating, BV, Netherlands, H. GERDES, R. BANDORF, F. LENZ, G. BRAEUER, Fraunhofer Institute für Schicht und Oberflächentechnik, Germany, T. KRUG, Hauzer Techno Coating, BV, Netherlands	
11:40 am		
12:00 pm	**Exhibition Closes Today 2:00 p.m.**	

Wednesday Afternoon, May 1, 2013

	Hard Coatings and Vapor Deposition Technology Room: Royal Palm 4-6 - Session B4-3 Properties and Characterization of Hard Coatings and Surfaces Moderators: J. Lin, Colorado School of Mines, ACSEL, US, B. Zhao, Exxon Mobile, US	Hard Coatings and Vapor Deposition Technology Room: Royal Palm 1-3 - Session B7-2 Computational Design and Experimental Development of Functional Thin Films Moderators: B. Alling, Thin Film Physics Division, IFM, Linköping University, Sweden, D. Holec, Montanuniversität Leoben, Austria
2:10 pm	B4-3-1 Invited Novel Method for Deposition of Protective Coatings on Internal Surfaces, T. CASSERLY, J. BAE, J. WICKERSHAM, Sub-One Technology, US, B. WILLIAMS, URS Flint, US	B7-2-1 On the Structure and Growth of Reactive Magnetron Sputtered Ta_2O_5, R. HOLLERWEGER, Christian Doppler Laboratory for Application Oriented Coating Development at Montanuniversitat Leoben and Vienna University of Technology, Austria, M. BARTOSIK, Vienna University of Technology, Austria, M. ARNDT, R. RACHBAUER, OC
2:30 pm	Invited talk continued.	B7-2-2 Probing Temperature-induced Ordering in $Ti_{0.33}Al_{0.67}N$ Coatings, C. ÄRHAMMAR, Sandvik Coromant R&D S-126 80 Stockholm, Sweden, J. ENDRINO, Instituto Abengoa Research S. L., Spain, M. RAMZAN, Uppsala University, Sweden, D. HORWAT, Université de Lorraine, Institut Jean Lamour, CNRS, Institut Jean Lamour, UMR 7198,
2:50 pm	B4-3-3 Prediction of DLC Friction Lifetime Based on a Local Archard Factor Density Approach, F. ALKELAE, S. FOUVRY, LTDS - Ecole Centrale de Lyon, France	B7-2-3 Lattice Ordering Effects on Toughness Enhancement in Transition Metal Nitride Thin Films, D. SANGIOVANNI, D. EDSTRÖM, V. CHIRITA, L. HULTMAN, Linköping University, IFM, Thin Film Physics Division, Sweden
3:10 pm	B4-3-4 Time- and Space-resolved High-throughput Characterization of Stresses during Sputtering and Thermal Processing of Al-Cr-N Thin Films, D. GROCHLA, Ruhr-Universität Bochum, Germany	B7-2-4 Invited Plasticity in Complex Crystals, C. WALTER, University of Cambridge, UK, J. WHEELER, R. RAGHAVAN, J. MICHLER, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland, W. CLEGG, University of Cambridge, UK
3:30 pm	B4-3-5 Mechanical Properties and Microstructures of Cr-O-N Coatings Deposited by Arc Ion Plating Method, T. MINAMI, S. NISHIO, Kanefusa Corporation, Japan, Y. MURATA, Nagoya University, Japan	Invited talk continued.
3:50 pm	B4-3-6 Effect of Bias Voltage on the Mechanical-tribological Properties of AlCrN Coatings, F. LOMELLO, DEN/DANS/DPC/SEARS/LISL CEA Saclay, France, A. BILLARD, IRTES-LERMPS-UTBM, France, F. SANCHETTE, LRC CEA-ICD LASMIS, Nogent International Center for CVD Innovation (Nicci), France, F. SCHUSTER, CEA Cross-Cutting	B7-2-6 Oxygen-deficient Zirconia Thin Films Synthesized by Reactive Magnetron Sputtering, S. KONSTANTINIDIS, G. GEUMEZ, T. VAN REGEMORTER, J. CORNIL, R. SNYDERS, University of Mons, Belgium
4:10 pm	B4-3-7 Influence of Substrate Bias on the Structure and Mechanical Properties of ZrN Thin Films Deposited by Arc Ion Plating, M. ZHANG, Liaoning Normal University, China, K. KWANG HO, Pusan National University, Republic of Korea, H. YE, H. XIAOGANG, P. YUNLI, Liaoning Normal University, China	
4:30 pm	B4-3-8 Effect of Cr/Al Content on Creep Resistance of AlCrN Coatings Applied by Reactive Magnetron Sputtering, Z. GASEM, S. ALAM, King Fahd University of Petroleum and Minerals, Saudi Arabia, A. MATTHEWS, University of Sheffield, UK	
4:50 pm		
5:10 pm		
5:30 pm	**Awards Convocation-5:45 p.m.** **San Diego Room** **Honorary Lecturer-William D. Sproul** **"40 Years of Advancement in PVD Technology"** **Awards Reception will follow the Convocation at 7:30 p.m. Poolside**	

Wednesday Afternoon, May 1, 2013

	Fundamentals and Technology of Multifunctional Thin Films: Towards Optoelectronic Device Applications Room: Sunset - Session C5-1 Thin Films for Active Devices Moderators: F. Tasnadi, Linköping University, Sweden, S. Moram, Imperial College London, UK	Tribology & Mechanical Behavior of Coatings and Engineered Surfaces Room: Golden West - Session E1-3 Friction, Wear, and Lubrication; Effects & Modeling Moderators: V. Fridrici, Ecole Centrale de lyon, France, O. Eryilmaz, Argonne National Laboratory, US, S.M. Aouadi, University of North Texas, US
2:10 pm	C5-1-1 Investigation on Plasma Treatment in Transparent Al-Zn-Sn-O Thin Film Transistor Application, C.H. CHANG, P.T. LIU, Y.T. WU, C.S. FUH, National Chiao Tung University, Taiwan, Republic of China	E1-3-1 Tribological Behavior of Multilayered Ti-Si-B/Zr-based Thin Film Metallic Glass Coatings with Various Si Contents, H.W. CHEN, Y.C. CHAN, National Tsing Hua University, Taiwan, Republic of China, J.-W. LEE, Ming Chi University of Technology, Taiwan, Republic of China, J.G. DUH, National Tsing Hua University, Taiwan,
2:30 pm	C5-1-2 IGZO Deposition - Sputtering Technologies Comparison, P. OZIMEK, W. GLAZEK, A. KLIMCZAK, P. ROZANSKI, Huettinger Electronic, Poland	E1-3-2 Invited A Simple In-situ Method of AFM Calibration for Tribological Characterization of Ultra-thin Transfer Films, D BURRIS, H. KHARE, University of Delaware, US
2:50 pm	C5-1-3 Low Temperature Electrochemical Hydrocarbon Sensor Based on Reactive Magnetron Co-sputtering Deposited Layers, E. DEREEPER, P. BRIOIS, A. BILLARD, IRTES-LERMPS-UTBM, France	Invited talk continued.
3:10 pm	C5-1-4 Growth of Carbon Nanotubes/ Diamond Double Layers for High Stable Field Electron Emission, L. YANG, C. ZHANG, Y. LI, Q. YANG, University of Saskatchewan, Canada	E1-3-4 Precession Electron Diffraction Studies to Determine Wear-induced Texture Formation and Grain Refinement in Tribological Coatings and Engineered Surfaces, H. MOHSENI, J.-E. MOGONYE, R. BANERJEE, P. COLLINS, T. SCHARF, University of North Texas, US
3:30 pm	C5-1-5 The Effect of Moisture on Oxygen Adsorption of InGaZnO Thin Film Transistors under Bias Stress, Y.C. CHEN, T.C. CHANG, National Sun Yat-Sen University, Taiwan, Republic of China	E1-3-5 Dry Friction Between Laser-patterned Surfaces: Role of Alignment and Structural Wavelength, A. ROSENKRANZ, C. GACHOT, Saarland University, Germany, N. PRODANOW, M. MUESER, Supercomputing Centre Juelich, F. MUECKLICH, Saarland University, Germany
3:50 pm		E1-3-6 Influence of Aspect Ratio of Silicon Patterned and Coated Surfaces on Wetting and Tribological Characteristics, S. PIAO, N. MACHAVALLAVAN, KIST, Republic of Korea, K.Y. JHANG, Hanyang University, Republic of Korea, E.-S. YOON, KIST, Republic of Korea
4:10 pm		E1-3-7 Laser Interference-induced Microstructural Architectures and Topographies in Gold Thin Films and their Effect under Dry Sliding Conditions, C. GACHOT, A. ROSENKRANZ, F. MUECKLICH, Saarland University, Germany
4:30 pm		E1-3-8 Stress Analysis of WS2 Coatings Using Scratch Testing and Raman Spectrocopy, J. RESTREPO, Universidad Nacional Autónoma de México, Mexico, J.M. GONZALEZ, Universidad Del Valle, Colombia, S. MUHL, Universidad Nacional Autónoma de México, Mexico, F. SEQUEDA, Universidad Del Valle, Colombia
4:50 pm		E1-3-9 Investigation of the Tribological Behavior of Electrocodeposited Ni-MoS_2 Composite Coatings, E. SARALOGLU GULER, İ. KARAKAYA, Middle East Technical University, Turkey, E. KONCA, Atilim University, Turkey, A. OZTURK, **M. ERDOĞAN**, Middle East Technical University, Turkey
5:10 pm		E1-3-10 Fretting Wear Behaviour of Ti-TiC Composite Alloys: Influence of the TiC Concentration, J. DUHART, S. FOUVRY, Ecole Centrale de lyon, France
5:30 pm		
6:10 pm 6:30 pm	**Awards Convocation-5:45 p.m.** **San Diego Room** **Honorary Lecturer-William D. Sproul** **"40 Years of Advancement in PVD Technology"** **Awards Reception will follow the Convocation at 7:30 p.m. Poolside**	

Wednesday Afternoon, May 1, 2013

	New Horizons in Coatings and Thin Films Room: Sunrise - Session F2-2 High Power Impulse Magnetron Sputtering Moderators: J. Sapieha, Ecole Polytechnique de Montreal, Canada, D. Lundin, Université Paris-Sud 11, France	New Horizons in Coatings and Thin Films Room: California - Session F3-1 New Boron, Boride and Boron Nitride Based Coatings Moderators: H. Hoegberg, Linkoeping University, Sweden, A. Inspektor, Kennametal Incorporated, US
2:10 pm	F2-2-1 Invited High Power Pulse Plasma Systems for the Reactive Deposition of Thin Films at Low Substrate Temperature, Z. HUBICKA, M. CADA, S. KMENT, Institute of Physics of the ASCR, v.v.i., Czech Republic, P. KSIROVA, J. OLEJNICEK, Institute of Physics ASCR, v.v.i., Czech Republic, T. KUBART, Uppsala University, Sweden, V. STRANAK, Insitute of Physics ASCR, v.,v.,i., Czech Republic	F3-1-1 Exploring New W-B Coating Materials for the Aqueous Corrosion-wear Protection of Stainless Steels, P. DEARNLEY, University of Southampton, UK, B. MALLIA, University of Malta, Malta
2:30 pm	Invited talk continued.	F3-1-2 Exploring Coating Materials Based on the Cr-B-N System for the Corrosion-wear Protection of Stainless Steels, P. DEARNLEY, University of Southampton, UK, M. STÜBER, Karlsruhe Institute of Technology, Germany, B. MALLIA, University of Malta, Malta
2:50 pm	F2-2-3 Mo_2BC a Stiff and Moderately Ductile Tool Coatings – from Ab Initio Predictions to HPPMS Synthesis in an Industrial Deposition System, H. BOLVARDI, J. EMMERLICH, D. MUSIC, RWTH Aachen University, Germany, M. ARNDT, H. RUDIGIER, OC Oerlikon Balzers AG, Liechtenstein, J. SCHNEIDER, RWTH Aachen	F3-1-3 Invited Magnetron Sputtering of Me-B-C coatings, U. JANSSON, N. NEDFORS, Uppsala University, Sweden, L. WANG, Lanzhou Institute of Chemical Physics, China
3:10 pm	F2-2-4 Influence of HPPMS Pulse Length and Inert Gas Mixture on the Properties of (Cr,Al)N Coatings, N. BAGCIVAN, K. BOBZIN, Surface Engineering Institute - RWTH Aachen University, Germany, G. GRUNDMEIER, C. KUNZE, University of Paderborn, Technical and Macromolecular Chemistry, Germany, R.H. BRUGNARA, Surface Engineering Institute - RWTH Aachen University, Germany	Invited talk continued.
3:30 pm	F2-2-5 Ultra-thin Poly-crystalline TiN Films Grown by HiPIMS on MgO(100) - *in-situ* Resistance Study of the Initial Stage of Growth, S. SHAYESTEHAMINZADEH, T.K. TRYGGVASON, University of Iceland, Iceland, F. MAGNUS, Uppsala University, Sweden, S. OLAFSSON, University of Iceland, Iceland, J.T. GUDMUNDSSON, Univ. of Michigan-Shanghai Jiao Tong University Joint Institute, China	F3-1-5 Synthesis of Very Thick PVD Boron Carbide Films for Potential Fusion Targets, P. MIRKARIMI, K. BETTENCOURT, N. TESLICH, K.J. WU, M. WANG, Lawrence Livermore National Laboratory, US, H. XU, General Atomics, Inc.,US, G. RANDALL, NIKROO, General Atomics, Inc., US
3:50 pm	F2-2-6 Influence of Ion Bombardment Energy on the Growth of CrN Films by Reactive Magnetron Sputtering and High Power Impulse Magnetron Sputtering, A.P. EHIASARIAN, Sheffield Hallam University, UK, B. HOWE, Air Force Research Lab, US, I. PETROV, University of Illinois at Urbana-Champaign, US	F3-1-6 Influences of Boron Contents on the Microstructure and Mechanical Properties of Ti-Zr-B-N Thin Films Deposited by Pulsed DC Reactive Magnetron Sputtering, W.S. LAI, National Taiwan University of Science and Technology, Taiwan, Republic of China, J.-W. LEE, Ming Chi University of Technology, Taiwan, Republic of China, C.J. WANG, National Taiwan University of Science and Technology, Taiwan, Republic of China
4:10 pm	F2-2-7 Properties of $Ti_{1-x}Si_xN$ Films Grown in Hybrid HIPIMS-DCMS Configuration, G. GRECZYNSKI, J. LU, J. JENSEN, Linköping University, 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, Sweden	F3-1-7 Invited Boron-10-Based Thin Films for the Next Generation of Neutron Detectors, C. HÖGLUND, European Spallation Source ESS AB/Linköping University, Sweden
4:30 pm	F2-2-8 A Comparative Study of AlN Films Deposited by Deep Oscillation Magnetron Sputtering and Pulse DC Magnetron Sputtering, B. WANG, Colorado School of Mines, US, I. DAHAN, Ben Gurion University of the Negev, Israel, J. MOORE, Colorado School of Mines, US, W. SPROUL, Reactive Sputtering, Inc., US, J. LIN, Colorado School of Mines, US	Invited talk continued.
4:50 pm	F2-2-9 Characterization of Hard Coatings Deposited by Constant Voltage HIPIMS and MPP Sputtering System and their Cutting Performance, T. SASAKI, K. INOUE, S. ABUSUILIK, Hitachi Tool Engineering, Ltd., Japan	F3-1-9 Tailoring the Mechanical and Tribological Properties of Boron Carbide Films by Adjusting the BC_x Stoichiometry, J.C. QIAN, Z.F. ZHOU, C. YAN, City University of Hong Kong, Hong Kong Special Administrative Region of China, D.J. LI, École Polytechnique de Montréal, Canada, M. AZZI, Notre Dame University, US, K.Y. LI, W.J. ZHANG, I. BELLO, City University of Hong Kong, Hong Kong Special Administrative Region of China, L. MARTINU, École Polytechnique de Montréal, Canada, J.E. KLEMBERG-SAPIEHA, Ecole Polytechnique de Montréal, Canada
5:10 pm	F2-2-10 Performance of RMS vs. HPPMS Cr/Cr_2O_3 Films in Protection against Metal Dusting, M. PÉREZ, O. SALAS, ITESM-CEM, Mexico, J. LIN, Colorado School of Mines, US, J. OSEGUERA, D. MELO-MAXIMO, ITESM-CEM, Mexico, R. TORRES, PUCPR, Brazil, C. LEPIENSKI, UFPR, Brazil, R. DE SOUZA, Usp, Brazil	F3-1-10 Modification of Multi-walled Boron Nitride Nanotubes by Metal Ion Implantation, D. SHTANSKY, E. OBRAZTSOVA, A. SHEVEKO, A.M. KOVALSKII, National University of Science and Technology "MISIS", Russian Federation, M. YAMAGUCHI, D.V. GOLBERG, National Institute for Materials Science, Japan
5:30 pm	**Awards Convocation-5:45 p.m.** **San Diego Room** **Honorary Lecturer-William D. Sproul** **"40 Years of Advancement in PVD Technology"** **Awards Reception will follow the Convocation at 7:30 p.m. Poolside**	

Thursday Morning, May 2, 2013

	Hard Coatings and Vapor Deposition Technology Room: Royal Palm 4-6 - Session B2-1 CVD Coatings and Technologies Moderators: E. Blanquet, CNRS, France, S. Ruppi, Walter AG, Germany	Tribology & Mechanical Behavior of Coatings and Engineered Surfaces Room: Golden West - Session E2-4 Mechanical Properties and Adhesion Moderators: M.T. Lin, National Chung Hsing University, Taiwan, R. Chromik, McGill University,Canada, D. Bahr, Washington State University, US
8:00 am	B2-1-1 Invited New Developments in the Field of CVD Hard Coatings, I. ENDLER, Fraunhofer IKTS, Germany	E2-4-1 3D Micro Scratch Tests in Combination with a Comprehensive Stress Analysis – a New Tool for the Understanding of Surface Failures, T. CHUDOBA, ASMEC Advanced Surface Mechanics GmbH, Radeberg, Germany, N. SCHWARZER, Saxonian Institute of Surface Mechancis, Germany, A. GIES, OC Oerlikon Balzers AG, Liechtenstein
8:20 am	Invited talk continued.	E2-4-2 A New Dynamic Impact and Sliding Wear Testing Method for the Tribological Evaluation of Treated Surfaces, P. EPAMINONDA, C. REBHOLZ, University of Cyprus, Cyprus
8:40 am	B2-1-3 CVD $Ti_{1-x}Al_xN$ Coatings for Mass Production, H. HOLZSCHUH, W. BUERGIN, SuCoTec AG, Switzerland	E2-4-3 Laser Shock Adhesion Test (LASAT) of EB-PVD TBCs: Towards an Industrial Application, G. BÉGUÉ, V. GUIPONT, M. JEANDIN, Mines-ParisTech, France, P. BILHE, J.Y. GUÉDOU, Snecma, SAFRAN Group, France
9:00 am	B2-1-4 The Development of a CVD Material for Thermally Oxidative Environments with High Hydrophobicity and Oleophobicity, and Good Wear Resistance with a Low Friction Coefficient, D. SMITH, J. MATTZELA, P. SILVIS, SilcoTek Corporation, US	E2-4-4 Self-organized Thin Film Buckling Patterns, S. GRACHEV, J.-Y. FAOU, Saint-Gobain Recherche, France, G. PARRY, SIMaP, France, E. BARTHEL, Saint-Gobain Recherche, France
9:20 am	B2-1-5 Phase Selective Deposition of α-Al_2O_3 by Thin Layers of TiO_2, B.E. BOMAN, D. FONDELL, S. MUNKTELL, Uppsala University, Angstrom Laboratory, Sweden, O. ALM, T. LARSSON, Seco tools AB, Sweden	E2-4-5 Determination of the Young´s Modulus of Hard Coatings on Soft Polymer Substrates, T. SANDER, S. TREMMEL, S. WARTZACK, Friedrich-Alexander-University Erlangen-Nuremberg, Germany
9:40 am	B2-1-6 Influence of the N/Al Ratio in Gas Phase on the Crystalline Quality of AlN Grown by HTCVD on c-sapphire., R. BOICHOT, N. COUDURIER, Grenoble INP, France, E. BLANQUET, M. PONS, CNRS, France	E2-4-6 Nanoscale Mechanical Mapping at a Wide Range of Deformation Rates with AFM, B. PITTENGER, S. MINNE, C. SU, Bruker Nano Surfaces Division, US
10:00 am	B2-1-7 Growth of HfC and Nanostructured Multilayer HfC/SiC Coatings by DLICVD, G. BOISSELIER, F. MAURY, CIRIMAT, France, F. SCHUSTER, CEA-Saclay, France	E2-4-7 The Effective Indenter Concept and its Extension into the Time Domain, N. BIERWISCH, N. SCHWARZER, Saxonian Institute of Surface Mechanics, Germany
10:20 am	B2-1-8 Industrial Scale Production of HFCVD Diamond Coatings, O. LEMMER, C. SCHIFFERS, M. FRANK, B. MESIC, CemeCon AG, Germany, M. RÜFFER, DiaCCon GmbH, Germany, S. ROSIWAL, University Erlangen-Nürnberg, Germany	E2-4-8 Determining Average Effective X-ray Elastic Constant (AEXEC) of Hard Coatings by Combining $\cos^2\alpha \sin^2\psi$ X-ray Diffraction and Laser Curvature Methods, A. WANG, G.P. YU, J.H. HUANG, National Tsing Hua University, Taiwan, Republic of China
10:40 am	B2-1-9 Gradient of Tribological and Mechanical Properties of Diamond-like Carbon Films Grown on Ti6Al4V Alloy with Different Condition of Interlayer Preparation, P. SILVA, G. MARTINS, J. MACHADO, E. CORAT, Instituto Nacional de Pesquisas Espaciais (INPE), Brazil, V. TRAVA-AIROLDI, Instituto Nacional de Pesquisas Espaciais (INPE, Brazil	E2-4-9 Fatigue Property Enhancements of Crystalline Metallic Substrates by Coating Thin Film Metallic Glasses, C.H. CHANG, J.P. CHU, C.M. LEE, National Taiwan Univ. of Sci. and Tech., Taiwan, Republic of China
11:00 am		E2-4-10 Bending Ductility Enhancement of Bulk Metallic Glass by Surface Treatment S, J.P. CHU, C.C. YU, National Taiwan Univ. of Sci. and Tech., Taiwan, Republic of China
11:20 am		E2-4-11 Crystal Orientation Effect on the Mechanical Behaviour of Al_2O_3 Coatings at Ambient Temperature, V. BHAKHRI, Imperial College London - South Kensington Campus, UK, R. MSAOUBI, Seco tools AB, F. GIULIANI, Imperial College London - South Kensington Campus, UK, E. BOUZAKIS, Fraunhofer Project Center for Coatings in Manufacturing (PCCM), Greece
11:40 am		
12:00 pm	**ICMCTF 2014 Planning Meeting** **12:00-1:15 p.m.** **Room: Royal Palm 4-6** **All Interested Parties are Welcome**	**VAMAS TWA 22 Annual General Meeting** **Mechanical Property Measurements of Thin Films and Coatings** **Room: Royal Palm 1-3** **12:15-1:15 p.m.**

Thursday Morning, May 2, 2013

	New Horizons in Coatings and Thin Films Room: Sunrise - Session F4-1 New Oxynitride Coatings Moderators: W. Kalss, OC Oerlikon Balzers AG, Liechtenstein, S. Ulrich, Karlsruhe Institute of Technology, Germany	Applications, Manufacturing, and Equipment Room: California - Session G6-1 Advances in Industrial PVD & CVD Deposition Equipment Moderators: N. Bagcivan, RWTH Aachen University, Germany, M. Schuisky, Sandvik Machining Solutions, Sweden
8:00 am	F4-1-1 Invited Oxynitride Coatings by Reactive Arc Evaporation, D. KURAPOV, OC Oerlikon Balzers AG, Liechtenstein	
8:20 am	Invited talk continued.	
8:40 am	F4-1-3 Nitride and Oxy-Nitride Coatings for Application on Injection Moulding Tools, N. BAGCIVAN, K. BOBZIN, Surface Engineering Institute - RWTH Aachen University, Germany, C. HOPMANN, Institute of Plastics Processing - RWTH Aachen University, Germany, R.H. BRUGNARA, Surface Engineering Institute - RWTH Aachen University, Germany	G6-1-3 Invited Recent Developments in Pulsed I-PVD Technology for Sputtering Thin Films of Oxides, Nitrides and DLC for Tribological, Optical, Electrical and other Applications, R. CHISTYAKOV, Zpulser LLC, US
9:00 am	F4-1-4 Effects of Si and Y in Structural Development of (Al,Cr,Si/Y)O_xN_{1-x} Thin Films Deposited by Magnetron Sputtering, H. NAJAFI, A. KARIMI, D. ALEXANDER, Ecole Polytechnique Fédérale de Lausanne, Switzerland, P. DESSARZIN, M. MORSTEIN, PLATIT AG, Switzerland	Invited talk continued.
9:20 am	F4-1-5 Two-phase Single Layer Al-O-N Nanocomposite Films with Enhanced Resistance to Cracking, R. JILEK, J. MUSIL, T. TOLG, R. CERSTVY, University of West Bohemia, Czech Republic	G6-1-5 Optical Emission Spectroscopy of HiPIMS Coatings at Industrial Scale, R. CREMER, T. TAKAHASHI, KCS Europe GmbH, Germany, S. HIROTA, Kobe Steel Ltd., Japan
9:40 am	F4-1-6 Phase Formation of TiAlNO Thin Films, M. TO BABEN, F. KRUSCHEWSKI, M. HANS, J. SCHNEIDER, RWTH Aachen University, Germany	G6-1-6 Advances in Process Technology and Deposition Equipment for HiPIMS Coatings for Cutting Tools, C. SCHIFFERS, T. LEYENDECKER, O. LEMMER, W. KÖLKER, CemeCon AG, Germany
10:00 am	F4-1-7 Thermodynamic Modeling in the Materials System Ti-Al-O-N, H.J. SEIFERT, Karlsruhe Institute of Technology, Germany	G6-1-7 QuadCoatings$^{4®}$, a New Generation of PVD Coatings for High-Performance Cutting Applications, A. LUEMKEMANN, M. MORSTEIN, P. DESSARZIN, T. CSELLE, PLATIT AG, Switzerland, B. TORP, PLATIT Inc., US, M. JILEK JR., PLATIT Pivot a.s., Czech Republic
10:20 am	F4-1-8 Design of Thermal Conductivity of Hard Oxynitride Coatings, M. BÖTTGER, V. SHKLOVER, ETH Zurich, Department of Materials, Switzerland, E. LEWIN, J. PATSCHEIDER, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland, D. CAHILL, University of Illinois at Urbana-Champaign, US, M. SOBIECH, OC Oerlikon Balzers AG, Liechtenstein	G6-1-8 About the Novel HI3 Deposition Technique, O. JARRY, G. ERKENS, J. VETTER, J. MUELLER, T. KRIENKE, Sulzer Metaplas, Germany
10:40 am	F4-1-9 Oxides, Nitrides and Oxinitrides of Silicon on Non-silicon Substrates with Tailored Mechanical, Optical, Electrical and Chemical Properties, U. BECK, A. HERTWIG, M. GRIEPENTROG, M. WEISE, BAM Berlin, Germany	G6-1-9 New Arc Evaporation Technology CARC^{+}: High Performance Coatings Deposited at High Deposition Speeds, M. EERDEN, F. PAPA, D. DERCKX, T. KRUG, Hauzer Techno Coating, BV, Netherlands
11:00 am	F4-1-10 The Consequence of Different Sputtering Parameters on Optical, Wettability and Structural Characterization of Chromium Oxynitride Thin films, S. RAWAL, Indian Institute of Technology Roorkee and Charotar Univ. of Science and Tech., India, A. CHAWLA, University of Petroleum and Energy Studies, India, R. JAYAGANTHAN, Indian Institute of Technology Roorkee and Indian Institute of Technology, India, A. JOSHI, G.H. Patel College of Engineering & Technology, India, R. CHANDRA, Indian Institute of Technology Roorkee, India	G6-1-10 The LAM Family – Tools for Production of ta-C Coatings with Excellent Properties, M. FALZ, M. HOLZHERR, K.-D. STEINBORN, T. SCHMIDT, VTD Vakuumtechnik Dresden GmbH, Germany, H.-J. SCHEIBE, A. LESON, V. WEIHNACHT, Fraunhofer-Institut für Werkstoff- und Strahltechnik, IWS Dresden, Germany
11:20 am		
11:40 am 12:00 pm	**ICMCTF 2014 Planning Meeting** **12:00-1:15 p.m.** **Room: Royal Palm 4-6** **All Interested Parties are Welcome**	**VAMAS TWA 22 Annual General Meeting** **Mechanical Property Measurements of Thin Films and Coatings** **Room: Royal Palm 1-3** **12:15-1:15 p.m.**

Thursday Morning, May 2, 2013

Topical Symposia
Room: Royal Palm 1-3 - Session TS2-1

Advanced Characterization of Coatings and Thin Films
Moderators: S. Korte, University of Erlangen-Nürnberg, Germany, M. Sebastiani, University of Rome "Roma Tre", Italy, F. Giuliani, Imperial College London - South Kensington Campus, UK

8:00 am	TS2-1-1 Correlative Analysis of Phase and Microstructural Evolution of Rapidly Solidified Metallic Multilayers by Transmission Electron Microscopy and Atom Probe Tomography, P. LEIBENGUTH, I. SCHRAMM, F. MÜCKLICH, Saarland University and Materials Engineering Center Saarland, Germany	
8:20 am	TS2-1-2 *In situ* Transmission Electron Microscopy Studies of Metal Diffusion on Ceramic Coatings, I. JOUANNY, C. NGO, University of California, Los Angeles, US, J. PALISAITIS, Linköping University, Sweden, P.H. MAYRHOFER, Vienna University of Technology, Austria, L. HULTMAN, P. PERSSON, Linköping University, Sweden, S. KODAMBAKA, University of California, Los Angeles, US	
8:40 am	TS2-1-3 Invited Advanced Transmission Electron Microscopy Methods: Going beyond Imaging, C. SCHEU, LMU Munich, Germany	
9:00 am	Invited talk continued.	
9:20 am	TS2-1-5 *In Situ* Transmission Electron Microscopy Studies of Thermochemical Stability of TiO_2/C Core/Shell Nanocrystals, I. JOUANNY, S. KODAMBAKA, University of California, Los Angeles, US	
9:40 am	TS2-1-6 Evaluation of Laboratory and Synchrotron Nanobeam X-Ray Diffraction Methods for the Characterization of Residual Stress Gradients in Hard Coatings, M. STEFENELLI, Materials Center Leoben Forschung GmbH, Austria, R. DANIEL, Montanuniversität Leoben, Austria, A. RIEDL, Materials Center Leoben Forschung GmbH, Austria, M. BARTOSIK, Montanuniversität Leoben, Austria, M. BURGHAMMER, European Synchrotron Radiation Facility, France, C. MITTERER, J. KECKES, Montanuniversität Leoben, Austria	
10:00 am	TS2-1-7 Cross-Sectional X-ray Nanodiffraction on a Graded Multiphase Cr-N Thin Film, M. BARTOSIK, Christian Doppler Laboratory for Application Oriented Coating Development at Montanuniversitat Leoben and Vienna University of Technology, Austria, J. KECKES, R. DANIEL, C. MITTERER, Montanuniversität Leoben, Austria, M. BURGHAMMER, European Synchrotron Radiation Facility, France, L. ZHOU, Vienna University of Technology and Montanuniversität Leoben, Austria, D. HOLEC, Montanuniversität Leoben, Austria, P.H. MAYRHOFER, Vienna Univ. of Technology, Austria	
10:20 am	TS2-1-8 Smart Approach of Surface Characterizations of Engineered Diamond-like Carbon (DLC) Coatings, D. CASCHERA, B. CORTESE, G. GIGLI, A. MEZZI, M. BRUCALE, G.M. INGO, T. DE CARO, G. PADELLETTI, CNR, Italy	
10:40 am	TS2-1-9 Multi-scale Residual Stress Analysis of AlN on (100)Si Substrate Deposited at Different Biases, M. RENZELLI, E. BEMPORAD, M. SEBASTIANI, University "Roma Tre" Rome, Italy	
11:00 am	TS2-1-10 Focused Ion Beam Milling for Localized Stress Measurement on Thin Films, M. KROTTENTHALER, F. HAAG, C. SCHMID, K. DURST, M. GÖKEN, University Erlangen-Nuremberg, Germany	
11:20 am	TS2-1-11 A New Methodology for the Analysis of Fracture Toughness and Residual Stress in Thin Hard Coatings, M. SEBASTIANI, E. BEMPORAD, University of Rome "Roma Tre", Italy, EG. HERBERT, GM. PHARR, University of Tennessee, US	
11:40 am		
12:00 pm	**ICMCTF 2014 Planning Meeting** **12:00-1:15 p.m.** **Room: Royal Palm 4-6** **All Interested Parties are Welcome**	**VAMAS TWA 22 Annual General Meeting** **Mechanical Property Measurements of Thin Films and Coatings** **Room: Royal Palm 1-3** **12:15-1:15 p.m.**

Thursday Afternoon, May 2, 2013

	Hard Coatings and Vapor Deposition Technology Room: Royal Palm 4-6 - Session B2-2 CVD Coatings and Technologies Moderators: E. Blanquet, CNRS, France, S. Ruppi, Walter AG, Germany	Tribology & Mechanical Behavior of Coatings and Engineered Surfaces Room: Golden West - Session E3-1+G Tribology of Coatings for Automotive and Aerospace Applications Moderators: S. Dixit, Plasma Technology Inc., US, G.L. Doll, University of Akron, US, A. Gies, OC Oerlikon Balzers AG, Liechtenstein
1:30 pm	B2-2-1 Invited Residual Stress and Crystallographic Texture in CVD Zirconia Thin Films, V. JI, M. ANDRIEUX, N. PRUD'HOMME, Université Paris-Sud 11, France	E3-1+G-1 Invited Friction Reduction Through Thermal Spray Coatings on Cylinder Running Surfaces of Internal Combustion Engines, PE. ERNST, Sulzer Metco AG (Switzerland), Switzerland
1:50 pm	Invited talk continued.	Invited talk continued.
2:10 pm	B2-2-3 The Deposition of Hydrogenated Silicon Films under Different H_2 and Ar Flow Rates by an ICP CVD System, C. LI, National Central University, Taiwan, Republic of China, J.H. HSIEH, Ming Chi University of Technology, Taiwan, Republic of China, K.L. HUANG, National Central University, Taiwan, Republic of China	E3-1+G-3 Thermal Treatment and Tribological Behaviour of Hybrid Coatings Deposited by Sol-gel Route on Martensitic Stainless Steel, S. RAHOUI, V. TURQ, J.P. BONINO, Université Paul Sabatier, France
2:30 pm	B2-2-4 High-rate PECVD with Metal Strip Magnetron for Hard and Other Functional Coatings, C. METZNER, B. SCHEFFEL, O. ZYWITZKI, Fraunhofer FEP, Germany	E3-1+G-4 Tribological Behavior of New Coatings for High Temperature Aeronautical Applications, M. BERNARD, V. FRIDRICI, P. KAPSA, LTDS - Ecole Centrale de Lyon, France
2:50 pm	B2-2-5 Study of the Uniformity of SiO_2 Films Developed in Atmospheric Plasmas, D. PAPPAS, J.H. YIM, V. RODRIGUEZ-SANTIAGO, A. BUJANDA, S.D. WALCK, US Army Research Laboratory, US	E3-1+G-5 Invited Thick TiSiCN-based Nanocomposite Coatings for Aerospace and Automotive Applications, R.H. WEI, Southwest Research Institute, US
3:10 pm	B2-2-6 Semi-empirical Modeling of the Optical Gap of Plasma-deposited a-C:H:F, a-C:H:Cl and a-C:H:Si:O:F Films, A. NETO, T. GONÇALVES, R. TURRI, UNESP, Brazil, W. SCHREINER, UFPR, Brazil, D. GALVÃO, UNICAMP, Brazil, S. DURRANT, UNESP, Brazil	Invited talk continued.
3:30 pm	B2-2-7 The $SiO_xC_yH_z$ Hydrophobic Film with Chemical and Mechanical Properties Using PECVD by Controlling the Plasma Process, J.S. LEE, S.B. JIN, CHOI, CHOI, HAN, Institute for Plasma-Nano Materials, Center for Advanced Plasma Surface Technology, Sungkyunkwan University, Korea	E3-1+G-7 In-situ Real Time Solid Particle Erosion Testing Methodology for Hard Protective Coatings, E BOUSSER, L. MARTINU, École Polytechnique de Montréal, Canada, J.E. KLEMBERG-SAPIEHA, Ecole Polytechnique de Montréal, Canada
3:50 pm	B2-2-8 Modeling Surface Processes and Kinetics of Compound Layer Formation during Plasma Nitriding of Pure Iron, F. CAZARES, A. JIMENEZ-CENISERO, ITESM-CEM, Mexico, J. OSEGUERA, ITESM-CEM,Mexico, F. CASTILLO, ITESM-CEM, Mexico	E3-1+G-8 Characterization and Tribological Investigation of $TiSi_xC_y$ Wear Protective Coatings, J. MATTHEY, Haute Ecole Arc Ingenierie, Switzerland
4:10 pm		E3-1+G-9 Effects TiN and TaN Barrier Layers on the Rmergence of Ag and Cu Particles and the Subsequent Mechanical and Antibacterial Properties of TaN-(Ag,Cu) Nanocomposite Films, J.H. HSIEH, Y.R. CHO, Y.T. SU, Ming Chi University of Technology, Taiwan, Republic of China
4:30 pm		
4:50 pm		
5:10 pm		
5:30 pm	**Poster Session 5:00-7:00 p.m. Grand Hall Reception begins at 6:00 p.m.**	

Thursday Afternoon, May 2, 2013

	New Horizons in Coatings and Thin Films Room: Sunrise - Session F5-1 Coatings for Compliant Substrates Moderators: B Beake, Micro Materials Ltd., UK, N. Moody, Sandia National Laboratories, US	Applications, Manufacturing, and Equipment Room: California - Session G5-1 Coatings, Pre-Treatment, Post-Treatment, and Duplex Technology Moderators: T. Takahashi, KCS Europe GmbH, Germany, S. Brahmandam, Kennametal, Inc., US
1:30 pm	F5-1-1 Deformation Domains of Nanostructured Metallic Thin Film onto Polyimide Substrate under Controlled Biaxial Deformation, P.O. RENAULT, E. LE BOURHIS, University of Poitiers, France, D. FAURIE, University of Paris 13, France, S. DJAZIRI, P.O. GOUDEAU, University of Poitiers, France, D. THIAUDIÈRE, C. MOCUTA, Synchrotron SOLEIL, France, G. GEANDIER, University of Lorraine, France	G5-1-1 Nitriding Duration Reduction with Improving Mechanical Characteristic and Fatigue Behavior, the Beneficial Effect of Prior Severe Shot Peening, A. MORIDI, S.M. HASSANI-GANGARAJ, Politecnico di Milano, Italy, S. VEZZÙ, Associazione Civen, Italy, M. GUAGLIANO, Politecnico di Milano, Italy
1:50 pm	F5-1-2 Stress Measurement in Thin Films: Micro-focus Synchrotron X-ray Diffraction Combined with Focused Ion Beam Patterning for d_o Evaluation, N. BAIMPAS, University of Oxford, UK, E. LE BOURHIS, Université de Poitiers, France, S. EVE, ENSICAEN, CRISMAT, France, D. THIAUDIÈRE, Synchrotron SOLEIL, France, C. HARDIE, A.M. KORSUNKY, University of Oxford, UK	G5-1-2 Growth Kinetics and Mechanical Properties of Boride Layers Formed at the Surface of ASTM F-75 Biomedical Alloy, I. CAMPOS-SILVA, D. BRAVO-BÁRCENAS, A. MENESES-AMADOR, Instituto Politecnico Nacional, Mexico, H. CIMENOGLU, Istanbul Tech. Univ., Turkey, U. FIGUEROA-LÓPEZ, ITESM-CEM, Mexico
2:10 pm	F5-1-3 Invited Wrinkling and Delamination of Thin Films on Compliant Substrates, R. HUANG, University of Texas at Austin, US	G5-1-3 Invited Combining Thermal Spraying and PVD Technologies: a New Aproach of Duplex Surface Engineering for Ti Alloys, F. CASADEI, M. TULUI, Centro Sviluppo Materiali SpA, Italy
2:30 pm	Invited talk continued.	Invited talk continued.
2:50 pm	F5-1-5 Interfacial Failure in a Model Polymer-metal Thin Film Structure, R. FRIDDLE, D. REEDY, E. CORONA, D. ADAMS, Sandia National Laboratories, US, M. KENNEDY, Clemson University, US, CORDILL, University of Leoben, Austria, D. BAHR, Washington State University, US, N. MOODY, Sandia National Laboratories, US	G5-1-5 Corrosion Testing by Potentiodynamic Polarization and EIS in Borided Steels, I. MEJÍA-CABALLERO, Instituto Politecnico Nacional, Mexico, H. HERRERA-HERNÁNDEZ, Universidad Autónoma Metropolitana- Azcapotzalco, Mexico, J. MARTÍNEZ-TRINIDAD, Instituto Politecnico Nacional, Mexico, M. PALOMAR-PARDAVÉ, M. ROMERO-ROMO, UAM-A, Mexico, I. CAMPOS-SILVA, Instituto Politecnico Nacional, Mexico
3:10 pm	F5-1-6 Fatigue-corrosion Behavior of Flexible Optoelectronic Device Electrodes, T. BEJITUAL, K. SIERROS, D. CAIRNS, West Virginia University, US	G5-1-6 Improved Adhesion of Diamond Coatings on Cemented Carbide Tools by Surface Reconstruction via MPCVD, M. MEE, S. MEIER, Fraunhofer IWM, Germany
3:30 pm	F5-1-7 Load Bearing Capacity of Hydrogenated Amorphous Carbon Coatings on Ultrafine Grained Al Substrates, C. SCHMID, C. SCHUNK, University of Erlangen-Nürnberg, Germany, S. MEIER, Fraunhofer Institute for Mechanics of Materials, IWM, Germany, M. GÖKEN, K. DURST, University Erlangen-Nuremberg, Germany	G5-1-7 Improvement in the Tribological Characteristics of Si-DLC Coating by Laser Surface Texturing at Elevated Temperatures, A. AMANOV, S. SASAKI, Tokyo University of Science, Japan
3:50 pm	F5-1-8 Three-dimensional Finite Element Analysis of Adhesive Failure on Coated Systems under Uniaxial Tensile Tests, N. FUKUMASU, University of São Paulo, Brazil, F. SILVA, Federal University of ABC, Brazil, R. SOUZA, University of São Paulo, Brazil	
4:10 pm	F5-1-9 Annealing Induced Structural Evolution and Optical Properties of Block Copolymer Templated Nanostructured Tungsten Oxide Films, C.L. WU, National Cheng Kung Univ., Taiwan, Republic of China, C.K. LIN, Taipei Medical University, Taiwan, Republic of China, C.K. WANG, National Cheng Kung Univ., Taiwan, Republic of China, S.C. WANG, Southern Taiwan University of Science and Technology, Taiwan, Republic of China, J.L. HUANG, National Cheng Kung Univ., Taiwan, Republic of China	
4:30 pm		
4:50 pm		
5:10 pm		
5:30 pm	**Poster Session 5:00-7:00 p.m.** **Grand Hall** **Reception begins at 6:00 p.m.**	

Thursday Afternoon, May 2, 2013

Topical Symposia
Room: Royal Palm 1-3 - Session TS3-1

Energetic Materials and Micro-Structures for Nanomanufacturing
Moderators: C. Rebholz, University of Cyprus, D. Adams, Sandia National Laboratories, US

1:30 pm	TS3-1-1 Invited Hermetic and Room-Temperature Wafer-Level-Packaging Based on Nanoscale Energetic Systems, J. BRAEUER, J. BESSER, Fraunhofer ENAS, Germany, E. TOMOSCHEIT, Chemnitz University of Technology, Germany, M. WIEMER, T. GESSNER, Fraunhofer ENAS, Germany	
1:50 pm	Invited talk continued.	
2:10 pm	TS3-1-3 Self-Sustained Deflagration Reactions in Sputter-deposited Al_xPt_y Multilayers, D. ADAMS, R. REEVES, M. RODRIGUEZ, E. JONES, JR., Sandia National Laboratories, US	
2:30 pm	TS3-1-4 Visualizing Mass Transport in theSself-propagating Formation of B2-RuAl from PVD Multilayers, C. PAULY, H. ABOULFADL, Saarland University, Germany, K. WOLL, Johns Hopkins University, US, F. MÜCKLICH, Saarland University, Germany	
2:50 pm	TS3-1-5 Ti/Al Multilayer Coating Releasing Heat During Slow Thermal Annealing, P. STUPKA, J. MUSIL, S. PROKSOVA, R. CERSTVY, P. ZEMAN, University of West Bohemia, Czech Republic	
3:10 pm	TS3-1-6 Invited Fabrication and Characterization of Microstructured Thermites Derived from Electrophoretic Deposition, A.E. GASH, K.T. SULLIVAN, J.W. KUNTZ, Lawrence Livermore National Laboratory, US	
3:30 pm	Invited talk continued.	
3:50 pm	TS3-1-8 Effect of Surface Functionalization of Fuels on Nanocomposite Thermites, K. KAPPAGANTULA, C. FARLEY, M. PANOTYA, Texas Tech University, US, J. HORN, Naval Research Laboratory, US	
4:10 pm	TS3-1-9 Exothermic Reactions in Spark Ignitable Green Compacts of Continuously Ball-milled Al/Ni Powders, A. HADJIAFXENTI, University of Cyprus, Cyprus, I. GUNDUZ, Northeastern University, US, C. DOUMANIDIS, C. REBHOLZ, University of Cyprus, Cyprus	
4:30 pm	TS3-1-10 Optimization and Functionalization of Anodized Titania Nanotubes for Redox Supercapacitor, Z. ENDUT, M. HAMDI, W.J. BASIRUN, University of Malaya, Malaysia	
4:50 pm		
5:10 pm		
5:30 pm	**Poster Session 5:00-7:00 p.m.** **Grand Hall** **Reception begins at 6:00 p.m.**	

Thursday Afternoon Poster Sessions

Coatings for Use at High Temperature
Room: Grand Hall - Session AP

Symposium A Poster Session
Moderators: A Bolcavage, Rolls Royce,US, B. Hazel, Pratt and Whitney, US

5:00 pm

AP1

Thermal Stability of Ir – Re Coatings Annealed in Oxygen Containing Atmospheres, LIN, National Tsing Hua University, Taiwan, Republic of China, Y.I. CHEN, National Taiwan Ocean University, Taiwan, Republic of China, H.Y. TSAI, National Tsing Hua University, Taiwan, Republic of China, K.C. LIU, National Taiwan Ocean University, Taiwan, Republic of China, Y.H. CHEN, Young Optics Inc.

AP2

Steam Oxidation of Al Slurry Coatings Deposited on Super304H, TP347H and TP347HFG, M. SERAFFON, A.T. FRY, National Physical Laboratory, UK

AP5

Structure of Pd-Zr and Pt-Zr Modified Aluminide Coatings Deposited by CVD Method on Nickel Superalloys, M. PYTEL, Rzeszów University of Technology, Poland, R. FILIP, M. GORAL, Rzeszow University of Technology, Poland, J. SIENIAWSKI, Rzeszów University of Technology, Poland

AP6

TBCs Deposited using New EB-PVD Smart Coater System, A. NOWOTNIK, Rzeszow University of Technology, Poland, M. GORAL, J. SIENIAWSKI, M. PYTEL, Rzeszów University of Technology, Poland

AP8

Influence of Deposition Parameters on Structure of Diffusion Aluminide Coatings Obtained by CVD Method on Rene 108 DS Superalloy, L. SWADZBA, B. WITALA, Silesian University of Technology, Poland, R. SWADZBA, Institute for Ferrous Metallurgy, Poland, M. HETMANCZYK, G. MOSKAL, B. MENDALA, Silesian University of Technology, Poland, L. KOMENDERA, AVIO Poland sp. z o.o., Poland

AP9

Research on High Temperature Property of Plasma Sprayed Lanthanum Cerium Oxide Thermal Barrier Coatings, R. WANG, T. WU, W. WANG, Beijing Aeronautical Technology Research Center, China

AP10

Calcium-Magnesium Aluminosilicate (CMAS) Reactions and Degradation Mechanisms of Advanced Environmental Barrier Coatings, N. AHLBORG, The Ohio State University, US, D. ZHU, NASA Glenn Research Center, US

AP11

An Experimental Method for Determining the Mode II Interfacial Toughness of Thermal Barrier Coatings, S.J. LOCKYER-BRATTON, J.A. EL-AWADY, K.J. HEMKER, Johns Hopkins University, US

AP12

Isothermal Oxidation of a Single Crystal N5 Superalloy in the Range of 1050°C to 1150°C, R. SWADZBA, Institute for Ferrous Metallurgy, Poland, B. WITALA, L. SWADZBA, Silesian University of Technology, L. KOMENDERA, AVIO Polska

AP13

Boron Distribution in High Temperature Silicide Coatings for Niobium Alloys: An Analytical Problem Which can be Solved using a Coupled WDS-EDS System, S. MATHIEU, L. PORTEBOIS, N. CHAIA, Université de Lorraine, France

AP14

Evaluation of EBPVD Top Coat Modulus Using Micro-beam Bending Techniques, B. ZHANG, K.J. HEMKER, Johns Hopkins University, US

Hard Coatings and Vapor Deposition Technology
Room: Grand Hall - Session BP

Syposium B Poster Session
Moderators: A. Anders, Lawrence Berkeley National Laboratory, US, C. Rebholz, University of Cyprus, Cyprus, J. Vetter, Sulzer Metaplas, Germany

5:00 pm

BP1

High Temperature Wettability of Ion Implanted Multicomponent CrAlSiN by Molten Glass, YY CHANG, H.M. LAI, National Formosa University, Taiwan, Republic of China, H.Y. KAO, MingDao University, Taiwan, Republic of China

BP2

Mechanical Properties and Impact Resistance of Multilayered CrAlSiN/TiN Coatings, Y.Y. CHANG, National Formosa University, Taiwan, Republic of China, Y.Y. LIOU, MingDao University, Taiwan, Republic of China

BP3

Mechanical Properties and Physicochemical Characteristics of CrN/Si_3N_4 Multilayers, C. AGUZZOLI, T. SOARES, Universidade de Caxias do Sul, Brazil, G. SOARES, Universidade Federal do Rio Grande do Sul, Brazil, C.A. FIGUEROA, Universidade de Caxias do Sul, Brazil, I. BAUMVOL, Universidade de Caxias do Sul, Brazil and Universidade Federal do Rio Grande do Sul, Brazil

BP4

Reliability Characteristics of Multi-Step Deposition-Annealed HfO_2 Film under Static and Dynamic Stress, YL CHENG, C.Y. HSIEH, National Chi-Nan University, Taiwan, Republic of China, T.C. BO, National Chi Nan University, Taiwan, Republic of China

BP5

Wear Properties and Microstructure Characterization of Various Fe-W-C-B-Cr System Clad Layers, Y.C. LIN, Y.C. CHEN, National Taiwan University, Taiwan, Republic of China

BP6

Effect of Cu Diffusion on Electrical and Reliability Characteristics for Low Dielectric Constant Dielectric, YM CHANG, National Chiao Tung University, Taiwan, Republic of China, YL CHENG, K.C. KAO, National Chi-Nan University, Taiwan, Republic of China, J.P. LEU, National Chiao Tung University, Taiwan, Republic of China, T.C. BO, National Chi-Nan University, Taiwan, Republic of China

BP7

Zirconium Modified Aluminide Coatings Obtained by the CVD and the PVD Methods., J. ROMANOWSKA, M. ZAGULA-YAVORSKA, J. SIENIAWSKI, Rzeszów University of Technology, Poland, J. MARKOWSKI, Wrocław University of Technology, Poland

BP8

Phase Stability, Thermal Stability and Oxidation Resistance of Arc evaporated Ti-Al-Ta-N Coatings, R. HOLLERWEGER, Christian Doppler Laboratory for Application Oriented Coating Development at Montanuniversitat Leoben and Vienna University of Technology, Austria, M. ARNDT, R. RACHBAUER, OC Oerlikon Balzers AG, Liechtenstein, P. POLCIK, PLANSEE Composite Materials GmbH, Germany, J. PAULITSCH, P.H. MAYRHOFER, Vienna University of Technology, Austria

BP9

Superhard and Corrosion Protective Coatings of Ta-Si-N and Nb-Si-N, G. RAMIREZ, Argonne National Laboratory, US, S. RODIL, S. MUHL, Universidad Nacional Autónoma de México - Instituto de Investigaciones en Materiales, Mexico, E. CAMPS, L. ESCOBAR-ALARCON, Instituto Nacional de Investigaciones Nucleares de Mexico

BP10

Simple Relationships Between Characteristics of Complex Nitrides and Electronegativities and Radii of Constituent Elements, V. PETRMAN, University of West Bohemia, Czech Republic, J. HOUSKA, University of West Bohemia - NTIS, Czech Republic

BP11

Internal Oxidation of Nanolaminated Nb–Ru Coatings, Y.I. CHEN, H.N. CHU, National Taiwan Ocean University, Taiwan, Republic of China

BP12

Phase Stability, Structural and Elastic Properties of Ternary $Cr_{1-x}TM_xN$ alloys: An Ab-initio Study, L. ZHOU, Vienna University of Technology and Montanuniversität Leoben, Austria, D. HOLEC, Montanuniversität Leoben, Austria, P.H. MAYRHOFER, Vienna University of Technology, Austria

BP13

Substrate Bias eEfects on the Wear and Hydrophobic Properties of CrAlN Coatings Prepared by Close Filed Unbalanced Magnetron Sputtering, Y.S. YANG, T.P. CHO, J.H. LIN, National Kaohsiung First Univ. of Sci. and Tech., Taiwan

BP14

Electrolyte-Insulator-Semiconductor (EIS) with Gd_2O_3-based Sensing Membrane for pH-Sensing Applications, H. CHEN, National Chi-Nan University, Taiwan, Republic of China, C.H. KAO, Chang Gung University, Taiwan

BP15

Reactive and Non-reactive Sputter Deposition of Metallic, Intermetallic and Ceramic Target Materials to Prepare Al-Cr-N Coatings, C. SABITZER, Christian Doppler Laboratory for Application Oriented Coating Development at the Institute of Materials Science and Technology, Vienna University of Technology, Austria, J. PAULITSCH, Vienna University of Technology, Austria, P. POLCIK, PLANSEE Composite Materials GmbH, Germany, M. ARNDT, R. RACHBAUER, OC Oerlikon Balzers AG, Liechtenstein, P.H. MAYRHOFER, Vienna University of Technology, Austria

BP16

The Young's Modulus of Composite Spacer Contributed on the Stress Effect of N-MOSFET with Contact-etch-stop Layer Stressor, Y.C. CHIOU, National Chiayi University, Taiwan, Republic of China, C.C. LEE, T.L. TZENG, Chung Yuan Christian University, Taiwan, Republic of China, C.C. HUANG, National Nano Device Laboratories, Taiwan, Republic of China

BP17

Thermal Stability and Oxidation Resistance of TiAlN/TaAlN Multilayer Coatings, C.M. KOLLER, Christian Doppler Laboratory for Application Oriented Coating Development at Montanuniversitat Leoben and Vienna University of Technology, Austria, R. HOLLERWEGER, Vienna University of Technology, Austria, R. RACHBAUER, OC Oerlikon Balzers AG, Liechtenstein, P. POLCIK, PLANSEE Composite Materials GmbH, Germany, J. PAULITSCH, Vienna University of Technology and Montanuniversität Leoben, Austria, P.H. MAYRHOFER, Vienna University of Technology, Austria

BP18

Investigation of Corrosion Properties in TiAlN/TiCrN Multilayer Coatings Deposited by CFUBMS, E. DEMIRCI, Atatürk University, Turkey, O. BARAN, Erzincan University, Turkey, Y. TOTIK, I. EFEOGLU, T. MORTEZA, Atatürk University, Turkey

BP19

Simulation of Neutral Gas Dynamics for PVD DC-MSIP and HPPMS Processes, K. BOBZIN, N. BAGCIVAN, S. THEISS, R.H. BRUGNARA, M. SCHÄFER, Surface Engineering Institute - RWTH Aachen University, Germany, R. BRINKMANN, T. MUSSENBROCK, Institute for Theoretical Electrical Engineering - Ruhr University Bochum, Germany, J. TRIESCHMANN, Surface Engineering Institute - RWTH Aachen University, Germany

BP20

Oxidation Resistance and Mechanical Properties of Ta – Si – N Coatings, Y.I. CHEN, K.Y. LIN, National Taiwan Ocean University, Taiwan, Republic of China

BP21

Structural and Optical Properties of Brominated Plasma Polymers, M. APPOLINARIO, A. NETO, UNESP, Brazil, W. SCHREINER, UFPR, Brazil, N. CRUZ, E. RANGEL, S. DURRANT, UNESP, Brazil

BP22

First Principles Study of Alloying Trends in Ti—Al—N and Cr—Al—N Systems, D. HOLEC, Christian Doppler Laboratory for Application Oriented Coating Development at Montanuniversitat Leoben and Vienna University of Technology, Austria, L. ZHOU, Vienna University of Technology and Montanuniversität Leoben, Austria, R. RACHBAUER, Montanuniversität Leoben, Austria, P.H. MAYRHOFER, Vienna University of Technology, Austria

BP23

Pulsed Laser Deposition of Tetrahedral Amorphous Carbon Layers (ta-C) – Properties in Dependence of Laser Fluence on the Target- Surface, K. GUENTHER, S. WEIBMANTEL, University of Applied Sciences Mittweida, Germany

BP24

Tribological Properties of TiN/TaN and TiN/TaN Doped CrY Multilayer Coatings at High Temperature, I. EFEOGLU, Atatürk University, Turkey, O. BARAN, Erzincan University, Turkey, E. DEMIRCI, Y. TOTIK, Atatürk University, Turkey

BP25

The Effect of Annealing Temperatures on the Hydrophobic Property of CrAlN Coatings, Y.S. YANG, T.P. CHO, J.H. LIN, S.H. YANG, National Kaohsiung First University of Science and Technology, Taiwan, Republic of China

BP26

Effect of CO Gas for CVD Ti(C,N,O) Coating Layers on MT-TiCN Ⅰ: CO Gas Effect, S. NA, J. KIM, E. LEE, D. KIM, S. SONG, M. SHARON, TaeguTec, Republic of Korea, B. MIN, Yeungnam University, Republic of Korea

BP27

Effect of CO Gas for CVD Ti(C,N,O) Coating Layers on MT-TICN Ⅱ: Temperature Effect, S. NA, E. LEE, J. KIM, D. KIM, S. SONG, H. HAN, TaeguTec, Republic of Korea, J. LEE, Yeungnam University, Republic of Korea

BP28

Wear and Oxidation Behaviors of Ti(C, N, O) Coatings, J.H. HSIEH, Y.L. LAI, Y.R. CHO, Ming Chi University of Technology, Taiwan, Republic of China

BP29

Improved Performance of Metal-based Dye-sensitized Solar Cells by Introducing a TiN Nanocrystalline Thin Film, W.L. TAI, F-Y. OUYANG, National Tsing Hua University, Taiwan, Republic of China

BP30

Super Smooth Nano-Structured Carbon Films with Cross-linked Graphitic Sheets Induced by ECR Ion Irradiation, X. FAN, Key Laboratory of Education Ministry for Modern Design and Rotor-Bearing System, School of Mechanical Engineering, Xi'an Jiaotong University, China, D.F. DIAO, School of Mechanical Engineering, Xi'an Jiaotong University; College of Mechatronics and Control Engineering, Shenzhen Univeristy, China, L. YANG, Key Laboratory of Education Ministry for Modern Design and Rotor-Bearing System, School of Mechanical Engineering, Xi'an Jiaotong University, China

BP31

Influence of the Bilayer Period on the Structure of AlN and the Mechanical Properties of CrN/AlN Multilayer Coatings, P.H. MAYRHOFER, Vienna University of Technology, Austria, M. SCHLÖGL, Vienna University of Technology and Montanuniversität Leoben, Austria, B. MAYER, V CHAWLA, D. HOLEC, Montanuniversität Leoben, Austria

BP34

Mechanical Properties and Interface Adhesion of Molybdenum Single Layer on Soda-lime Glasses, H.H. SUNG, National Chung Hsing University, Taiwan, Republic of China, Z.C. CHANG, National Chin-Yi University of Technology, Taiwan, Republic of China, L.Y. KUO, F.S. SHIEU, National Chung Hsing University, Taiwan, Republic of China

BP35

Effects of Silicon Content on the Structure and Mechanical Properties of (AlCrTaTiMo)N Coatings by Reactive Magnetron Sputtering, D.C. TSAI, F.S. SHIEU, National Chung Hsing University, Taiwan, Republic of China

BP36

Effect of In-Situ Crystallization on the Microstructural and Photo-induced Properties of TiO_2 Coatings Prepared by Magnetron Sputtering, I. SAYAH, M. ARAB POUR YAZDI, LERMPS-IRTES, France, F. SCHUSTER, CEA-Saclay, France, A. BILLARD, Lrc Cea/irtes-Lermps, France

BP37

Thermal Stability of Quaternary TiZrAlN Sputtered Thin Films, G. ABADIAS, Institut P' - Universite de Poitiers, France, I. SALADUKHIN, S. ZLOTSKI, V. UGLOV, Belarussian State University, Belarus

BP38

The Development and Application on the Process Technique of $(Zr_xHf_{1-x})N$ Thin Film, Y.W. LIN, Instrument Technology Research Center, National Applied Research Laboratories, Taiwan, Republic of China, J.H. HUANG, Department of Engineering and System Science National Tsing Hua University, Taiwan, Republic of China, G.P. YU, Institute of Nuclear Engineering and Science National Tsing Hua University, Taiwan, Republic of China

BP39

Deposition of TiN Films by High Power Impulse Magnetron Sputtering, W. WU, S. SHIH, P. CHEN, C.L. CHANG, D.Y. WANG, MingDao University, Taiwan, Republic of China

BP40

Development of Uniform Coating Technique of Tetrahedral Amorphous-Carbon Film by T-shape Filtered-Arc-Deposition with Deflected Plasma beam and Multi-Motion Substrate Holder for Semispherical Object, H. TANOUE, H. OKUDA, Y. SUDA, H. TAKIKAWA, Toyohashi University of Technology, Japan, M. KAMIYA, Itoh Optical Industrial Co., Ltd., Japan, M. TAKI, Y. HASEGAWWA, N. TSUJI, Onward Ceramic Coating Co., Ltd., Japan

BP41

Optical Emission Spectroscopy of Cr-Al-C Arc Ion Plating Plasma, T. TAKAHASHI, R. CREMER, P. JASCHINSKI, KCS Europe GmbH, Germany

BP42

Growth of Boron Nitride with a High Temperature Chemical Vapor Deposition (HTCVD) Reactor using BCl3 and NH3 as Precursors, N. COUDURIER, R. BOICHOT, Grenoble INP, France, E. BLANQUET, M. PONS, CNRS, France

BP43

Novel TiAlN Nanostructured CVD Coatings with Superior Oxidation Resistance, J. KECKES, R. DANIEL, V. TERZIYSKA, C. MITTERER, Montanuniversität Leoben, Austria, A. KÖPF, R. WEIßENBACHER, R. PITONAK, Böhlerit GmbH, Kapfenberg, Austria

BP44

Silicon Carbide Interlayers for HFCVD Diamond on Cemented Carbide Cutting Tools, U. HECKMAN, Fraunhofer Institute for Surface Engineering and Thin Films, Germany, A. HAGEMANN, Fraunhofer Institute for Surface Engineering and Thin Films IST, Germany, J.A. OYANEDEL FUENTES, Institute for Machine Tools and Factory Management (IWF), TU Berlin, Germany, J. GÄBLER, M. HÖFER, Fraunhofer Institute for Surface Engineering and Thin Films IST, Germany, F. SAMMLER, Institute for Machine Tools and Factory Management (IWF), TU Berlin, Germany, L. SCHÄFER, Fraunhofer Institute for Surface Engineering and Thin Films IST, Germany, E. UHLMANN, Institute for Machine Tools and Factory Management (IWF), TU Berlin, Germany

BP45

Role of the Si-addition on the Mechanical and Tribological Properties of AlCrN-based Films Deposited by Cathodic Arc Deposition, A. BILLARD, IRTES-LERMPS-UTBM, France, F. LOMELLO, DEN/DANS/DPC/SEARS/LISL CEA, France, F. SANCHETTE, ICT, France, F. SCHUSTER, M. TABARANT, CEA, France

BP46

Influence of RF and Plasma Parameters on Film Properties for Layer Transfer by an Advanced PECVD Process Control Method, T. GROTJAHN, Fraunhofer IWM, Germany, R. ROTHE, Plasmetrex GmbH, Germany, S. MEIER, Fraunhofer IWM, Germany

BP47

Arc evaporated coatings for machining application, D. SCHLEGEL, ESTA, France, M. ARAB POUR YAZDI, IRTES-LERMPS-UTBM, France, F. LOMELLO, DEN/DANS/DPC/SEARS/LISL CEA, France, F. SANCHETTE, ICT, France, A. BILLARD, IRTES-LERMPS-UTBM, France, F. SCHUSTER, CEA, France

BP48

Structure and Properties of CrN/TiN Multilayer Coatings Deposited by Modulated Pulsed Power and Pulsed dc Magnetron Sputtering, Y. OU, J. LIN, Colorado School of Mines, US, I. DAHAN, Ben Gurion University of the Negev, Israel, B. WANG, J. MOORE, Colorado School of Mines, US, W. SPROUL, Reactive Sputtering, Inc., US, M. LEI, Dalian University of Technology, China

BP49

Hardness and Structure Evolution of Annealed Zr-TiAlN Films, R. PILEMALM, Linköping University, Sweden

BP50

Synthesis of the CrZrSiN Thin Films and its High Temperature Tribological Properties, D.J. KIM, J.H. LA, S.M. KIM, S.Y. LEE, Korea Aerospace University, Republic of Korea

BP51

Improvement of Wear Resistance of Nitrile Rubber Surfaces by Hydrocarbon Plasma Treatments, R. DOS SANTOS, E. SANTOS JR., S. CAMARGO JR., Federal University of Rio de Janeiro, Rio de Janeiro, RJ, Brazil.

BP53

Preparation and Characterization of Ti-Al-N Thin Films Deposited by Reactive Crossed Beam Pulsed Laser Deposition, L. ESCOBAR-ALARCON, Instituto Nacional de Investigaciones Nucleares de Mexico, Mexico, D. SOLIS-CASADOS, Universidad Autonoma del Estado de Mexico, Mexico, S. ROMERO, J. PEREZ-ALVAREZ, Instituto Nacional de Investigaciones Nucleares de Mexico, Mexico, G. RAMIREZ, Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de Mexico, México, S. RODIL, Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de Mexico, México, Mexico

BP54

Characterization of Diamond-like Carbon Film Synthesized by HIPIMS System for Medical Application, M.H. SHIH, W.C. CHEN, C.L. CHANG, D.Y. WANG, MingDao University, Taiwan, Republic of China

BP55

Design and Fabrication of Bilayer Wire Grid Polarizers (B-WGPs) with Sub-wavelength Metal Gratings, J.J. KIM, T.Y. KIM, W.Y. KIM, B.H. KU, P. PAZHANISAMI, C. HWANGBO, Inha University, Republic of Korea

BP56

Alumina Coatings for use under High Radiation Conditions, F. MAJID, S. RIAZ, S. NASEEM, University of the Punjab, Pakistan, I. AHMAD, G. HUSNAIN, National Centre of Physics, Pakistan

BP57

A Detailed Investigation into the Preparation and Properties of ZrO_2- Fe_2O_3 Coatings for Bio-Medical Applications, S. RIAZ, S. NASEEM, University of the Punjab, Pakistan

BP58

Preparation and Characterization of CIGAS Thin Films and Their Solar Cells, S. NASEEM, S. RIAZ, University of the Punjab, Pakistan

BP59

Effect of Droplet Inclusion in Arc-evaporated Multilayer Coatings on the Anisotropy of Thermal Conductivity, M. BÖTTGER, ETH Zurich, Department of Materials, Switzerland, A. GUSSAROV, ENISE, France, V. SHKLOVER, ETH Zurich, Department of Materials, Switzerland, J. PATSCHEIDER, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland, M. SOBIECH, OC Oerlikon Balzers AG, Liechtenstein

BP60

Structural, Electrical Conductivity and Mechanical Properties of TiN_x Thin Films, J. GOUPY, CEA Grenoble, France, P. DJEMIA, LSPM-CNRS, Université Paris 13, Sorbonne Paris-Cité, France, S. POUGET, CEA Grenoble, France, L. BELLIARD, UPMC-Institut des NanoSciences de Paris, France, G. ABADIAS, Institut P' - Universite de Poitiers, France, J.C. VILLÉGIER, CEA Grenoble, France, J.L. SAUVAGEOT, C. PIGOT, CEA Saclay, France

BP61

Tribological and Electrochemical Properties of HVOF Sprayed CrC-40NiCr and WC-40NiCr Coatings, P. OLUBAMBI, Z.H. MASUKU, B. OBADELE, T. RAPOO, Tshwane University of Technology, South Africa

BP62

TiCrN/NiMnSb Thin Film Heterostructures for Vibration Damping in MEMS, N. CHOUDHARY, D. KAUR, Indian Institute of Technology Roorkee, India

BP63

Characterization of a Cylindrical Planar Hollow Cathode and it's use for the Preparation of Bi Nanoparticles, S. MUHL, Universidad Nacional Autónoma de México - Instituto de Investigaciones en Materiales, Mexico, A. PEREZ, Universidad Nacional Autonoma de Mexico, Mexico, A. TENORIO, Universidad Nacional Autónoma de México - Instituto de Investigaciones en Materiales, Mexico

BP64

Theinfluence of the Inert and Reactive Gas Inlet Temperature and Pressure on the Reactive Sputtering Process Outcomes, S. FADDEEVA, J. OSEGUERA, ITESM-CEM, Mexico

BP65

Hardness and Elastic Modulus of Hard Coatings at High Temperatures, M. REBELO DE FIGUEIREDO, University of California Berkeley, M. TKADLETZ, Materials Center Leoben Forschung GmbH, R. HOLLERWEGER, Christian Doppler Laboratory for Application Oriented Coating Development at the Institute of Materials Science and Technology, Vienna University of Technology, Austria, A.J. HARRIS, Micro Materials Ltd, UK, M. ABAD, University of California Berkeley, P.H. MAYRHOFER, Vienna University of Technology, Austria, C. MITTERER, Montanuniversität Leoben, Austria, P. HOSEMANN, University of California Berkeley

BP66

Electrochemical and Impact Wear Behavior of TiCN, TiSiCN, TiCrSiCN, and TiAlSiCN Coatings, D. SHTANSKY, K.A. KUPTSOV, PH.V. KIRYUKHANTSEV-KORNEEV, A. SHEVEKO, National University of Science and Technology "MISIS", Russian Federation

BP67

A Study of Thermal Stability, Structural and Mechanical Properties of $Zr_xW_{1-x}N_y$ Coatings Deposited by DC/RF Reactive Magnetron Sputtering, P. DUBEY, R. CHANDRA, A. VIVEK, D. SINGH, V. DAVE, Indian Institute of Technology Roorkee, India

BP68

The Investigation of the Adhesion, Wear and Friction Properties of TiN/TaN Multilayer Coatings, O. BARAN, Erzincan University, Turkey, E. DEMIRCI, I. EFEOGLU, Y. TOTIK, Atatürk University, Turkey

BP69

Rapid Annealing of TaN-(Ag,Cu) Thin Films Deposited on PEEK Polymer Substrate by Pulse Current Heating, J.H. HSIEH, Y.T. SU, Ming Chi University of Technology, Taiwan, Republic of China

BP70

Synthesis and Characterization as Hydrocarbon Sensors of Nanostructured ZnO Sputter-deposited Coatings, M. ARAB POUR YAZDI, IRTES-LERMPS-UTBM, France, J. SANCHEZ, Umr Cnrs 6249, France, E. MONSIFROT, Sarl Dephis, France, P. BRIOIS, IRTES-LERMPS-UTBM, France, F. BERGER, UMR CNRS 6249 University of franche comte, France, A. BILLARD, IRTES-LERMPS-UTBM, France

BP71

A New Dedicated DLC Coating System for Threading in Titanium, M. MORSTEIN, P. DESSARZIN, PLATIT AG, Switzerland, K. GERSCHWILER, RWTH Aachen University, H. FRANK, M. SCHIFFLER, GFE Schmalkalden e.V., Germany

BP72

Study on the Characteristics of MoN Doping Cu Amorphous Thin Film Fabricated by Pulse Magnetron Sputtering Process, C.H. HUANG, W.S. HWANG, National Cheng Kung University, Taiwan, Republic of China, C.W. CHU, Metal Industries Research & Development Centre, Taiwan, Republic of China, S.J. LIU, H.Y. CHU, National Unversity of Tainan, Taiwan, Republic of China

BP73

Thermal Stability and Oxidation Behavior of Reactively Sputtered TaN Coatings, F.B. WU, K.Y. LIU, National United University, Taiwan, Republic of China

BP74

Electrochemical Impedance Spectroscopy Evaluation of Aluminium-Based PVD Coatings Exposed to Salt-Spray Corrosion, F. INDEIR, O. FASUBA, A. MATTHEWS, A. LEYLAND, University of Sheffield, UK

BP75

Comparison Between Single Phase Ti and Cr-nitrides Thin Films Deposited by Different Processing Routes, F. LOMELLO, DEN/DANS/DPC/SEARS/LISL CEA Saclay, France, M. ARAB POUR YAZDI, IRTES-LERMPS, France, D. SCHLEGEL, ESTA, France, A. BILLARD, IRTES-LERMPS-UTBM, France, F. SANCHETTE, LRC CEA-ICD LASMIS, Nogent International Center for CVD Innovation (Nicci), France, F. SCHUSTER, CEA Cross-Cutting Programme on Advanced Materials, France, M. TABARANT, DEN/DANS/DPC/SEARS/LISL CEA Saclay, France

BP76

Improving the Corrosion Resistance of Electroplated Chromium Coatings on AISI H13 Steel by Gaseous Nitriding in Vacuum, H. CIFUENTES, J.J. OLAYA, Universidad Nacional de Colombia Bogotá, Colombia

BP77

Enhancement of Mechanical and Tribological Properties in NiTi Shape Memory Alloy Thin Films by Using Graded AlN/Al Multilayer Coating, N. KAUR, D. KAUR, Indian Institute of Technology Roorkee, India

BP78

Property Evaluation in Humid Environments of Silicon-doped DLC Films Deposited by Plasma Immersion Assisted Deposition, C. LIU, J. COOPER, H. LI, M. AUDRONIS, A. MATTHEWS, A. LEYLAND, University of Sheffield, UK

BP79

First-principles Calculations on the Thermodynamic and Mechanical Properties of Ti-Al-(Zr, Hf)-N Wear-resistant Coating Systems, A. WANG, National Center for Quality Supervision and Inspection of Building Decoration Materials, China, W. WANG, Y. DU, L. CHEN, State Key Laboratory of Powder Metallurgy, Central South University, P.R. China

BP80

Interfacial Structure of Ti2AlN Thin Film Deposited on MgO(111): Experimental and Computational Study, H. JIN, Institute of High Performance Computing, Singapore

BP81

Study of the Mechanical Properties of PVD Metallic Nanocomposite Cr(N)-based Coatings with Combined Additions of Silver and Copper, X. LIU, M. AUDRONIS, A. YEROKHIN, A. MATTHEWS, A. LEYLAND, University of Sheffield, UK

BP82

Improving the Corrosion and Tribological Performance of Magnesium Alloys by Using Duplex Surface Treatments, L. LIU, M. AUDRONIS, A. YEROKHIN, A. MATTHEWS, A. LEYLAND, University of Sheffield, UK

Fundamentals and Technology of Multifunctional Thin Films: Towards Optoelectronic Device Applications

Room: Grand Hall - Session CP

Syposium C Poster Session

Moderators: E. Schubert, University of Nebraska-Lincoln, US, M. Cremona, Pontificia Universidade Católica do Rio de Janeiro, Brazil

5:00 pm

CP1

Electrical and Optical Properties of AZO/Ag Bilayer Prepared by Transfer Printing Method, M.S. KIM, D.H. LEE, Y.H. CHA, B.H.O. O, S.G. LEE, S.G. PARK, Inha University, Republic of Korea

CP2

Characterization of Hysteresis Phenomena in Indium Zinc Oxide Thin Film Transistors with Double-channel Layers via Capacitance-voltage Measurement, W. KIM, S.H. LEE, J.S. PARK, Hanyang University, Republic of Korea

CP3

Effects of RF Power and Oxygen Gas on the Characteristics of Thin Film Transistors with Co-sputtered Silicon Zinc Oxide Channel Layers, S.H. LEE, W. KIM, Hanyang University, Republic of Korea, H.S. UHM, Samsung Display, Republic of Korea, J.S. PARK, Hanyang University, Republic of Korea

CP6

Effect of Thickness on the Structure and Optical Properties of Yttrium-Doped Hafnium Oxide Nanocrystalline Thin Films, C. RAMANA, A. ORTEGA, M. NOOR-A-ALAM, A. KONGU, University of Texas at El Paso, US

CP7

Impact of Mechanical Strain on Hot Carrier Degradation for Partially Depleted Silicon-On-Insulator n-channel Metal-Oxide-Semiconductor-Field-Effect-Transistors, W.H. LO, T.C. CHANG, J.Y. TSAI, National Sun Yat-Sen University, Taiwan, Republic of China

CP8

Abnormal Threshold Voltage Shift under Hot Carrier Stress in $Ti_{1-x}N_x/HfO_2$ p-channel MOSFETs, J.Y. TSAI, T.C. CHANG, W.H. LO, National Sun Yat-Sen University, Taiwan, Republic of China

CP9

Electrical Enhancement of Nitrogen Doped Amorphous In-Ga-Zn-O Thin Film Transistors by Microwave Annealing, C.S. FUH, P.T. LIU, S.M. SZE, S.W. HUANG, M.J. LIU, C.H. CHANG, National Chiao Tung University, Taiwan, Republic of China

CP10

Chemical Bath Deposited Zn-Cd-S Buffer Layer for $Cu(In,Ga)Se_2$ Solar Cells, Y.C. LIN, National Chung Hsing University, Taiwan, Republic of China, Z.C. CHANG, National Chin Yi University of Technology, Taiwan, Republic of China, F.S. SHIEU, National Chung Hsing University, Taiwan, Republic of China

CP11

Investigation on Amorphous InGaZnO Based Resistive Switching Memory with Low-power, High-speed, High Reliability and Good Flexibility, Y.S. FAN, C.H. HSU, P.T. LIU, National Chiao Tung University, Taiwan, Republic of China

CP12

Effect of Sn-layer Addition to Precursors on Characteristics of $Cu_2ZnSn(S,Se)_4$ Thin Film Solar Cell Absorber, K. SAMMI, K. WOO KYOUNG, O. MISOL, L. SOOBIN, J. SOYOUNG, Yeungnam University, Republic of Korea

CP13

Rapid Sulfurization of CuGaIn/Se Precursors, L. SOOBIN, Yeungnam University, Republic of Korea, C. HYUN-IL, S. CHANGGIL, A. DONGGI, K. BYOUNGDONG, Samsung SDI, Republic of Korea, K. WOO KYOUNG, Yeungnam University, Republic of Korea

CP14

Electrical and Optical Properties of Magnesium Doped Delafossite Structure $CuCr_{1-x}Mg_xO_2$ Reactively co Sputter Deposited Coatings, P. BRIOIS, M. ARAB POUR YAZDI, IRTES-LERMPS-UTBM, France, J.F. PIERSON, Institut Jean Lamour, France, A. BILLARD, IRTES-LERMPS-UTBM, France

CP15

High Power Impulse Magnetron Sputtering of Transparent Conducting Oxides, L.C. CHANG, C.K. CHANG, S.C. WANG, Ming Chi University of Technology, Taiwan, Republic of China

CP16

Synthesis of Silver Nanowire by Polyol Method for Transparent Conductive Film Application, J.J. HUANG, MingDao University, Taiwan, Republic of China, J.Y. LIN, National Yunlin University of Science and Technology, Taiwan, Republic of China, C.N. CHEN, Asia University, Y.L. HSUEH, National Yunlin University of Science and Technology, Taiwan, Republic of China, M.W. TSAI, MingDao University, Taiwan, Republic of China

CP17

Performance Improvement of Hybrid Solar Cells with Thermally Evaporated Cuprous Oxide as a Hole Transport Layer, Y. YU, Y. WANG, M. HSU, Ming Chi University of Technology, Taiwan, Republic of China

CP18

Nanocomposite Anti Bacterial Sputter Deposited Coatings, E. MONSIFROT, Dephis, France, F. SANCHETTE, ICT, France, A. BILLARD, IRTES-LERMPS-UTBM, France, F. SCHUSTER, CEA, France

CP19

Organic Thin-film Transistors with Polymer–nanoparticle Hybrid Dielectrics Layer, Y. YU, M. CHEN, Ming Chi University of Technology, Taiwan, Republic of China

CP20

Investigation of Sputtered GAZO Films for CIGS Photovoltaics, C.-H. HUANG, National Dong Hwa University, Taiwan, Republic of China, H.-L. CHENG, Natioanl Dong Hwa University, Taiwan, Republic of China

CP21

Investigation of Green and Yellow Luminescence from Alpha and Beta Zinc Silicate Thin Films Doped with Manganese, Y.K. CHO, J.H. KIM, Chungbuk National University, Republic of Korea

CP22

Effect of the Thin Ga_2O_3 Layer in n^+-ZnO/n-Ga_2O_3/p-Cu_2O Heterojunction Solar Cells, Y. NISHI, T. MIYATA, T. MINAMI, Kanazawa Institute of Technology, Japan

CP23

Influence of Crystallographical Properties on Obtainable Texture-etched Surface Structure in Transparent Conducting Impurity-doped ZnO Thin Films, T. MIYATA, J. NOMOTO, T. FUJITA, T. MINAMI, Kanazawa Institute of Technology, Japan

CP24

Co-Sputtering and RTA Process for Preparation of CIGS Thin Films Using Gallium, Indium and Copper Diselenide Alloy Targets, E. BLEZA, S. OH, G. CHO, N. KIM, Chosun University, Korea

CP25

Analysis of Coatings in Matrix of Conformation Fasteners in Stainless Steel Austenitic, W. MATTES, J. PAIVA JUNIOR, Centro Univesitário Catolica de Santa Catarina, Brazil

CP26

Influence of Rapid Thermal Annealing Treatment on Transparent Conducting Impurity-Doped ZnO Thin Films for Thin-Film Solar Cell Applications, J. NOMOTO, T. MIYATA, T. MINAMI, Kanazawa Institute of Technology, Japan

CP29

Hole Trapping-induced Anomalous Gate Current Hump after Dynamic Negative Bias Stress in p-MOSFETs with HfO_2 and $Hf_xZr_{1-x}O_2$/Metal Gate Stacks, S.H. HO, National Chiao Tung University, Taiwan, Republic of China, T.C. CHANG, National Sun Yat-Sen University, Taiwan, Republic of China, T.Y. TSENG, National Chiao Tung University, Taiwan, Republic of China

CP30

Temperature Dependent Instability of Drain Bias Stress in Amorphous Indium-Gallium-Zinc-Oxide Thin Film Transistors, G.W. CHANG, National Chiao Tung University, Taiwan, Republic of China, T.C. CHANG, National Sun Yat-Sen University, Taiwan, Republic of China, Y.H. TAI, National Chiao Tung University, Taiwan, Republic of China, Y.E. SYU, National Sun Yat-Sen University, Taiwan, Republic of China

CP31

Temperature Dependence on Positive Gate Bias Instability in HfO_2/TiN p-MOSFETs, H.M. CHEN, National Chiao Tung University, Taiwan, Republic of China, T.C. CHANG, National Sun Yat-Sen University, Taiwan, Republic of China, Y.H. TAI, National Chiao Tung University, Taiwan, Republic of China, W.H. LO, National Sun Yat-Sen University, Taiwan, Republic of China

CP32

Investigation of Random Telegraph Signal in PD SOI nMOSFETs between Moderate and Strong Inversion Region, C.E. CHEN, National Chiao Tung University, Taiwan, Republic of China, T.C. CHANG, B. YOU, National Sun Yat-Sen University, Taiwan, Republic of China, T.Y. TSENG, National Chiao Tung University, Taiwan, Republic of China

CP33

Self Current Compliance Bipolar Resistance Switching Characteristics for Nonvolatile Memory Application, H.C. TSENG, National Sun Yat-Sen University, Taiwan, Republic of China

CP35

Study of the Surface Chemical Composition and Evaluation of Corrosion Resistance of $Bi_XTi_YO_Z$ Thin Films Deposited by RF Magnetron Sputtering, J. ALFONSO, J.J. OLAYA, M. PINZÓN, National University of Colombia, Colombia, J.F. MARCO, CSIC

CP36

Light Extraction Enhancement by Metallic Photonic Crystal Nanostructures Embeded in Gallium Nitride Diodes, G.M. WU, Chang Gung MemoUniversity, Taiwan

CP37

Effects of Intermediate GAZO Layer Thickness on the Properties of GAZO/Ag/GAZO/Ag/GAZO Film, Y.S. JUNG, H.W. CHOI, K.H. KIM, Gachon University, Republic of Korea

Thursday Afternoon Poster Sessions

Coatings for Biomedical and Healthcare Applications
Room: Grand Hall - Session DP

Syposium D Poster Session
Moderators: J. Piascik, RTI International, R. Hauert, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland

5:00 pm

DP1

Albumin Adsorption on Zirconium Oxide Thin Films: the Influence of Atomic Ordering, P. SILVA-BERMUDEZ, Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de Mexico, México, Mexico, S. RODIL, Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de Mexico, México

DP2

Hydroxyapatite Growth Behavior and Osteocompatible Performance of Biomedical Polymer Coated with Titanium Dioxide Interlayer, M.H. CHI, Feng Chia University, Taiwan, Republic of China, H.K. TSOU, Feng Chia University, Taiwan; Taichung Veterans General Hospital, Taiwan, Republic of China, C.J. CHUNG, Central Taiwan University of Science and Technology, Taiwan, Republic of China, J.L. HE, Feng Chia University, Taiwan, Republic of China

DP3

Deposition, Characterization and In Vivo Performance of Parylene Coating on General-purposed Silicone for Biocompatible Surface Modification, C.M. CHOU, Taichung Veterans General Hospital; National Yang-Ming University, C.J. SHIAO, Feng-Chia University, Taiwan, Republic of China, C.J. CHUNG, Central Taiwan University of Science and Technology, Taiwan, Republic of China, J.L. HE, Feng Chia University, Taiwan, Republic of China

DP4

The Biological Characteristics of MG-63 Human Osteosarcoma Cell Line and Human Gingival Fibroblast Cells on Tantalum Doped Carbon Films, M.T. TSAI, Hungkuang University, Taiwan, Republic of China, Y.Y. CHANG, National Formosa University, Taiwan, Republic of China, YC CHEN, MingDao University, Taiwan, Republic of China, J.T. HSU, H.L. HUANG, China Medical University, Taiwan, Republic of China

DP5

Cytocompatibility and Antibacterial Properties of Zirconia Coatings with Different Silver Contents on Titanium, H.L. HUANG, China Medical University, Taiwan, Republic of China, YY CHANG, National Formosa University, Taiwan, Republic of China, YC CHEN, MingDao University, Taiwan, Republic of China, C.H. LAI, MYC CHEN, China Medical University, Taiwan, Republic of China

DP7

Adhesion and Corrosion Performance of Amorphous Titanium Oxide Films on Stainless Steel, V. GARCIA-PEREZ, Facultad de Odontología, Universidad Nacional Autónoma de México, Mexico, P. SILVA-BERMUDEZ, Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de Mexico, México, A. ALMAGUER-FLORES, Facultad de Odontología, Universidad Nacional Autónoma de México, Mexico, J. RESTREPO, Universidad Nacional Autónoma de México - Instituto de Investigaciones en Materiales, Mexico, S. RODIL, Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de Mexico, México

DP8

Blood Compatibility and Adhesion of Collagen/Heparin Multilayers Coated on Two Titanium Surfaces by a Layer-by-layer Technique, C.-C. CHOU, H.-J. ZENG, National Taiwan Ocean University, Taiwan, Republic of China, C.-H. YEH, Chang Gung Memorial Hospital, Keelung, Taiwan, Republic of China, S.-C. LIU, National Taiwan Ocean University, Taiwan, Republic of China

DP11

Effect of Nitrogen Plasma Immersion Ion Implantation Treatment on Corrosion Resistance of Ni-free ZrCuFeAl Bulk Metallic Glass, H.M. HUANG, Y.S. SUN, H.H. HUANG, National Yang-Ming University, Taiwan

DP12

Tribocorrosion and Properties of TiAlN/TiB_2 Coatings Deposited onto Ti6Al4V Alloy by DC/RF Magnetron Sputtering, O. JIMENEZ, J. REYES, M. FLORES, E. RODRIGUEZ, Universidad de Guadalajara, Mexico

DP13

The Tribocorrosion Behavior of CoCrMo Alloys Coated with TIALPtN in Simulated Body Fluid, M. FLORES, Universidad de Guadalajara, Mexico, E. ANDRADE, Universidad Nacional Autónoma de México, Mexico, O. JIMENEZ, E. RODRIGUEZ, Universidad de Guadalajara, Mexico

DP14

101 Million Cycle Simulator Wear Characterization of Diamond lLke Carbon Coated CoCrMo Articulating Implants, K. THORWARTH, U. MÜLLER, R. FIGI, B. WEISSE, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland, G. THORWARTH, DePuy Synthes Companies, Switzerland, R. HAUERT, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland

DP15

Preparation of a Composite Bioceramic HA/Ag Coating and Effect on Insertion Torques of the Coated Ti6Al4V Screws, T. CHENG, X. NIE, Y. CHEN, University of Windsor, Canada

DP16

Scratch Resistance of Coated Orthodontic Archwires, E. SANTOS JR., D. DA SILVA, A. RUELLAS, S. CAMARGO JR., C. MATTOS, Federal University of Rio de Janeiro, Brazil

DP17

AC Impedance Behavior of HA/TiN Coated Ti-25Ta-xZr Alloy by RF Sputtering and EB-PVD for Dental Implant, H.J. KIM, Y.H. JEONG, Y.M. KO, Chosun University, Korea, S.W. EUN, Polytechnic V Colleges, Korea, H.C. CHOE, Chosun University, Korea

DP18

Hydroxyapatite Precipitation on Nanotubular Film Formed Ti-25Nb-xHf Alloys for Biomedical Application, S.H. KIM, Y.H. JEONG, Y.M. KO, H.C. CHOE, Chosun University, Korea

DP19

HA/TiN Multilayer Coating on the Ti-30Nb-xTa Alloys by RF Sputtering for Biocompatibility, E.S. KIM, Y.H. JEONG, Y.M. KO, H.C. CHOE, Chosun University, Korea

DP20

Electrochemical Behaviors of an Interface Between Si/HA Coated Ti-Nb-Zr Alloy and HOB Cell, Y.H. JEONG, H.C. CHOE, Chosun University, Korea

DP21

Hydroxyapatite Coating on Micro-pore formed Ti-35Ta-xNb Alloy by Electron Beam-Physical Vapor Deposition, C.I. JO, Y.H. JEONG, Y.M. KO, H.C. CHOE, Chosun University, Korea, S.W. EUN, Polytechnic V Colleges, Korea

Thursday Afternoon Poster Sessions

Tribology & Mechanical Behavior of Coatings and Engineered Surfaces
Room: Grand Hall - Session EP

Syposium E Poster Session
Moderators: N.M. Jennett, National Physical Laboratory, UK, T. Scharf, University of North Texas, US

5:00 pm

EP1

Controlled Vacuum Annealing of TiZrN Thin Film on Si (001) and AISI 304 Stainless Steel Deposited by Unbalanced Magnetron Sputtering, P-H. WU, J.H. HUANG, G.P. YU, National Tsing Hua University, Taiwan, Republic of China

EP2

Fracture Toughness Measurement of ZrN Hard Coatings, Y-H. CHEN, G.P. YU, J.H. HUANG, National Tsing Hua University, Taiwan, Republic of China

EP3

Producing Thick TiN Films by Controlling Deposition Parameters in Magnetron Sputtering, M-L. CAI, G.P. YU, J.H. HUANG, National Tsing Hua University, Taiwan, Republic of China

EP4

Wear Behavior and Failure Mechanism of a Solid Lubricant Coating on One Side or Both Sides of Counterbodies, J. YANG, V. FRIDRICI, P. KAPSA, Ecole Centrale de lyon, France

EP5

Investigation of Internal Stress Levels and Characteristics during Electrocodeposition of Ni-MoS_2 Composite Coatings, E. SARALOGLU GULER, İ. KARAKAYA, Middle East Technical University, Turkey, E. KONCA, Atilim University, Turkey, M. **ERDOĞAN**, Middle East Technical University, Turkey

EP6

Impact Wear Resistance of CrN, CrAlN and TiAlN PVD Coatings on Cemented Carbide and M2 Steel Substrates, J.L. MO, M.H. ZHU, Southwest Jiaotong University, China, S. BANFIELD, University of Sheffield, UK, J. HOUSDEN, Tecvac Ltd, UK, A. LEYLAND, A. MATTHEWS, University of Sheffield, UK

EP7

Examples for the Time Dependent Effective Indenter Concept, N. BIERWISCH, Saxonian Institute of Surface Mechanics, Germany, N. SCHWARZER, Saxonian Institute of Surface Mechancis, Germany, A. EL SEWEIFI, Forum Zehlendorf, Germany, M. GRIEPENTROG, P. REINSTÄDT, BAM Berlin, Germany

EP8

Effect of Implant Diameter and Length on Stress Distribution for Titanium and Zirconia İmplants with 15° Angled Abutment by using Finite Element Analysis (FEA), F. KARABUDAK, R. YESILDAL, F. BAYINDIR, Atatürk University, Turkey

EP9

Coated Polymers for Low Friction and Wear of Roller Bearing Cages in Lightweight Design, T. SANDER, B. VIERNEUSEL, S. TREMMEL, S. WARTZACK, Friedrich-Alexander-University Erlangen-Nuremberg, Germany

EP10

Tribological Properties of Hard a-C:H:F Coatings, C. JAOUL, Université de Limoges - CNRS, France, O. JARRY, Sulzer Sorevi, P. TRISTANT, Université de Limoges - CNRS, France, E. LABORDE, Université de Limoges - CNRS, M. COLAS, J.P. LAVOUTE, Université de Limoges - CNRS, France, L. KILMAN, Sulzer Sorevi, H. AGEORGES, C. DUBLANCHE-TIXIER, Université de Limoges - CNRS, France

EP11

Microtribological Properties of Extremely Thin Diamond-like Carbon Films Deposited using Bend-type Filtered Cathodic Vacuum Arc and Electron Cyclotron Resonance Chemical Vapor Deposition Techniques, S. YAMAZAKI, S. MIYAKE, Nippon Institute of Technology, Japan

EP12

Deposition and Tribological Properties of Multilayer and Mixed Films Composed of Gold and Diamond-like Carbon, S. TAKANORI, M. SHOJIRO, Nippon Institute of Technology, Japan

EP14

Deposition and Characterization of Bismuth Containing Hard Coatings, R. MIRABAL, S. RODIL, P. SILVA-BERMUDEZ, S. MUHL, G. RAMIREZ, Universidad Nacional Autónoma de México - Instituto de Investigaciones en Materiales, Mexico, J. OLIVEIRA, A. CAVALEIRO, Faculdade Ciencias E Tecnologia Da Universidade De Coimbra, Portugal

EP15

A Laboratory-scale Pin-sliding Instrument for Triboluminescence Measurement, S. LEELACHAO, S. MURAISHI, Tokyo Institute of Technology, Japan

EP16

An Overview of Interfacial Fracture Energy Predictions for Stacked Thin Films Using Four-Point Bending Framework, C.C. LEE, Y.J. LAI, Chung Yuan Christian University, Taiwan, Republic of China, C.C. HUANG, National Nano Device Laboratories, Taiwan, Republic of China

EP17

Thermo-mechanical Failure Behavior of Copper TSV Induced by Transient Selective Annealing Technology, C.C. LEE, Y.H. LIN, Chung Yuan Christian University, Taiwan, Republic of China, C.C. HUANG, National Nano Device Laboratories, Taiwan, Republic of China

EP18

Global Elastic Anisotropy of Polycrystalline Metallic Thin Films and Multilayers, D. FAURIE, P. DJEMIA, LSPM-CNRS, Université Paris 13, Sorbonne Paris-Cité, France, E. LE BOURHIS, P.O. RENAULT, Institut P' - Universite de Poitiers, France, O. CASTELNAU, PIMM, ENSAM Paris, France, R. BRENNER, UMPC, Paris, France, P.O. GOUDEAU, Institut P' - Université de Poitiers, France

EP19

On the Meaning and Requirements of the Concept of an Effective Indenter, M. FUCHS, Chemnitz University of Technology, Germany

EP21

Friction Characteristics Degradation of Cup Anemometer used for Wind Energy Potential Measurements, M. ZLATANOVIC, School of Electrical Engineering, Serbia, D. ROMANIC, Republic Hydrometeorogical Service, Serbia

EP22

Characterization of Zr-Ti-Fe Thin Film Metallic Glasses Containing Different Fe Contents, L.T. CHEN, National Taipei University of Technology, Taiwan, Republic of China, J.-W. LEE, Ming Chi University of Technology, Taiwan, Republic of China, Y.C. YANG, National Taipei University of Technology, Taiwan, Republic of China

EP23

Enhanced Wear Resistance and Mechanical Properties of the WC-12%Co HVOF Thermally Sprayed Coatings Doped with MWCNTs, M. RODRIGUEZ, Universidad Central de Venezuela (UCV), Venezuela (Bolivarian Republic of), J. CARO, Fundació CTM Centre Tecnològic, Spain, E. ANGLARET, N. FRÉTY, Université Montpellier II, France, L. GIL, Universidad Nacional Experimental Politécnica (UNEXPO), Vicerrectorado Puerto Ordaz, Venezuela (Bolivarian Republic of)

EP24

Evaluations of the Residual Stress in the Plasma Sprayed Multi-layer Electrodes of the Solid Oxide Fuel Cell, Y.C. YANG, Y.C. WANG, National Taipei University of Technology, Taiwan, Republic of China, C.S. HWANG, C.H. TSAI, Institute of Nuclear Energy Research

EP25

Microstructure and Properties of WC-Co Carbides Coatings Obtained by Different Methods of High Velocity Thermal Spray Process, K. SZYMAŃSKI, G. MOSKAL, H. MYALSKA, Silesian University of Technology, Poland

EP27

Characteristics of Structure and Selected Properties of High Velocity Oxy-fuel Thermal Sprayed WC-Co Type Coatings with the use of Ultra-fine Powders, A. IWANIAK, Silesian University of Technology, Poland, G. WIECLAW, K. ROSNER, Certech Sp. z o.o., Poland

EP28

Deformation and Failure Mechanisms of Magnetron Sputtered Cu/TiN Multilayers, R. RAGHAVAN, D. ESQUÉ-DE LOS OJOS, A. MONTAGNE, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland, E. ALMANDOZ, G. FUENTES, AIN-Centre of Advanced Surface Engineering, Spain, J. MICHLER, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland

Thursday Afternoon Poster Sessions

New Horizons in Coatings and Thin Films
Room: Grand Hall - Session FP

Syposium F Poster Session
Moderators: A.P. Ehiasarian, Sheffield Hallam University, Sweden, U. Helmersson, Linköping University, Sweden, IFM, Plasma and Coatings Physics, Sweden, S. Kodambaka, University of California, Los Angeles, US
5:00 pm

FP1

Mechanical Properties of Patterned Oxide Structures on Compliant Substrates for Flexible Optoelectronics, K. SIERROS, West Virginia University, T. BEJITUAL, N. MORRIS, D. CAIRNS, West Virginia University, US

FP2

Influence of H-radical Irradiation on the Properties of a Ge/SiC Nanodot/SiC Stacked Structure, K. SATOU, Y. ANEZAKI, Nagaoka University of Technology, Japan, M. SUEMITSU, Tohoku University, Japan, H. NAKAZAWA, Hirosaki University, Japan, Y. NARITA, Yamagata University, Japan, A. KATO, T. KATO, Nagaoka University of Technology, Japan, K. YASUI, Nagaoka Univeversity of Technology, Japan

FP3

Shape Controllability and Photoluminescence Properties of ZnO Nanorods Grown by Chemical Bath Deposition, T. TERASAKO, T. MURAKAMI, Graduate School of Science and Engineering, Ehime University, Japan, M. YAGI, Kagawa National College of Technology, Japan, S. SHIRAKATA, Graduate School of Science and Engineering, Ehime University, Japan

FP4

Optical Properties of La_2O_3 Thin Films Deposited by RF Magnetron Sputtering, S.B. BRACHETTI-SIBAJA, M.A. DOMÍNGUEZ-CRESPO, A.M. TORRES-HUERTA, Instituto Politécnico Nacional, Mexico, S. RODIL, Universidad Nacional Autónoma de México, Mexico

FP5

ZnO Nanostructures as Efficient Antireflection Layers in High Efficiency Non-selenized Cu(In,Ga)Se2 Solar Cells, B.T. JHENG, National Tsing Hua University, Taiwan, Republic of China, P.T. LIU, National Chiao Tung University, Taiwan, Republic of China, Y.P. CHANG, Nan Kai University of Technology Nantou, Taiwan, M.C. WU, National Tsing Hua University, Taiwan, Republic of China

FP7

Phase Stability of Bi_2O_3 Thin Films prepared by Reactive Magnetron Sputtering, O. DEPABLOS-RIVERA, P. SILVA-BERMUDEZ, S. RODIL, Universidad Nacional Autónoma de México - Instituto de Investigaciones en Materiales, Mexico, E. CAMPS, Instituto Nacional de Investigaciones Nucleares de Mexico

FP8

Photocatalytic Activity of Bismuth Oxide Thin Films, J.C. MEDINA, S. RODIL, M. BIZARRO, P. SILVA-BERMUDEZ, Universidad Nacional Autónoma de México - Instituto de Investigaciones en Materiales, Mexico

FP9

Synthesis and Characterization of Copper Nanoparticles by Solution Plasma Processing, S.M. KIM, S.C. KIM, S.H. JIN, Korea Aerospace University, Republic of Korea, G.J. YOON, S.W. NAM, J.W. KIM, University of InCheon, Republic of Korea, S.Y. LEE, Korea Aerospace University, Republic of Korea

FP10

A Study of Microstructure and Electrical Properties of Strontium Doped Ceria Thin Films Deposited by High Power Impulse Magnetron Sputtering, C.T. CHANG, National Taipei University of Technology, Taiwan, Republic of China, J.-W. LEE, Ming Chi University of Technology, Taiwan, Republic of China, Y.C. YANG, National Taipei University of Technology, Taiwan, Republic of China

FP12

Effect of Substrate Bias and Hydrogen Addition on the Residual Stress of Hexagonal Boron Nitride Film Prepared by Sputtering of B_4C Target with Ar/N_2 Reactive Gas, J.K. PARK, J.H. LEE, W.-S. LEE, Y.J. BAIK, Korea Institute of Science and Technology, Republic of Korea

FP13

In-situ Biaxial Loading During X-Ray Diffraction and Digital Image Correlation Measurements: Application to Metallic Thin Films Supported by Polyimide Substrates, P.O. RENAULT, E. LE BOURHIS, University of Poitiers, France, D. FAURIE, University of Paris 13, France, G. GEANDIER, University of Lorraine, France, P.O. GOUDEAU, University of Poitiers, France, D. THIAUDIÈRE, Synchrotron SOLEIL, France

FP14

Antimicrobial Brass Coatings Prepared on Poly(ethylene terephthalate) Textile by High Power Impulse Magnetron Sputtering, Y.H. CHEN, G.W. CHEN, J.L. HE, Feng Chia University, Taiwan, Republic of China

FP16

Influences of Various Feedstocks on Characteristics of the Plasma Sprayed NiO/YSZ Anode in Solid Oxide Fuel Cell, Y.C. YANG, H.C. TSENG, C.T. CHENG, National Taipei University of Technology, Taiwan, Republic of China

FP17

Effect of Mo Content on Structure and Corrosion Resistance of Arc Ion Plated Ti-Mo-N Films on 316L Stainless Steel as Bipolar Plates for Polymer Exchange Membrane Fuel Cells, M. ZHANG, Liaoning Normal University, China, K. KWANG HO, Pusan National University, Republic of Korea, S. ZHIGANG, Dalian Institute of Chemical Physics, P. YUNLI, H. XIAOGANG, H. YE, Liaoning Normal University, China

FP18

The Smoke Density Evaluation of Acrylic Emulsion and Intumescent, Z. LI, H. WANG, W. ZHAO, W. LU, J. ZHAO, Marine Chemical Research Institute, State Key Lab of Marine Coatings, China

FP19

Effects of Duty Cycle and Pulse Frequency on the Fabrication of AlCrN Thin Films Deposited by High Power Impulse Magnetron Sputtering, Y. C. HSIAO, National Taipei University of Technology, Taiwan, Republic of China, J.-W. LEE, Ming Chi University of Technology, Taiwan, Republic of China, Y.C. YANG, National Taipei University of Technology, Taiwan, Republic of China

FP20

Enhancing the Thermal Stability and Oxidation Resistance of the Cr Zr N Films by Adding Oxygen, D.J. KIM, J.H. LA, S.M. KIM, Y.S. HONG, S.Y. LEE, Korea Aerospace University, Republic of Korea

FP21

Novel Synthesis of Conductive Nano-crystalline Carbon Film by Advanced Magnetron Sputtering, JEONG. HAN, SUNGI. KIM, J.D. NAM, Sungkyunkwan University, South Korea

FP22

Reactive Sputtering Al2O3 and Cr2O3 Coatings using Arc Free High Power Pulsed Magnetron Sputtering, J. LIN, W. SPROUL, B. WANG, Y. OU, Colorado School of Mines, US

Thursday Afternoon Poster Sessions

Applications, Manufacturing, and Equipment
Room: Grand Hall - Session GP

Symposium G Poster Session
Moderators: D. Pappas, EP Technologies, LLC,US, K. Yamamoto, Kobe Steel Ltd., Japan

5:00 pm

GP2

Preparation of Phosphor-doped TiO_2 Particle/Passivating Layer and their Applications in Dye-sensitized Solar Cells, T.S. EOM, K.H. KIM, C.W. BARK, H.W. CHOI, Gachon University, Republic of Korea

GP3

Dual Frequency ICP Discharge: Effect of Pressure and Gas Ratio on EEDF and Discharge Parameters, A. MISHRA, T.H. KIM, K.N. KIM, G.Y. YEOM, Sungkyunkwan University, Republic of Korea

GP4

Failure Behavior of Thick Single and Multilayered TiSiCN Coatings under Impact-sliding Forces, J.F. SU, X. NIE, H. HU, University of Windsor, Canada, R.H. WEI, Southwest Research Institute, US

GP5

Evolution of Reliability on Electroplated and Sputtered Ni-Zn films for Under Bump Metallization with Sn-3.0Ag-0.5Cu Solder Attached During Liquid Reactions, H.M. LIN, J.G. DUH, National Tsing Hua University, Taiwan, Republic of China

GP6

Improvement of Air Plasma Spraying Parameters for the Fabrication of Thermal Barrier Coatings, S. LISCANO, L. GIL, M. ROMERO, UNEXPO, Venezuela (Bolivarian Republic of)

GP7

Surface Recrystallization of Tungsten Carbide by MPCVD due to Controlled Oxidation and Deoxidation in an Equilibrium Process, M. MEE, S. MEIER, Fraunhofer IWM, Germany

GP8

Understanding of Wear Mechanisms of Coated Solid Carbide Endmills During Machining of Ti-Al6-V4, S. STEIN, R. RACHBAUER, M. ARNDT, OC Oerlikon Balzers AG, Liechtenstein

Topical Symposia
Room: Grand Hall - Session TSP

Syposium TS Poster Session
Moderator: C. Muratore, University of Dayton, US

5:00 pm

TSP1

Fine Micro- and Nano-Imprinting onto DLC Coating via Controlled Oxygen Plasma Etching, T.A. ZHO, Shibaura Institute of Technology, Japan, K.M. MIZUSHIMA, Shibaura Institute of Tchnology, Japan, T.F. FUKUDA, Mitsue Mold Engineering, Co. Ltd.

TSP2

Comparison of Flow Curves of Thin Films Determined by Different Finite Element Models and Nanoindenter Geometries, K. BOBZIN, N. BAGCIVAN, R.H. BRUGNARA, J. PERNE, Surface Engineering Institute - RWTH Aachen University, Germany

TSP3

Micro-chemical and -morphological Features of Heat Treated Plasma Sprayed Zirconia-based Thermal Barrier Coatings, B. CORTESE, D. CASCHERA, T. DE CARO, G.M. INGO, CNR, Italy

TSP6

Deposition, Structural and Optoelectronic Properties of Bi_2O_3 Thin Films Deposited by Magnetron Sputtering, C.L. GOMEZ, Universidad Nacional Autonoma de Mexico, Mexico, S. RODIL, P. SILVA-BERMUDEZ, Universidad Nacional Autónoma de México, Mexico, M. LEJEUNE, S. CHARVET, A. ZEINERT, Universite de Picardie Jules Verne, France, E. CAMPS, Instituto Nacional de Investigaciones Nucleares de Mexico

TSP8

Relationship Between the Microstructure and Thermoelectric Properties of n-type Bi-Se-Te by Using RF Sputtering, T.S. CHEN, C.C. SHIH, H.D. FU, M.S. LEU, Industrial Technology Research Institute, Taiwan

TSP9

Surfactant-assisted Dispersion of Polyimide/multi-walled Carbon Nanotube Nanocomposites Films with Ultrahigh Electrical Conductivity, H.P. YU, National Chin-Yi University of Technology, Taiwan, Republic of China, Y.C. HUANG, National Chiao Tung University, Taiwan, Republic of China, I.H. TSENG, TSAI, National Chin-Yi University of Technology, Taiwan, Republic of China

TSP10

Poly(amide-imide) / Graphene Oxide Nanocomposite Films for Anticorrosion Application, C.W. CHANG, I.H. TSENG, M.-H. TSAI, National Chin-Yi University of Technology, Taiwan, Republic of China, J.M. YEH, Chung-Yuan Christian University, Taiwan, Republic of China

TSP11

Aberration-corrected HRSTEM Characterization of Nanolaminate Copper Diffusion Barriers Grown by PEALD, C.N. HSIAO, B.H. LIOU, National Applied Research Laboratories, G.S. CHEN, Feng Chia University, Taiwan, Republic of China, Y.J. CHENG, National Chi Nan University, Y.S. Y. S. LAI, National Applied Research Laboratories

TSP12

Kinetics of Spinodal Decomposition in Au-Ni Nanolaminates near Room Temperature, A. JANKOWSKI, Texas Tech University, US

TSP13

Synthesis of CdS Thin Films with Hexagonal Orientation Through an Ammonia-free System, K.Y. CHEN, S.C. HSIAO, B.J. YANG, L.H. CHOU, National Tsing Hua University, Taiwan, Republic of China

TSP14

Electrical Characteristics and Stability of Metal Electrodes for Pyrite Ultra-thin Film Solar Cells, B.K. CHEN, S.C. HSIAO, L.H. CHOU, National Tsing Hua University, Taiwan, Republic of China

TSP15

Nanostructure Formation of Al_2O_3 Layer Carried Out in a Three-Component Electrolyte, M. KUBICA, University of Silesia, Poland, M. BARA, W. SKONECZNY, Univesrsity of Silesia, Poland

TSP16

Performance Characterisation of Metallic Substrates Coated by HVOF WC-Co, A. VENTER, Necsa Limited; DST/NRF Centre of Excellence in Strong Materials, South Africa, P. OLADIJO, DST/NRF Centre of Excellence in Strong Materials, South Africa; University of the Witwatersrand, South Africa, V. LUZIN, ANSTO (Australian Nuclear Science & Technology Organisation), Australia, L. CORNISH, N. SACKS, DST/NRF Centre of Excellence in Strong Materials, South Africa; University of the Witwatersrand, South Africa

TSP17

Micromechanical Characterisation of a-C:H Coating Systems with Si-based Adhesion Layers, C. SCHMID, C. SCHUNK, M. KROTTENTHALER, V. MAIER, M. GÖKEN, K. DURST, University of Erlangen-Nürnberg, Germany

Friday Morning, May 3, 2013

	Tribology & Mechanical Behavior of Coatings and Engineered Surfaces Room: Golden West - Session E3-2+G Tribology of Coatings for Automotive and Aerospace Applications Moderators: S. Dixit, Plasma Technology Inc., A. Gies, OC Oerlikon Balzers AG, Liechtenstein, G.L. Doll, University of Akron, US	New Horizons in Coatings and Thin Films Room: Sunrise - Session F6-1 Coatings for Fuel Cells & Batteries Moderators: G.V. Dadheech, General Motors Research and Development Center, US, L. Lei, Shanghai Jiaotong University, China
8:00 am	E3-2+G-1 Tribological and Mechanical Analysis of the Interest of DLC in Cold Rolling of High Carbon Steel Strips, C. CHOUMAD-OULD, HEF, CEMEF, France, X. BADICHE, HEF, France, P. MONTMITONNET, CEMEF, France, Y. GACHON, HEF, France	F6-1-1 Invited Prototyping Solid-Oxide Fuel Cells with Pulsed Laser Deposition, S. MAO, Lawrence Berkeley National Laboratory, US
8:20 am	E3-2+G-2 Invited Formation and Characterization of Reconstructive Coatings, H. LIANG, Texas A&M University, US	Invited talk continued.
8:40 am	Invited talk continued.	F6-1-3 High Performance Nano-Coatings for Ferritic Stainless Steel Strips used as Solid Oxide Fuel Cell Interconnects, J.G. GROLIG, J. FROITZHEIM, L.G. JOHANSSON, J.E. SVENSSON, Chalmers University of Technology, Sweden
9:00 am	E3-2+G-4 Plasma Electrolytic Oxidation for Surface Treatment of Engine Cylinder Bores, H. EILIAT, X. NIE, University of Windsor, Canada	F6-1-4 Strontium Diffusion in Magnetron Sputtered Gadolinia-doped Ceria Thin Film Barrier Coatings for Solid Oxide Fuel Cells, S. SONDERBY, P. LUNCA POPA, J. LU, Linköping University, Sweden, BH. CHRISTENSEN, KP. ALMTOFT, L. PLETH NIELSEN, Danish Technological Institute, Denmark, P. EKLUND, Linköping University, Sweden
9:20 am	E3-2+G-5 Invited Understanding Wear of Diamond-like Carbon Coatings for use in High-pressure Diesel Injection Engines, U. MAY, M. DJOUFACK, Robert Bosch GmbH, Diesel Systems, Germany	F6-1-5 High Performance Duplex Coatings for PEMFC Metallic Bipolar Plates by CFUBMSIP and HIPIMS Technology, H. SUN, K. COOKE, P. HAMILTON, Teer Coatings Limited, Miba Coating Group, UK, P. HOVSEPIAN, A.P. EHIASARIAN, A. SUGUMARAN, Sheffield Hallam University, UK
9:40 am	Invited talk continued.	F6-1-6 Industrial, Low Cost Ceramic MaxPhase™ Protective Coatings for Stainless Steel Bipolar Plates, H. LJUNGCRANTZ, K. NYGREN, M. SAMUELSSON, Impact Coatings, Sweden
10:00 am	E3-2+G-7 Characterization and Tribological Investigations of Arc Evaporated Mo-based Coatings, J. BECKER, Oerlikon Balzers Coating Germany GmbH, Germany, M. DÖBELI, Ion Beam Physics ETH Zürich, Switzerland, A. GIES, T. HUBEN, J. RAMM, H. RUDIGIER, F. SEIBERT, B. WIDRIG, OC Oerlikon Balzers AG, Liechtenstein	F6-1-7 Pre-coated Steel Stripes for PEMFC and SOFC Interconnects, G.V. DADHEECH, General Motors Research and Development Center, US, H. HOLMBERG, Sandvik Coromant R&D Materials and Processes, Sweden, M. SCHUISKY, Sandvik Machining Solutions, Sweden
10:20 am	E3-2+G-8 Development of New Oxidation Resistant Coating for Dry Hobbing, M. ABE, K. YAMAMOTO, Y. YAMAMOTO, Kobe Steel Ltd., Japan	F6-1-8 R.F. Magnetron Sputtered Li-Mn-O Thin Films, J. FISCHER, T. BERGFELDT, Karlsruhe Institute of Technology, Germany, K. CHANG, RWTH Aachen University, Germany, H. LEISTE, T. SCHERER, S. ULRICH, H.-M. BRUNS, Karlsruhe Institute of Technology, Germany, C. ZIEBERT, Karlsruhe Institute of Technology, Germay, H.J. SEIFERT, Karlsruhe Institute of Technology, Germany
10:40 am	E3-2+G-9 Third Body Behavior During Dry Sliding of Al-Al_2O_3 Composite Coatings: *in situ* Tribometry and Microanalysis, J.M. SHOCKLEY, McGill University, Canada, S. DESCARTES, Université de Lyon - CNRS, INSA-Lyon, France, E. IRISSOU, J.-G. LEGOUX, National Research Council Canada, R. CHROMIK, McGill University, Canada	F6-1-9 The Effect of Reactive Element Coatings on the Oxidation Properties of Ferritic Steels for Solid Oxide Fuel Cell Interconnect Applications, R. SACHITANAND, J. FROITZHEIM, J.E. SVENSSON, L.G. JOHANSSON, Chalmers University of Technology, Sweden
11:00 am		
11:20 am		
11:40 am	**2014 ICMCTF April 28 – May 2, 2014**	**2014 Abstract Submission Deadline October 1, 2013**
12:00 pm	**Thank You & See You Next Year Party Trellis Courtyard near Pool 12:30 – 1:30 pm**	**Awards Nominations Deadline October 1, 2013**

Friday Morning, May 3, 2013

	Applications, Manufacturing, and Equipment Room: California - Session G5-2 Coatings, Pre-Treatment, Post-Treatment, and Duplex Technology Moderator: T. Takahashi, KCS Europe GmbH, Germany	Topical Symposia Room: Royal Palm 4-6 - Session TS1-1 Surface Engineering for Thermal Transport, Storage and Harvesting Moderators: B. Cola, Georgia Technical Institute, US, C. Muratore, University of Dayton, US
8:00 am	G5-2-1 Invited Surface Modification for Metal using a Newly Developed Atmospheric Controlled Induction-heating Fine Particle Peening (AIH-FPP) System, J.K. KOMOTORI, Keio University, Japan	TS1-1-1 Direct Thermal Conductivity Measurement of Nanostructured Coatings Using a Modified Photoacoustic Technique, T. BOUGHER, Georgia Institute of Technology, US, B. COLA, Georgia Technical Institute, US
8:20 am	Invited talk continued.	TS1-1-2 Thermo-Mechanical Modeling of Carbon Nanotube Arrays for Thermal Interface Applications, S. SADASIVAM, S. HODSON, T. FISHER, Purdue University, US
8:40 am	G5-2-3 Number of Passes and Thickness Effect on Mechanical Characteristics of Cold Spray Coating, A. MORIDI, S.M. HASSANI-GANGARAJ, M. GUAGLIANO, Politecnico di Milano, Italy, S. VEZZÙ, Associazione Civen, Italy	TS1-1-3 Invited Heat Transfer in Encased Graphene, C. DAMES, University of California, Berkeley, US
9:00 am	G5-2-4 Effects of Intermediate Surface Treatments on Corrosion Resistance of Cathodic Arc PVD Hard Coatings, S. ABUSUILIK, K. INOUE, Hitachi Tool Engineering, Ltd., Japan	Invited talk continued.
9:20 am	G5-2-5 Microstructure and Dielectric Nature of Plasma Sprayed Ultra Purity Aluminum Oxide Coatings, S. DIXIT, Plasma Technology Inc., US	TS1-1-5 Limited Thermal Conductance of Metal-carbon Interfaces, J. GENGLER, Spectral Energies, LLC/Air Force Research Laboratory, Materials and Manufacturing Directorate, Nanoelectronic Materials Branch, USA, S. SHENOGIN, UES/Air Force Research Laboratory,Materials and Manufacturing Directorate, Nanoelectronic Materials Branch, USA, J. BULTMAN, UDRI/Air Force Research Laboratory, Materials and Manufacturing Directorate, Nanoelectronic Materials Branch, USA, A. ROY, C. MURATORE, A. VOEVODIN, Air Force Research Laboratory, Materials and Manufacturing Directorate, Nanoelectronic Materials Branch, US
9:40 am	G5-2-6 The Fracture Toughness of Boride Coating Improved by a Diffusion Annealing Process, I. CAMPOS-SILVA, M. FLORES-JIMÉNEZ, G. RODRIGUEZ-CASTRO, Instituto Politecnico Nacional, Mexico, E. HERNANDEZ-SANCHEZ, Universidad Autonoma Metropolitana-Azc, Mexico, J. MARTÍNEZ-TRINIDAD, L. JIMÉNEZ-TINOCO, Instituto Politecnico Nacional, Mexico	TS1-1-6 Invited Thermoreflectance Microscopy of Thin Films, A. SCHMIDT, Boston University, US
10:00 am		Invited talk continued.
10:20 am		TS1-1-8 Hydrogen Absorption and Desorption Properties of Pd/Mg/Pd Tri-layers Prepared by Magnetron Sputtering, Y.K. GAUTAM, R. CHANDRA, Indian Institute of Technology Roorkee, India, M. KUMAR, Indian Institute of Technology Delhi, India
10:40 am		TS1-1-9 Invited Interface Engineering for Optimized Thermal Transport in Copper/Diamond System, V. SINHA, UES/Air Force Research Laboratory,Materials and Manufacturing Directorate, US, J. GENGLER, Spectral Energies, LLC/Air Force Research Laboratory, Materials and Manufacturing Directorate, Nanoelectronic Materials Branch, US, C. MURATORE, Air Force Research Laboratory, Materials and Manufacturing Directorate, Nanoelectronic Materials Branch, US, J. SPOWART, Air Force Research Laboratory, Materials and Manufacturing Directorate, US
11:00 am		Invited talk continued.
11:20 am		TS1-1-11 Synthesizing MnO2/Graphene Composites by a Hydrothermal Method for use to Enhance the Performance of Supercapacitor, P.R. SO, J.M. TING, K.S. RAO, National Cheng Kung University, Taiwan
11:40 am	**2014 ICMCTF April 28 – May 2, 2014**	**2014 Abstract Submission Deadline October 1, 2013**
12:00 pm	**Thank You & See You Next Year Party Trellis Courtyard near Pool 12:30 – 1:30 pm**	**Awards Nominations Deadline October 1, 2013**

Friday Morning, May 3, 2013

Topical Symposia
Room: Royal Palm 1-3 - Session TS2-2

Advanced Characterization of Coatings and Thin Films
Moderators: S. Korte, University of Erlangen-Nürnberg, Germany, M. Sebastiani, University of Rome "Roma Tre", Italy, F. Giuliani, Imperial College London - South Kensington Campus, UK

8:00 am	TS2-2-1 Correlation Between the Rockwell Indentation Test and the Progressive Load Scratch Test for Assessment of Coating Adhesion, N. RANDALL, CSM Instruments, Switzerland, R. BETHKE, Fraunhofer IST, Germany, G. FAVARO, CSM Instruments, Switzerland	
8:20 am	TS2-2-2 How to Make Tribological Tests Physical, N. SCHWARZER, Saxonian Institute of Surface Mechancis, Germany	
8:40 am	TS2-2-3 Depth Profiling >40-μm Anodized Coatings Using Glow Discharge Optical Emission Spectroscopy, F. LI, J. LAIDUC, W. YORK, W. RIVELLO, Air Liquide Electronics-Balazs NanoAnalysis, US	
9:00 am	TS2-2-4 Mechanical Properties of Nanocrystalline Coatings Revealed by Bending Tests on Fabrication-Unaffected Micro-Cantilevers, A. RIEDL, Materials Center Leoben Forschung GmbH, Austria, R. DANIEL, Montanuniversität Leoben, Austria, M. STEFENELLI, Materials Center Leoben Forschung GmbH, Austria, T. SCHÖBERL, O. KOLEDNIK, C. MITTERER, J. KECKES, Montanuniversität Leoben, Austria	
9:20 am	TS2-2-5 Cyclic and Monotonic Mechanical Properties of Micro Samples Acquired with Custom Built Setups Working up to 1000 Hz – CuAl10Ni5Fe4, 3Y-PZT, T. KENNERKNECHT, Fraunhofer Institute for Mechanics of Materials, IWM, Germany, S. PELLETIER, T. STRAUB, Karlsruhe Institute of Technology, Germany, C. EBERL, Fraunhofer Institute for Mechanics of Materials, IWM, Germany	
9:40 am	TS2-2-6 High Cycle Fatigue of Al and Cu Thin Films by a Novel High-Throughput Method, S. BURGER, C. EBERL, Karlsruhe Institute of Technology, Germany, A. SIEGEL, A. LUDWIG, Ruhr University of Bochum, Germany, O. KRAFT, Karlsruhe Institute of Technology, Germany	
10:00 am	TS2-2-7 Structural, Morphological and Mechanical Characterization of Mo Sputtered Coatings, S.M. DEAMBROSIS, E. MIORIN, M. FABRIZIO, CNR, Italy, M. SEBASTIANI, E. BEMPORAD, University "Roma Tre" Rome, Italy	
10:20 am	TS2-2-8 Effect of AlN Layer on the Growth and on the Structure of Reactive Sputtered TiAlN Thin Films and Multilayers, A. RIZZO, D. VALERINI, L. MIRENGHI, R. TERZI, L. TAPFER, ENEA, Italy, R. GIANNOCCARO, U. GALIETTI, Politecnico di Bari, DIMEG, Italy	
10:40 am	TS2-2-9 Structural Characterization of Amorphous GdTM2 (TM=Fe, Ni and Co) from First-principles, R. LIZARRAGA, E. HOLMSTROM, Universidad Austral de Chile, Chile	
11:00 am	TS2-2-10 Influence of Stoichiometry and Architecture on Mechanical Properties of Cathodic Arc Deposited Ti-Al-Cr-N Coatings, S. PEMMASANI, International Advanced Research Centre for Powder Metallurgy and New Materials (ARCI), India, R. GUNDAKARAM, International Advanced Research Centre for Powder Metallurgy and New Materials(ARCI), India, K. RAJULAPATI, University of Hyderabad, India, R. MANTRIPRAGADA, S. KOPPOJU, K. VALLETI, S. JOSHI, International Advanced Research Centre for Powder Metallurgy and New Materials(ARCI), India	
11:20 am	TS2-2-11 Fabrication and Characterization of Polymethylmethacrylate (PMMA) Thin Film by Plasma Polymerization, C. LI, National Central University, Taiwan, Republic of China, J.H. HSIEH, Ming Chi University of Technology, Taiwan, Republic of China, Y.H. LIN, National Central University, Taiwan	
11:40 am	**2014 ICMCTF April 28 – May 2, 2014**	**2014 Abstract Submission Deadline October 1, 2013**
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Monday Morning, April 29, 2013

Plenary Talk
Room: Town & Country - Session PL

Plenary Lecture

8:00am **PL1 Designer Materials for Unconventional Electronics**, ***Marks*** *(t-marks@northwestern.edu)*, Northwestern University **INVITED**

This lecture focuses on the challenging design and realization of new materials for creating unconventional electronic circuitry to achieve functions not possible with conventional electronic materials, such as large-area coverage, optical transparency, and mechanical flexibility. Fabrication methodologies to achieve these goals include high-throughput, large-area printing techniques. Materials design topics to be discussed in this lecture include: (1) rationally designed high-mobility p- and n-type organic semiconductors for printed organic CMOS, (2) self-assembled and printable high-*k* nanodielectrics enabling ultra-large capacitance, low leakage, high breakdown fields, minimal trapped interfacial charge, and device radiation hardness, (3) polycrystalline and amorphous oxide semiconductors for transparent and mechanically flexible electronics, and (4) combining these materials sets to fabricate a variety of high-performance thin-film transistor-based devices.

Coatings for Use at High Temperature
Room: San Diego - Session A1-1

Coatings to Resist High Temperature Oxidation, Corrosion and Fouling
Moderator: L.G. Johansson, Chalmers University of Technology, Sweden, F. Perez Trujillo, Universidad Compultense de Madrid, M. Weaver, University of Alabama

10:00am **A1-1-1 Oxidation and Coatings for High Temperature Mo-Si-B Alloys**, ***J. Perepezko*** *(perepezk@engr.wisc.edu)*, University of Wisconsin-Madison, US, *R. Sakidja*, The University of Alabama, US **INVITED**

Multiphase Mo-Si-B alloys with compositions, that yield the ternary intermetallic Mo_5SiB_2 (T_2) phase as a key microstructure constituent together with the Mo and Mo_3Si phases, offer an attractive balance of high melting temperature, oxidation resistance and mechanical properties. Mo-Si-B alloys respond to high temperature oxidation in two distinct stages. First, there is a transient stage with an initial high recession rate that corresponds to the evaporation of volatile MoO_3 due to the oxidation of the molybdenum rich phases. The steady state stage of the

oxidation begins when a borosilica layer that initiated in the transient period becomes continuous and protects the alloy from further rapid oxidation. Then, the oxidation rate is limited by oxygen diffusion through the borosilicate layer. In order to improve the oxidation performance of the Mo-Si-B alloys, it is necessary to minimize the transient stage. The three phases, Mo (solid solution), Mo_3Si (A15) and Mo_5SiB_2 (T_2), composing the Mo-Si-B alloys play different roles in

the transient stage. The interaction of the three phases with a reduced microstructure scale can reduce considerably the transient oxidation stage. As a further approach to inhibit the transient stage, a kinetic biasing strategy has been developed to capitalize on the reactions between different phases to develop useful reaction products and alloy compositions that evolve toward a steady state of a compatible system. In order to achieve a compatible interface coating together with enhanced oxidation resistance, a pack cementation process has been adopted to apply

diffusion coatings. From this basis kinetic biasing is used together with pack cementation to develop Mo-Si-B based multilayered coatings with an aluminoborosilica surface and in-situ diffusion barriers with self-healing characteristics for enhanced oxidation resistance. While a combustion environment contains water vapor that can accelerate attack of silica based coatings, the Mo-Si-B based coatings provide oxidation resistance in water vapor up to at least 1500°C. An exposure to hot ionized gas species generated in an arc jet confirms the robust coating performance in extreme environments. To extend the applications beyond Mo-based systems a two-stage process has been implemented to provide effective oxidation resistance for refractory metal cermets, SiC and ZrB_2 ultra-high temperature composites.

10:40am **A1-1-3 Oxidation Performance Evaluation of Niobium Silicide Coatings for Aeronautical Gas Turbines**, ***S. Mathieu*** *(stephane.mathieu@ijl.nancy-universite.fr)*, *L. Portebois*, *M. Vilasi*, Universite de Lorraine, France

Progresses in the field of gas-turbine engine for aircraft are controlled by the availability of structural materials able to withstand the higher-temperature hostile environments (very significant flow conditions containing aggressive elements such as water vapor, at more than 1150°C). Niobium silicide in situ composite alloys are potentially capable of operating in those conditions. The efficiency of intermetallics silicides $Ti_3X_3CrSi_6$ (M_7Si_6-TiX with X=Fe,Co or Ni) as protective coating for niobium alloys against oxidation was demonstrated through many works. All these compounds develop a duplex protective chromia and silica oxide scale, in which both species are not mixed, due to the non-solubility of chromia into silica melts. Under the oxidizing conditions previously described, interaction of water vapor with oxides can lead to the formation of volatile metal hydroxides as $CrO_2(OH)_2$ and also to the formation of Si(OH) volatile species.

In the present work, both coatings and intermetallic single phases $Ti_3X_3CrSi_6$ were elaborated by uniaxial hot pressing. Their characterization (SEM+XRD) showed that the nature of the metal X influenced on the chromium content. Isothermal oxidation behavior at 1200°C was investigated for 100h in thermobalance using industrial dry air (1,5L/H). Steam oxidation test (=7,5% using a flow of 2,5L/h) at 1200°C during 100h and 500h were also carried out. XRD analysis and FEG-SEM observations highlighted that all phases developed a duplex chromia and silica protective layer, with a ratio chromia/silica depending on the nature of X. Formation of low chromium content phases under oxide scale ($TiXSi_2$ or $Ti_4X_4Si_7$) due to the selective oxidation of chromium were detected, ensuring the development of a thin protective silica layer in dry oxidation conditions. Under water vapour atmosphere, the protective behaviour of the oxide scale was function of the nature of X. Indeed Co- and Ni-containing specimens developed pure chromia during oxidation whereas Fe ones develop $(Cr_xFe_{1-x})_2O_3$, reducing drastically the CrO_3 volatilization from the upper chromia scale, and ensuring the durability of the silica layer.

11:00am **A1-1-4 Effect of Water Vapor on Thermally-Grown Alumina Scales on Pt-modified and Simple Aluminide Bond Coatings**, ***M.J. Lance*** *(lancem@ornl.gov)*, *K.A. Unocic*, *J.A. Haynes*, *B.A. Pint*, Oak Ridge National Laboratory, US

Photo-stimulated luminescence spectroscopy (PSLS), 3D microscopy and focused ion beam (FIB) SEM evaluations were made at increasing cyclic oxidation exposures on the same region of simple and Pt-modified aluminide bond coatings on several superalloy substrates. Each sample coupon was cut in half and one half was tested in 10%H2O and the other in dry air in order to understand the effect of water vapor on samples with a thermal barrier coating. With one exception, water vapor did not increase the roughness of the bond coating surface over the increase due to thermal cycling in air. The roughness increase for all samples was due to large and small bond coating grains rising and sinking, respectively, with thermal cycling. This caused the compressive stress in the Al2O3 scale to decrease on the bond coating grain boundary regions eventually leading to scale cracking in the simple aluminide bond coatings. Water addition retards the θ to α-Al2O3 phase transformation in the Pt-modified bond coatings but it is unclear if this affects scale adherence at later stages. Stress histograms produced by PSLS mapping help to elucidate Al2O3 scale damage accumulation in each sample while not identifying a consistent difference for all samples between wet and dry conditions.

Research sponsored by the U. S. Department of Energy, Office of Fossil Energy, Coal and Power R&D

11:20am **A1-1-5 NiAl-Based Metallic Coatings for Advanced Single Crystal Superalloys**, ***H.B. Guo*** *(guo.hongbo@buaa.edu.cn)*, Beihang University, China **INVITED**

NiAl-based intermetallic compounds have attracted increasing attentions because of their promising potential as candidates for metallic coatings or the bond coats in thermal barrier coating (TBCs) to protect the underlying superalloy against high-temperature oxidation and corrosion. Some important aspects should be considered before NiAl compounds are explored as the protective coatings for advanced single crystal (SC) superalloys, such as poor oxide scale adherence of NiAl coating when subjected to cyclic oxidation and severe interdiffusion between the coating and SC superalloy during high-temperature exposure. It is well admited that Secondary reaction zone (SRZ) and need-like topologically-closed packed phases (TCP) formed in SC alloys, partially due to interdiffusion, would result in a significant degradation of mechanical properties of the alloys. In this work, minor reactive elements doped RuNiAl coatings were produced on SC alloys by a combination of electro-plating and electron beam physical vapor deposition (EB-PVD). Cyclic oxidation and interdiffusion of the RuNiAl coated alloy were researched. 0.05at% Dy doped RuNiAl coating revealed not only much improved cyclic oxidation life but also lower oxidation rate as compared to the NiAl coating. And, Dy and Hf co-doping could even behave better in improving cyclic oxidation life than single RE doping. In the RuNiAl coated alloy, SRZ and needle-like TCP phases didn't occur after 200 h annealing at 1373 K, whereas SRZ and TCP was observed in a NiAl coated alloy after 100 h annealing, with a thickness of ~100 μm, indicating that the RuNiAl coating effectively suppressed the formation of SRZ and TCP as a diffusion barrier. The associated mechanisms for the diffusion barrier effect of the RuNiAl coating was discussed via diffusion couples.

Keywords: NiAl; Oxidation; Diffusion; Secondary reaction zone (SRZ); Reactive element effect (REE).

Hard Coatings and Vapor Deposition Technology
Room: Royal Palm 4-6 - Session B1-1

PVD Coatings and Technologies

Moderator: J.H. Huang, Department of Engineering and System Science National Tsing Hua University, S. Weiβmantel, University of Applied Sciences Mittweida

10:00am **B1-1-1 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-Institut für Werkstoff- und Strahltechnik, IWS Dresden, 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.

10:40am **B1-1-3 Hard DLC Coatings Developed by Using HIPIMS Technology**, ***H. Gerdes*** *(holger.gerdes@ist.fraunhofer.de), R. Bandorf, M. Ebert, M. Petersen, G. Bräuer*, Fraunhofer Institute for Surface Engineering and Thin Films IST, Germany

Sputtering carbon containing coatings with high power impulse magnetron sputtering (HIPIMS) is discussed to suffer from the low ionization probability of carbon to significantly modify the resulting coating properties compared to state of the art technology. But B.M. De Koeven et al. reported in 2003 on an increased density for HIPIMS deposited carbon films of 2.7 g/cm^3, mainly attributed to the Ar ion bombardment connected with a very low hardness of only ~ 7 GPa. Coating hardness up to 25 GPa were published by R. Chistyakov et al. using modulated pulse power sputtering (MPP).

In this paper a reactive C-DLC deposition using HIPIMS technology will be reported. Within this study optical emission spectroscopy was carried out and ionized carbon was detected. When adding C_2H_2 to the HIPIMS sputtering of the graphite target the CII emission line increased even more. The deposited layers were investigated in dependence off of the acetylene content in the process and the applied bias voltage especially regarding their hardness. By modification of the deposition parameters DLC films with a plastic hardness of 65 GPa (indentation hardness of 41 GPa) were realized, while the deposition rate was well above 1 µm/h.

11:00am **B1-1-4 Tribological Properties of Tetrahedral amorphous Carbon layers on HSS- steel Drillers**, ***K. Guenther*** *(guenthe2@hs-mittweida.de), S. Scholze, S. Weißmantel*, University of Applied Sciences Mittweida, Germany

Several micrometer thick super-hard tetrahedral amorphous carbon (ta-C) films have been prepared by pulsed laser deposition on polished High-Speed-Steel (HSS)- substrates and HSS- driller. The first aim was to investigate if and how various process parameters influence the tribological properties and the wear parameters of these ta-C layers on polished steel substrates.

Furthermore the influences of an intermediate layer and of internal stress in these ta-C layers on the drill process were analyzed . It will be shown, that an intermediate layer of tungsten carbide optimizes the adhesion of the ta-C layers at the HSS- drillers. Built up edge and wear of the drillers is reduced by improving the mechanical properties of the ta-C layers by adjusting the ablation process and stress reduction process.

Drill- tests with these ta-C coated HSS- drillers in an aluminium cast alloy (G-AlSi12(Cu)) with minimal quantity lubrication shows a high reduction of the demand for energy as well as a strong increase of the durability of these drillers up to 400 times and more. Hence it is possible to elevate the cost effectiveness in case of ta-C coated drillers.

11:20am **B1-1-5 Preparation of Sharp Cutting Edges by Coating Processes in Nanostructured AlCrN Based Films**, ***F. Kaulfuss***, *O. Zimmer (otmar.zimmer@iws.fraunhofer.de)*, Fraunhofer IWS, Germany

Tool coating processes have increasingly gained importance during the last years. Hard protective films such as AlTiN, AlCrN and other types can improve the performance and the lifetime of the tools. The films are deposited by PVD- or CVD- methods, such as arc-technology, sputtering or APCVD.

The coating of cutting edges is a technical challenge because of a possible edge rounding. Often the strictly convex zones are exposed to an extensive ion bombardment during the coating process. Consequently a local overheating and re- sputtering can occur. On the other hand, the deposition of a thicker film causes an edge rounding because of geometrical reasons.

To solve this problem a process has been developed to sharpen the cutting edges during the deposition of the protective coating. The solution is a combination of a certain adjustment of the ion energies of the coating plasma and the materials composition of the film. Thus it is possible to stop and to reverse the rounding of the edges.

For example, with an 8 micron-thick Si-doped AlCrN/TiN film the cutting edge radius can be reduced from 3 micron at the tool blank to 300 nanometers at the surface of the coating.

Due to this process new perspectives of tool coating technologies can be opened.

11:40am **B1-1-6 Pulsed Laser Deposition of Fe-SiC Multilayers for Spintronic Applications**, ***M. Kumar*** *(mukesh232@gmail.com), R. Chandra*, Indian Institute of Technology Roorkee, India, *R. Mishra, R. Tiwari, A. Saxena*, Division, Defence Materials & Stores Research & Development Establishment (DMSRDE) Kanpur, India

The present study explored the deposition of Fe/SiC multilayers on Si (100) substrate at 400ºC using pulsed laser deposition (PLD). These samples were annealed isochronally at temperatures of 800ºC and 1000ºC for 2 h under an inert environment. XRD pattern revealed the amorphous nature of SiC films deposited at 400ºC and crystalline nature in the samples annealed at 800 ºC. On further increasing the annealing temperature to 1000ºC, a number of secondary phases like Fe_3C, SiO_2 and $FeSiO_3$ starts forming in the XRD pattern, causes reaction of SiC, Fe and oxygen at their interface and the interdiffusion of either matrix at higher annealing temperatures. A weak reflection from Fe (100) detected in all samples. X-ray photoelectron spectroscopy (XPS) study shows the binding energy of iron incorporated with iron carbide, iron silicon carbide and binding energy of Si and C incorporated with SiC. FESEM analysis revealed the formation of pyramidal like morphology in SiC films annealed at 800 and 1000ºC. Room temperature ferromagnetism with significant increment in the remnant magnetization and decrease in coercively was observed in Fe/SiC multilayers. The enhanced structural and magnetic properties of Fe/SiC multilayers could be a better approach towards spintronics applications at microscale.

Hard Coatings and Vapor Deposition Technology
Room: Royal Palm 1-3 - Session B5-1

Hard and Multifunctional Nanostructured Coatings

Moderator: J. Paulitsch, Vienna University of Technology, J. Houska, University of West Bohemia - NTIS

10:00am **B5-1-1 Complexity in Characterization of Self Organized Structures in Nitride Nanocomposites**, ***N. Ghafoor*** *(naugh@ifm.liu.se), M. Odén*, Linköping University, Sweden **INVITED**

The present research on transition metal nitrides is focused on introducing new multifunctional materials boosting functionality such as hardness, thermal stability and corrosion resistance of coatings used for metal cutting tools. One limiting factor in understanding the structural complexity of superhard self organized nano-composites is the detection limitations of available characterization techniques. For instance, the internal interfaces and the related hardness enhancement in nc-TiN/*a*-Si_3N_4 nano-composites are heavily debated topics in literature since their individual interfacial

structure has yet not been possible to determine. Similarly, there is a gap in the understanding of the onset of isostructural decomposition at elevated temperatures and the subsequent phase evolution in metastable TiAlN coatings. A well controlled synthesis of model systems of varying composition and growth temperature is an appropriate approach to elucidate phase evolution, decomposition, and interfaces in related structures. This is illustrated in the present work for $Zr_{1-x}Al_xN$ and $Zr_{1-x}Si_xN$ alloys as well as $Zr_{1-x}Al_xN$/ZrN and $Zr_{1-x}Si_xN$/ZrN superlattices synthesized by reactive magnetron sputter deposition onto single-crystal MgO(001) and Al_2O_3(0001) substrates at 500-800°C. High temperature epitaxial growth allows for phase separation during growth and makes it possible to design the structure of the internal interfaces by controlling the composition. It is shown that the maximum hardness in $Zr_{0.64}Al_{0.36}N$ or $Zr_{0.8}Si_{0.2}N$ is associated with unique self-organized nanostructures that form at higher temperatures. With the combination of aberration corrected high resolution STEM imaging, EDX elemental mapping and X-ray pole figure measurements using high energy synchrotron radiation we characterize the structure, draw conclusions regarding its growth, and discuss the underlying processes causing the ordering. Furthermore, crystallographic relationships determined in multilayer structures are related to 3D nano-composites.

10:40am **B5-1-3 High Speed Machining of Hardened Steel Using AIP Deposited Nano-multilayer Coating**, ***K. Yamamoto*** *(yamamoto.kenji1@kobelco.com)*, Kobe Steel Ltd., Japan, *G. Fox-Rabonovich*, McMaster University, Canada, *B Beake*, Micro Materials Ltd., UK

Recently a family of hard mono- and multilayer TiAlCrSiYN-based PVD coatings has been introduced for improving the cutting performance at extremely high cutting speed ranges. These coatings were developed for ultra high speed machining of hardened alloy steels. The multilayer coating was deposited by AIP method. It is alternating layer of TiCrAlSiYN and TiCrAlN with period of a few tens of nanometers. Cutting test was conducted using WC-Co ball nose end-mills against hardened die Steel (H13, HRC55) with cutting speed up to 800 m/min. Result of the cutting test indicated that tool life (as defined by 300um flank wear) of monolayer TiCrAlN is 50 m at cutting speed of 300m/min. Whereas it is increased up to 150m at 500m/min in case of TiCrAlSiYN monolayer coating. However, if multilayer structure is used tool life can be increased to 180m at 600m/min and 120m at cutting speed of 700m/min. TEM analysis of the worn surface of the endmill revealed that bending of the column structure is observed for the monolayer coating suggesting microstructure if destroyed by frictional force during the cutting process. Whereas no bending of the columnar structure was observed in case of the multilayer coating. Different analytical tests were conducted to identify the difference in cutting performance between mono- and multilayer coating. Hardness at room temperature indicate that there is no substantial difference between these three coating system. Then Micro-mechanical characteristics were investigated at elevated temperatures (up to 600 C) using a Micro Materials NanoTest System. Change in the hardness depending on the temperature indicates that hardness of two monolayer coatings decreased by approximately 30 % at 450 degree C. Whereas the hardness of multilayer coating was retained up to 500 degree and hardness decrease only started at 600 degree C. The high hot hardness combined with a crack-deflection ability due to the nano-multilayer structure is very beneficial in severe cutting conditions.This is considered as one of the major reasons (together with protective tribo-films formation on the friction surface) for improved wear resistance of the multilayer coating.

11:00am **B5-1-4 Understanding the Structure of Metastable Multicomponent Nitride Thin Films by First Principles Calculations - Possibilities and Limitations**, ***B. Alling*** *(bjoal@ifm.liu.se)*, Thin Film Physics Division, IFM, Linköping University, Sweden, *I. Abrikosov*, Theoretical Physics Division, IFM, Linköping University, Sweden, *L. Hultman*, Thin Film Physics Division, IFM, Linköping University, Sweden

Holleck proposed that the structure of as-deposited metastable thin films of ternary nitrides could be predicted from analysis of the energetics of solid solutions. As the growth process could prevent phase separation due to limited diffusion, the most likely resulting structure was that of the disordered solid solutions having the lowest free energy.[1] The mixing enthalpies, as a first step to the free energies, of several $M_{1-x}Al_xN$ (M=transition metal) was later calculated from first-principles and used to predict, analyze, and validate experimental results, see, e.g., [2-6]. However, several other aspects of the out-of-equilibrium synthesis conditions, like the structure of the substrate, the growth temperature, the nitrogen pressure, and the bias voltage are of importance and predictions based on energetic arguments should be made with caution. In this work we review theoretical calculations and compare them with experimental results for several technologically important $M_{1-x}Al_xN$ materials such as $Ti_{1-x}Al_xN$, $Zr_{1-x}Al_xN$, $Nb_{1-x}Al_xN$,$Y_{1-x}Al_xN$, and $Sc_{1-x}Al_xN$. As an example, in the latter case a NaCl structure seed layer could promote growth of cubic $Sc_{1-x}Al_xN$ film with Al content as high as x=0.5-0.6 [2], while calculations show that the hexagonal wurtzite structure has a lower enthalpy for x>0.4 [3]. Based on the result for those different systems we discuss the possibilities and limitations for understanding metastable phase formation in thin films using first principles calculations.

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11:20am **B5-1-5 High Temperature Wear Resistance of TiCrAlCN/TiAlN Multilayer PVD Coatings on M2 High Speed Steel**, ***I. Efeoglu***, *E. Demirci (eedemirci@atauni.edu.tr)*, Atatürk University, Turkey, *O. Baran*, Erzincan University, Turkey, *Y. Totik*, Atatürk University, Turkey

The mechanical and tribological properties of TiN-based coatings can be improved with the addition of different alloy elements such as B, Cr, Al, C, Si, etc.. For this purpose, in this study, TiN co-sputtered with Cr, Al and C were deposited on M2 steel substrates and silicon wafers by Closed-Field Unbalanced Magnetron Sputtering (CFUBMS) and TiCrAlCN/TiAlN multilayer films were obtained. The structural and properties of TiCrAlCN/TiAlN multilayer films were analyzed by using XRD and SEM. The hardness properties of films were investigated by microhardness tester. The high temperature wearproperties of TiCrAlCN/TiAlN multilayer coatings were determined by using a high temperature pin-on-disc tribometer. The effect of deposition parameters and Ti, Cr, Al, C and N content on crystallographic orientation and friction coefficient and wear rate at the high temperature was examined.

Key Words: TiN-based coatings, alloy elements, CFUBMS, high temperature wear resistance, M2 steels.

11:40am **B5-1-6 Wear Characteristics of Nitrogen-doped Al-Ti-Ni Nanocomposite Coatings Deposited on Austenitic Stainless Steel**, ***J. Lawal***, *M. Audronis, A. Matthews, A. Leyland (a.leyland@sheffield.ac.uk)*, University of Sheffield, UK

Non-ferritic engineering alloys (e.g. austenitic stainless steels, nickel alloys and alloys of Titanium, Aluminium, Magnesium) are increasingly used for engineering components, owing to combinations of desirable functional properties such as high specific strength, toughness, corrosion resistance and durability in extreme environments. However, it is well known that such alloys tend to exhibit poor tribological properties – especially under conditions of sliding wear and/or abrasion

Nanostructured coatings comprising a hard nanocrystalline phase embedded in an amorphous matrix have been found to exhibit improved tribological properties in various conditions. This study investigates the wear characteristics of nitrogen-doped Al-Ti-Ni nanocomposite coatings prepared by magnetron sputtering. The sliding and abrasive wear behaviour of the coating-substrate system were studied using a reciprocating ball-on-flat test and an abrasive wear test respectively in dry and lubricated conditions in different environments. SEM, with EDS and XRD were conducted to check the composition and measure the thickness of the coatings. Hardnesses and elastic modulii were also determined. The addition of nitrogen enhanced the formation of a hard phase in the amorphous matrix which had a significant influence on the wear behaviour of the substrate. This work provides a comprehensive report of the wear rates in different environments in both dry and lubricated conditions.

Fundamentals and Technology of Multifunctional Thin Films: Towards Optoelectronic Device Applications
Room: Sunset - Session C1-1

Recent Advances in Optical Thin Films
Moderator: J.H. Hsieh, Ming Chi University of Technology

10:00am **C1-1-1 Recent Progress in Plasmonics Applied to Optoelectronic Devices**, ***K. Okamoto*** *(okamoto@ms.ifoc.kyushu-u.ac.jp)*, Kyushu University, Japan **INVITED**

Plasmonics is the technique to control and utilize surface plasmon (SP) generated around nano-structured metals. In 2004, for the first time, we have reported that the plasmonics is very useful to increase the emission

efficiencies of light emitting materials. Huge enhancement of the photoluminescence from InGaN/GaN-based QWs was obtained when nano-structured Ag layers were deposited 10 nm above the QWs[1]. The coupling between the exciton and the SP becomes remarkable when the emission energy is close to the SP frequency[2]. The SP-enhanced internal quantum efficiencies (IQEs) can reach almost 100% at the blue emission region[3]. One of the most important advantages of this technique is the ability to apply to not only InGaN-based materials but also various materials. We observed similar huge enhancement effcts for several organic films, CdSe-based nanoparticles and also silicon-based nanostructures, etc. The SP-exciton coupling would lead to high efficiency optoelectronic devices such as "plasmonic LEDs" and "Plasmonic solar cells".

Until now, several types of the plasmonic LEDs and solar cells have been proposed and reported, however, these are still far from practical utilizations. Further optimization of the metal nanostructure and tuning of the SP coupling process are required to develop both devices. Therefore we are designing more effective plasmonic nanostructures by using the 3-dimensional finite difference time domain (3D-FDTD) calculations and the nanofabrication processes with several bottom-up techniques. For example, we can control the resonance spectra of localized SP (LSP) mode by using the Ag nanoparticles with various diameters. By optimization of the Ag particle size, we achieved high efficient green emission from InGaN/GaN QWs, which has been very difficult to improve the emission efficiency. Moreover we succeeded to control the LSP resonance spectra with much wider wavelength region by employing 2 dimensional (2D) nanosheet structure of Ag nanoparticles with 5nm diameter[4]. These plasmonic nanostructures would bring the new type of high-efficiency LEDs and solar cells. The detail of the recent progress in plasmonics applied to several optoelectronic devices will be discussed at the conference.

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10:40am **C1-1-3 Influence of Sputtering Pressure on the Structural, Optical and Hydrophobic Properties of Sputtered Deposited HfO_2 Coatings**, ***V. Dave***, *H. Gupta, R. Chandra (ramesfic@gmail.com),* Indian Institute of Technology Roorkee, India

The aim of this work is to develop hydrophobic coatings for outdoors insulators using sputtering technique. Hafnium oxide is characterized by high dielectric constant, large band gap (5.6eV), high refractive index (2.1) , and good mechanical ,thermal and chemical properties. Hence HfO2 is suitable as a protective coating for outdoor insulators used in the transmission line and transformers. Hafnium oxide coatings were deposited on glass substrates by DC magnetron sputtering technique at sputtering pressure of 10mtorr, 15mtorr and 20mtorr.The film was characterized by techniques like X ray diffraction(XRD),atomic force microscopy(AFM),water contact angle meter and UV-NIR spectrophotometer. The average crystallite size calculated from XRD peaks shows that it increases with increase in sputtering pressure. The roughness calculated from AFM images shows the similar trend. The hydrophobicity was investigated using water contact angle meter and found correlation with the roughness calculated from AFM. The effect of sputtering pressure was also investigated on optical band gap and refractive index calculated from transmission and absorption data.

11:00am **C1-1-4 Influence of the Parameters the Fabrication in Optical Properties of $Bi_xTi_yO_z$ Thin Films**, ***J. Alfonso***, *J. Olaya, M. Pinzon (mjpinzonc@unal.edu.co),* National University of Colombia, Colombia

In the last decade, the different compositions of Bismuth Titanate Oxide (BixTiyOz) has been researched it due to their physical properties such as: electric, ferroelectric and optoelectronic behavior that allow it be used as ceramic capacitors, transducers, sensors, memory devices, optoelectronic devices, piezoelectric technology, acousto-electronics and acousto-optics applications. For these reasons in this work, we present the results obtained in the growth of the $Bi_xTi_yO_z$ thin films through rf magnetron sputtering The films were grown on common glass substrate and has been evaluated the microstructure and optical behavior as a function of the substrate temperature and power applied at target. The microstructure analysis was carried out by x-ray diffraction (XRD) and optical response was evaluated by means transmittance measurements. The XRD results have shows that the films growth from room temperature to 573 K and power from 100 W to 200W are amorphous. Moreover, the films growth at 623 K and power from 150 to 200 W shows preferential orientation along (622) plane of $Bi_2Ti_2O_7$ cubic face centered phase.

Using the transmittance values and through Swanepoel method we calculated the refractive index, thickness and absorption coefficient of the amorphous and crystalline films. The mean values in amorphous films found are: n=2.43 (λ=463nm); α= $1.3x10^4$ cm^{-1}; 285nm and in crystalline films n=3.31 (λ=424nm); 255.68nm and α= $2.2x10^4$ cm^{-1}. The energy gap was determined used the Urbach's formula (2.8 eV). The values of refractive index and energy gap are very near of the $Bi_2Ti_2O_7$.

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

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

Moderator: M. Stack, University of Strathclyde, M. Mathew, Rush University Medical Center, J. Geringer, Ecole Nationale Superieure des Mines

10:00am **D2-1-1 Why Does Titanium Alloy Wear Cobalt Chrome Alloy Despite Lower Bulk Hardness: a Nanoindentation Study?**, ***S Bull*** *(steve.bull@ncl.ac.uk),* Newcastle University, UK, *O. Sayginer,* Newcastle University, UK, Turkey, *N. Moharrami,* Newcastle University, UK

Titanium-based and cobalt-chrome alloys have been widely used in orthopaedic applications as these materials can significantly enhance the quality of human life as implant materials. The longevity of these materials is highly influenced by their mechanical properties. In some devices cobalt chrome components articulate with titanium alloy counterfaces (e.g. in the taper connections of stems and femoral heads in modern modular designs) and damage has been reported of the harder cobalt chrome by the softer titanium alloy component. This study attempts to understand why this might occur by investigating bulk and surface mechanical properties (such as hardness and Young's modulus) of a number of hip implants and test samples using a Hysitron triboindenter. AFM images were also obtained to determine the contact area and hence pile-up correction factors.The results were compared for samples before being used in the body, to account for surface mechanical response due to implant manufacture, and after to account for the materials response to long-term cyclic loads. To assess the effects of oxidation, the alloys were treated electrochemically with NaCl solution at body temperature. It was found that titanium oxidised preferentially compared with cobalt-chrome alloys. Furthermore, the oxidised titanium showed significantly higher hardness values therefore damaging the unoxidised cobalt-chrome material. The implications for device design and manufacture will be discussed.

10:20am **D2-1-2 Metal - Metal Oxide Thin Film-Biological Interfaces and the Role of Bio-mechano-electro-chemical Processes**, ***J.L. Gilbert*** *(gilbert@syr.edu), V. Swaminathan, M. Haeri, S. Mali,* Syracuse University, US **INVITED**

Metallic Biomaterials continue to serve as the major class of materials used in a wide array of medical devices today. The primary alloy systems used come from the titanium, cobalt-chromium, and stainless steel families and are extraordinarily corrosion resistant and biocompatible with the human body. The major source of these characteristics are the nanometer-scale oxide thin films that spontaneously form on their surface. While these are known as passive films because of their ability to resist corrosion, they are not passive in their structure, properties or behavior when implanted in the biological milieu. Importantly, when these medical devices experience mechanical interactions at their surface, significant coupled processes interact to result in major changes to the surface and its properties and performance. In this presentation, the effects and consequences of mechanical abrasion of immersed oxide films on metallic substrates will be described. The coupled processes of surface mechanics with electrochemical effects will be explored in the context of the biological system. This includes explaining how oxide abrasion results in dramatically increased corrosion processes, large excursions in voltage, changes in oxide film electrical properties (impedance), altered solution chemistry and how these changes can influence the cells and proteins immediately adjacent to the implant surface. Large cathodic voltage excursions are possible and these shifts lower surface impedance characteristics and result in significant alteration in adsorbed protein conformation and behavior, and induce an apoptotic cell death in-vitro that may have a significant clinical effect on implant performance. Test methods for the exploration of fretting crevice corrosion will be described for both material surface studies and implant studies.

11:00am **D2-1-4 Dominant Role of Molybdenum in the Electrochemical Deposition of Biological Macromolecules on Metallic Surfaces**, *E. Martin (elizabeth-martin@u.northwestern.edu)*, Northwestern University, US, *R. Pourzal*, ***M. Mathew***, Rush University Medical Center, US, *K. Shull*, Northwestern University, US

The corrosion of CoCrMo, an alloy frequently used in orthopedic implants, was studied with an electrochemical quartz crystal microbalance (QCM) in three physiologically relevant solutions. Mass changes were measured during potentiodynamic tests, showing material deposition in protein solutions at potential levels that caused mass loss when the proteins were not present. X-ray photoelectron spectroscopy (XPS) data indicated that the deposited material was primarily organic, and therefore was most likely derived from proteins in the electrolyte. Material deposition consistently occurred at a critical potential and was not dependent on the current density or total charge released into solution. Corrosion studies on pure Co, Cr and Mo in protein solutions only found material deposition on Mo. We hypothesize that organic deposition results from the interaction of Mo(VI) with proteins in the surrounding solution. The organic layer is reminiscent of tribochemical reaction layers that form on the surface of CoCrMo hip bearings, suggesting that these types of layers can be formed by purely electrochemical means.

11:20am **D2-1-5 Engineering Nanostructured Cubic Zirconia Coating for Enhanced Biointegration of Orthopaedic Implants**, ***F. Namavar*** *(fnamavar@unmc.edu)*, University of Nebraska Medical Center, US, *R. Sabirianov*, University of Nebraska at Omaha, US, *A. Rubenstein, R. Miralami, G.M. Thiele, J.G. Sharp, K.L. Garvin*, University of Nebraska Medical Center, US

Failure of osseointegration prevents long-term stability, which results in pain, implant loosening, and infection, all of which can necessitate revision replacement surgery. Hydroxyapatite (HA) and bioactive glasses have been studied for decades because of their bioactive properties. However, concerns have been raised about the bioabsorption of the HA layer, the mechanical strength of the HA layer [1, 2], and the HA layer debonding from the metal implant [2, 3]. We designed and produced nanostructurally stabilized pure cubic zirconia ceramic [4] coatings by an ion beam assisted deposition (IBAD) with nanostructures comparable to the size of adhesive proteins (with 2-25 nm grain size). Our ceramic coatings exhibit high hardness (16±1.7 GPa) and a zero contact angle with serum and possess excellent adhesion to all orthopaedic materials. Adhesion and proliferation experiments were performed with a mesenchymal stromal cell cell line (OMA-AD) on the nano-structured coatings and compared to Cobalt Chrome, Titanium, and HA. Our results with Alamar blue, direct cell counting, and scanning electron microscopy, clearly indicated that nano-engineered cubic zirconia is superior in supporting growth, adhesion, and proliferation. Further adhesion experiments with fibronectin (FN) from human plasma using an ELISA based technique resulted in higher FN adsorption on nanoengineered surfaces as compared to other conventional orthopedic materials. These experiments indicate a clear correlation between cell and FN adhesion. Since the absorption of adhesive proteins such as FN is a key factor in cell adhesion and bone formation at an implant surface, we are proposing a phenomenological concept based on electrostatic and steric complementarity that may explain the enhanced adhesion of cells, through modification of adhesive protein absorption, to the engineered nanostructured surfaces as compared to conventional smooth surfaces [5]. 1. A. El-Ghannam, Expert Review Medical Devices, 2 (1), 87-101, 1340-1347 (2005). 2. B.D. Ratner, Journal of Dental Education, 65 (12), 340-1347 (2001). 3. O. Reikeras, R.B.Gunderson, Acta Orthop Scand. 73 (1), 104-108 (2002). 4. F. Namavar, C.L. Cheung, R.F. Sabirianov, et. al, Nano Lett., 8, 988 (2008). 5. R.F. Sabirianov, A. Rubinstein, F. Namavar, Phys. Chem. Chem. Phys. 13, 6597, (2011).

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

Mechanical Properties and Adhesion
Moderator: M.T. Lin, National Chung Hsing University, Taiwan, R. Chromik, McGill University, D. Bahr, Washington State University

10:00am **E2-1-1 Time Resolved Synchrotron X-ray Strain Measurement in Biaxially Loaded Au Thin Films**, ***D. Faurie*** *(faurie@univ-paris13.fr)*, LSPM-CNRS, Université Paris 13, Sorbonne Paris-Cité, France, *P.O. Renault*, Institut P' - Universite de Poitiers, France, *G. Geandier*, Institut Jean Lamour, France, *E. Le Bourhis*, Institut P' - Universite de Poitiers, France, *C. Mocuta, D. Thiaudière*, Soleil Synchrotron, France

Synchrotron x-ray radiation was used for *in situ* strain measurements in gold films on polyimide substrate during biaxial deformation tests. We have used an area detector that allows inspecting multiple directions in the polycrystalline thin film without serial sectioning during straining. We show in this paper the configuration used and the attainable orientations on a pole figure for which the x-ray strains are measured. Moreover, we show how to detect the onset on plasticity, by comparing x-ray strains and macroscopic strains measured by Digital Image Correlation.

This experimental Setup offers several possibilities that will be described in this talk:

(i) Continuous biaxial tensile tests

(ii) Continuous biaxial cyclic tests

(iii) Complete strain pole figure measurements during biaxial loading steps

A few examples of studies about elastic-plastic behavior of Au thin films with thicknesses below 100 nm will be shown.

10:20am **E2-1-2 Grain Growth in Nanocrystalline Copper During Indentation at Very Low Temperatures**, ***C.C. Battaile*** *(ccbatta@sandia.gov)*, *B.L. Boyce, S.M. Foiles, K.M. Hattar*, Sandia National Laboratories, US, *E.A. Holm*, Carnegie Mellon University, US, *E.R. Homer*, Brigham Young University, US, *H. Padilla, G.J. Tucker*, Sandia National Laboratories, US

The properties of most engineering materials are strongly influenced by the characteristics of their internal structures. A material's internal structure greatly affected not only by thermal and/or mechanical processing during fabrication, but also during service or storage through the influence of temperature or stress. Temperature influences a material's evolution partly through the modification of the migration kinetics of its internal interfaces, and stress does so by storing energy in the material inhomogeneously. Nanocrystalline metals exhibit properties that are advantageous to a wide variety of applications, but the relatively high energy (per unit volume) and curvature of the internal interfaces render these materials relatively unstable. Thus, it is important that we achieve an understanding, and thus enhance our ability to control, the microstructural stability of nanocrystalline metals. In this presentation, we will discuss experiments and simulations on grain growth in pure, nanocrystalline copper. Vickers indentation of thin films at various temperatures - including 4K, 77K, and 273K - demonstrates that substantial grain growth can occur even at very low temperatures. Precession TEM characterization and in-situ TEM cryo-indentation help elucidate the nature and character of the interfaces responsible for this anomaly. Molecular dynamics simulations of the migration of individual grain boundaries suggest that the mobilities of some special boundaries can increase with decreasing temperature, contrary to conventional wisdom. Coupled continuum simulations of grain growth and mechanical deformation demonstrate that the acceleration of grain growth at low temperatures might be explained by the mitigation of plastic deformation as a stress relief mechanism.

10:40am **E2-1-3 Inhomogeneous Stresses, Texture Transformations and Anomalous Grain Growth in Thin Metal Films**, ***S. Baker*** *(spb14@cornell.edu)*, Cornell University, US **INVITED**

Thin metal films on substrates often form fiber textures during deposition and processing. Since film properties depend strongly on texture, it is important to be able to predict what texture components will form. However, existing models are incomplete. For example, a simple thermodynamic model predicts that FCC films should form (111) texture to minimize interface energy when sufficiently thin, and (100) texture to minimize strain energy when sufficiently thick. While this texture trend is observed experimentally, evidence suggests that the driving forces are not

so simple—e.g. films transform even when no substrate is present to provide the requisite strain energy. We have developed a novel high-throughput test and used it to study the thermodynamics and kinetics of texture transformations. Up to 100 samples with a range of thicknesses and different interface energies are produced in a single deposition run, eliminating variations due to fluctuating impurity levels. Texture and stress levels are determined using x-ray diffraction and grain structure is characterized by EBSD. We find that texture transformation occurs by anomalous grain growth, resulting in stable, thickness-dependent mixed (111)/(100) textures over a wide range of thicknesses. The final stress state does *not* correlate well with the strain energy, or the presence or absence of an adhesion layer. Transformation kinetics are strongly thickness dependent, with maximum transformation rates occurring at intermediate film thicknesses. These results suggest that variations in initial nucleus density with film thickness control the transformation kinetics. An explanation based on inhomogeneous stresses is proposed to account for the thickness-dependent mixed texture.

11:20am **E2-1-5 Microstructure and Mechanical Properties of Nanodiamond Enhanced Diamond-like Carbon Thin Films on Ti Alloys**, ***C. Zhang***, *H. Niakan, L. Yang, Y. Li, Q. Yang (qiy866@mail.usask.ca)*, University of Saskatchewan, Canada

Diamond nanoparticles (DNP) have been proven to be effective in enhancing adhesion between DLC thin film and Ti6Al4V substrate. In this research, the effect of DNP density on the adhesion and mechanical properties of DLC on Ti alloy were investigated in order to optimize the conditions. Initially, DNP with different density from separate particles to semi-continuous thin film were deposited on Ti6Al4V substrates by microwave plasma assisted chemical vapor deposition. A DLC thin film was then deposited on them by direct ion beam deposition. Scanning electron microscopy, Atomic force microscopy, Raman spectroscopy, synchrotron near-edge X-ray absorption fine structure, Nano analyzer and Rockwell indentation were used to evaluate the microstructure, mechanical properties and adhesion of the deposited films. Results show that the density of DNP has significant effect on the adhesion and other mechanical properties of the films: higher density resulted in higher adhesion, higher hardness and lower friction coefficient.

11:40am **E2-1-6 Residual Stress Analysis in Thin Films using Focused Ion Beam and Digital Image Correlation - Stress Analysis by Raman Spectroscopy on Diamond Films**, *F. Ahmed, M. Krottenthaler, C. Schmid,* ***K. Durst*** *(Karsten.Durst@ww.uni-erlangen.de)*, University Erlangen-Nuremberg, Germany

The residual stresses in thin films are caused by thermomechanical mismatch and deposition process. These stresses affect the in-service mechanical performance and can reduce the lifetime of a coated component. The analysis and control of residual stresses is important for understanding the fracture and delamination behaviour of the coatings and to improve the adhesion.

In this work, crystalline diamond thin films on titanium substrate were used, which in general have compressive residual stresses after deposition. In order to evaluate these stresses at sub-micron scale, a semi-destructive trench cutting method based on focused ion beam (FIB) milling was employed. Using FIB tool, some rectangular bars were milled with trenches along the longer sides. These trenches introduced the strain relief in the coating perpendicular to the longer sides of the bar. To evaluate the strain change in film by digital image correlation (DIC), high resolution images of the concerned area were recorded with FIB microscope before and after the milling. The displacement produced in the film was determined with DIC and plotted against pixel positions on the image to determine the strain change. To get the magnitude of residual stress from this strain change, FIB-milled bar was modelled using finite element method (FEM) in three dimensions. A residual stress of -5 GPa (determined with Raman spectroscopy) was used as input material property for the coating. The resulting strain change measured on the simulated bar was very close to the DIC value. This result validated the stress value measured by Raman spectroscopy. Afterwards, the FIB-milled bars were scanned with micro-Raman spectroscopy to analyse the stress relief along the edges of the bar. The results showed a full relaxation of compressive stress from ~ -5 GPa to zero value. Furthermore, the stress profiles made with Raman spectroscopy, along the edges of the milled bar, were compared to the FEM based stress profiles and these showed the similar stress relaxation trend.

Applications, Manufacturing, and Equipment
Room: California - Session G4-1+E

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

Moderator: M. Arndt, OC Oerlikon Balzers AG, X. Nie, University of Windsor

10:00am **G4-1+E-1 Advanced Coatings and Tool Materials for Hobbing - a Major Step Forward in Productivity**, ***P. Immich*** *(pimmich@lmt-fette.com), Kretzschmann, M. Rommel, T. Falk, R. Fischer*, LMT Fette Werkzeugtechnik GmbH & Co. KG, Germany **INVITED**

Today without gear wheels almost nothing is turning. Manufacturers produce these components by the million for use in automotive gearboxes or in the gears of large wind turbines. Gear hobs have proven themselves for more than a hundred years now in the manufacture of gear wheels and other tooth-cutting tasks.

The ever increasing demand for higher productivity in manufacturing gears requires advanced hard coatings and new substrate materials. Up to now in this field of gear hobbing different substrate materials are used for single-piece hobs: powder metallurgy high-speed steel (PM-HSS) and cemented carbide. Today PM-HSS has a market share around 70% offering limited cutting speeds for wet and dry conditions. On the other hand cemented carbide offers strong performance related features like high cutting speeds up to 400 m/s. But due to the fact, that hobs have a typical life cycle time of 10-15 recondition cycles– hobs are often demounted – packed and shipped – decoated- regrinded and coated again- could cause small handling or production damages that result in a shorter tool life time and less reliability of the production process.

On the substrate side – there is a new generation of intermetallic phase substrate on the market offering compared to conventional PM-HSS higher hot hardness and as result from these higher cutting speeds. On the coating side the development focus is on introducing new coatings allowing new cutting features. In fact today hobs are coated and e.g. dry gear cutting is only possible with coated tools due to the prevention of chip welding. Today hob coatings that are available on the commercial market mainly based on TiAlN system. Now there is a significant switch in the market towards the system Cr-Al-N offering higher oxidation resistance and higher wear resistance. As a result of these developments it is possible to increase cutting speeds up to 50% compared to conventional coatings

For large modules hobs with inserts are offering an economic way of producing gears. There are gear milling cutters (single tooth method) and ICI hobs available. The selection of the best type of tool depends on the lot size to be manufactured and the corresponding number of teeth. Gear hobbing is the most productive method for cutting large-module gears with a high number of teeth. Gear milling cutters are especially to be preferred for low numbers of teeth or small lot sizes. In the last years the performance of these tools are driven by new cutting material grades like new ultra-fine grain carbide combined with new thick PVD coatings and special micro-surface preparation.

10:40am **G4-1+E-3 Physicochemical, Mechanical and Tribological Properties of Si_3N_4-MoS_2 Thin Films Deposited by Magnetron Sputtering**, *R. Trentin, A. Bandeira, C. Aguzzoli, I. Baumvol, M. Moré Farias,* ***C.A. Figueroa*** *(cafiguer@ucs.br)*, UCS - Caxias do Sul University, Brazil

Hard coatings are widely used in surface engineering for wear protection of tools and mechanical components. Nowadays, dry machining technologies are emerging techniques due to both saving costs and environmental issues. Such type of coatings to be applied in tools for dry machining must combine not only high hardness and structure stability but also tribological aspects like ultra-low friction. Si_3N_4 thin films show outstanding performance, in terms of wear and corrosion resistance, in cutting tools at higher temperatures than 1000 ^oC. However, the incorporation of MoS_2 in Si_3N_4 thin films could reduce the friction coefficient maintaining high values of hardness in these thin films.

In this work, Si_3N_4-MoS_2 thin films were deposited on Si(100) substrates by dual rf and dc reactive magnetron sputtering from Si and MoS_2 targets in a Ar/N_2 plasma with different MoS_2 amounts. The composite thin films were characterized by glancing angle X-ray diffraction, Rutherford backscattering spectrometry, glow-discharge optical emission spectroscopy, nanohardness at different temperatures (23^{o}C to 400^{o}C) and nano-scratch and friction measurements at room temperature. In the whole layer both Si_3N_4 and MoS_2 compounds are stoichiometric and the deposition rate is 0.12 $nm.s^{-1}$. Moreover, the structure is amorphous and homogenous. The MoS_2 content in the composite thin film goes from 0.2 at. % to 4 at. %. In contrast to previous results where the hardness of the TiN-MoS_2

nanocomposite system decreases monotonously following the mixture rule when MoS_2 is incorporated, our Si_3N_4-MoS_2 thin films show a maximum hardness of 28.5 ± 1.5 GPa at a MoS_2 content of 1.6 at. %. The hardness of these Si_3N_4-MoS_2 thin films decrease slightly as a function of temperature. Finally, the friction coefficient tendency of the Si_3N_4-MoS_2 thin films will be discussed and compared to the TiN-MoS_2 nanocomposite system where a minimum friction coefficient is reached at intermediate MoS_2 contents.

11:00am **G4-1+E-4 Effect of Silicon Content on Pvd Nitride Film Mechanical Properties and Cutting Performance of Coated Cemented Carbide Inserts**, *K.D. Bouzakis (bouzakis@eng.auth.gr)*, Aristoteles University of Thessaloniki, Greece, ***E. Bouzakis***, Fraunhofer Project Center for Coatings in Manufacturing (PCCM), Greece, *S. Kombogiannis, G. Skordaris, S. Makrimallakis, M. Batsiolas*, Aristoteles University of Thessaloniki, Greece, *R. M'Saoubi, J. Andersson*, Seco Tools AB, Sweden

The effect of Si content on TiSiN and TiAlN/TiSiN films' mechanical strength, brittleness, fatigue and adhesion is introduced. These films were deposited on cemented carbide inserts using cathodic arc evaporation method. Moreover, cutting performance investigations in milling stainless steel by these inserts are presented. According to previous research works, the addition of Si would lead to a linear PVD film structure, since the columnar one of a standard TiAlN coating is substituted by a dense nano-composite structure. Thus, on one hand, TiSiN films may possess improved mechanical properties in comparison to TiAlN ones. On the other hand, the adhesion of TiSiN films compared to TiAlN coatings is deteriorated. For overcoming potential film adhesive failures when cutting with TiSiN coated inserts, an adhesive TiAlN layer prior to the TiSiN film is deposited. In this way, it was possible to investigate the influence of the Si-content on the wear behaviour of TiAlN/TiSiN coated tools at the same adhesion quality level, as that of TiAlN films on cemented carbide inserts. In the conducted investigations, specimens coated with TiAlN/TiSiN films of various Si-contents were applied. For determining coating strength properties, nanoindentations were carried out. Based on these data and a FEM continuous simulation of nanoindentation, films' elasto-plastic laws were determined. Moreover, nano-impact tests were conducted for capturing the influence of Si-content on TiSiN film brittleness. The fatigue properties of the examined coatings at ambient and elevated temperatures were encountered through perpendicular impact tests. The coatings' adhesion was evaluated by inclined impact tests and by Rockwell indentations. Finally, milling experiments were carried out for investigating coated inserts cutting performance at various cutting speeds and consequently temperatures, using as workpiece material stainless steel 304 L. According to the obtained results, the beneficial effect of Si on the cutting performance of PVD coated tools was detected in an optimum cutting speed range. Moreover, a superficial TiSiN layer on TiAlN coated cemented carbide tools, leads to improved compound mechanical properties; these as well as the cutting performance depend on the TiSiN-film Si content.

11:20am **G4-1+E-5 A Study on Friction and Wear Properties of Carbide Cutting Tools with MoS_2 Coating Deposited by Electrostatic Spray Coating**, ***U. Paturi*** *(maheshpaturi@gmail.com), S. Narala*, BITS-Pilani, India

In an attempt to explore the application of self-lubricant coatings on tribological components and to understand its influence in dry machining operations during tool-work sliding interaction, a laboratory based tribological simulation was conducted. To realize this, a wear test between Ti-6Al-4V alloy (counterface) and uncoated and coated cemented tungsten carbide-cobalt (WC-Co) alloy (pin specimen) at different sliding conditions was carried out using a pin-on-disc wear testing machine. The characteristics of wear rate, coefficient of friction and surface roughness were investigated with and without self-lubricant coatings on the carbide cutting tool specimen. In this work, electrostatic spray coating process was employed in deposition of molybdenum disulphide (MoS_2) solid lubricant powder particles on specimens. Microstructure of specimen and counter surface was analyzed using scanning electron microscopy and optical microscopy. The results showed that the presence of solid lubricant film on specimen will greatly influence the sliding performance and improves the wear resistance through reduction in the mechanical energy given in the sliding contact due to presence of MoS_2 lamellar structure as a transfer film.

Keywords: cemented carbide, solid lubricant, electrostatic spray coating, wear rate, friction, sliding performance

11:40am **G4-1+E-6 Enhanced Cutting Performance of Tools Coated with Al2O3 –Based Coatings**, ***M. Jilek*** *(jilek.jr@shm-cz.cz), M. Sima*, SHM, Czech Republic, *V. Maixner*, Pramet Tools, Czech Republic

From the point of view of oxidation and high-temperature wear resistance, Al_2O_3-based coatings are among the best available. This is especially useful for dry high-speed milling or turning of materials from the groups M 10 – 25 and K 10 – 20. We will report about the preparation and cutting performance of $(Al_{1-x}Cr_x)_2O_3$ coatings deposited by vacuum arc technology in the coating system PLATIT π311, which uses rotating cylindrical cathodes made of pure Al and Cr targets in an oxygen-containing reactive gas atmosphere, where poisoning of the Al cathode was controlled by the deposition of metallic Cr onto the Al cathode surface . This procedure significantly improved the uniformity of the erosion of the Al cathode and reduced the roughness of the deposited coatings. The deposited coatings have been evaluated in terms of their surface roughness, hardness, and structure. The life time of tools coated wi th the new Al_2O_3-based coating during machining has been compared with other coatings.

Coatings for Use at High Temperature
Room: San Diego - Session A1-2

Coatings to Resist High Temperature Oxidation, Corrosion and Fouling
Moderator: L.G. Johansson, Chalmers University of Technology, Sweden, M. Weaver, University of Alabama, F. Perez Trujillo, Universidad Compultense de Madrid

1:30pm **A1-2-1 Oxidation Behavior of Co-Doped NiCrAl Alloys in Dry and Wet Air**, ***K.A. Unocic*** *(unocicka@ornl.gov), B.A. Pint*, Oak Ridge National Laboratory, US

Cast NiCrAl alloys with additions of Y, La, Hf and Ti were evaluated at 1100°C in wet (10 and 50% H2O) and dry air in order to optimize such dopants for superalloy bond coatings. The results suggest that the typical Y addition in most coatings could be replaced by La. Also, scale adhesion in cyclic testing was improved with the co-addition of Hf with La or Y. Ti was added to investigate its incorporation in coatings on superalloys containing significant Ti additions. Particularly with co- doped alloys, the addition of Ti had little effect. Water vapor increased spallation, especially for the least adherent alloys, such as Y,Ti-doped NiCrAl, water vapor increased scale spallation. For the co- doped compositions with Hf, water vapor had a limited effect on scale adhesion on the alumina growth rate in isothermal exposures. In addition to specimen mass change, beta phase depletion in the substrate was evaluated. Analytical transmission electron microscopy showed that Y, La and Hf co- segregated to the alumina scale grain boundaries and formed dopant rich oxide precipitates in the scale.

Research sponsored by the U. S. Department of Energy, Office of Fossil Energy, Coal and Power R&D.

1:50pm **A1-2-2 Platinium Diffusion in Pure Nickel**, *M. Zagula-Yavorska*, ***J. Romanowska*** *(jroman@prz.edu.pl), J. Sieniawski*, Rzeszów University of Technology, Poland

The diffusion behavior of Pt deposited on pure nickel by the electroplating process was examined by the analysis of Pt concentration profiles against the distance in pure nickel specimens for various diffusion times (2, 4, 6, 8, 10, 12 and16 hours) at 1323K. Platinum diffusion coefficient was calculated by the use of the finite differences method. In solving the equations, it was accepted , that for a c(x) function, it is possible to approximate its derivative (slope/tangent) at a certain point by: the slope of the arc described as the difference of functions at the end of the calculation area or by the slope of the arc described as a reverse difference of functions – close to the samples surface;or by the slope of AB arc given as a central difference of functions – inside the sample. The platinum diffusion coefficient varied from $2.28x10^{-14}$ (for 2 hours) to $8.96x10^{-14}$(for 16 hours). The thickness of the diffusion zone is proportional to the a power function of the diffusion time. The exponent *m* of the power function is 0.4. As the *m* coefficient is slightly smaller than 0.5, we may expect, that the volume diffusion predominantly controls the layer growth and the boundary diffusion lightly contributes to the rate-controlling process.

2:10pm **A1-2-3 Microstructure Degradation of EB-PVD TBCs on Pt and Pd/Pt-modified Aluminide Coatings under Cyclic Oxidation Conditions**, ***R. Swadzba*** *(rswadzba@gmail.com)*, Institute for Ferrous Metallurgy, Poland

The study concerns comparison of Pt and Pd/Pt-modified aluminide bond coatings for

EB-PVD TBCs on N5 superalloy in terms of microstructural evolution during cyclic oxidation tests.

The coatings were deposited by Pt and Pd+Pt electroplating, followed by high activity vapor phase aluminizing at 1050°C and pre-oxidation heat treatment in order to form α-alumina TGO. The 7wt.% yttria stabilized zirconia TBC was deposited using electron beam physical vapor deposition. Cyclic oxidation tests of the coatings were performed at 1100°C in 1h cycles in laboratory air. The microstructures of the coatings in the as-deposited state as well as after cyclic oxidation tests were studied using SEM, EDS and EBSD. The evolution and phenomena occurring at the interface between the bond coating, thermally grown oxide and TBC during high temperature exposure were studied in detail using high resolution CTEM and S/TEM. The samples for S/TEM analysis were prepared using FIB (Focused Ion Beam). The study is mostly focused on the growth of TGO during high temperature exposure and the overall performance of the Pd/Pt-modified aluminide coatings as a cost effective alternative to Pt-modified aluminide coatings commonly used as EB-PVD bond coats.

2:30pm **A1-2-4 Ferritic-Martensitic Steels: Improvement of the Oxidation Behavior in Steam Environments via Diffusion Coatings**, ***D. Schmidt*** *(d.schmidt@dechema.de), M. Galetz, M. Schütze*, DECHEMA-Forschungsinstitut, Germany

Modern heat resistant ferritic-martensitic steels are of high interest as superheater materials in fossil fuel power plants. They have much better heat transfer behavior and a lower coefficient of thermal expansion, as well as lower costs in comparison to austenitic steels and nickel base alloys. Modern 9% Cr-steels have sufficient creep strength up to 650°C, however their corrosion resistance particularly in H_2O containing environments needs further improvement. The inner side of the superheater tubes is exposed to steam, which leads to increased corrosive attack.

Results pertaining to the enrichment of chromium and manganese in the metal subsurface region of P91 and P92 using a diffusion process (pack cementation) without altering the bulk phase will be presented. The diffusion treatment developed is based on thermodynamic considerations for the design of the coating process. High temperature oxidation exposure of uncoated and coated samples at 650°C in argon with 50% H_2O, a gas which was shown before to yield the same oxidation behavior such as pure steam oxidation, shows the improved behavior. The paper discusses the coating process parameters and the oxidation behavior.

2:50pm **A1-2-5 Oxidation under Pure Steam: Protective Oxides and Coatings**, ***A. Agüero*** *(agueroba@inta.es), V. González, M. Gutiérrez*, Instituto Nacional de Técnica Aeroespacial, Spain, *R. Muelas*, Ingeniería y Servicios Aeroespaciales, Spain **INVITED**

Although at temperatures of 900º C and higher, the formation, transformation and failure of protective oxides in air has been deeply studied, there is significantly less available information of these processes when they take place under pure steam and in the lower temperature range pertinent to steam power plants. New designs for these plants are expected to operate at 625-700º C, at which the candidate ferritic/martensitic steels exhibit very low steam oxidation resistance. In this paper, available knowledge of the behaviour of protective oxides formed under steam at 650º C will be presented. It is already known that on ferritic/martensitic steels with a Cr content lower than ~9 wt. % in Cr, such as P22, CB2, P91 and P92, a non protective, thick dual later composed of Fe_3O_4 and $(Fe, Cr)_3O_4$ forms. However, significantly higher steam oxidation resistance has been recently found when exposing NPM1, a 9 wt. % Cr martensitic steel rich in W and Co, to pure steam at 650º C. In this case a protective, very thin multilayer forms, with alternating Fe_3O_4 and $(Fe, Cr, Mn)_3O_4$. Fe based, Cr rich coatings, both diffusion and overlay, develop in most cases a protective spinel, which may also contain Cr_2O_3 depending on the Cr content. On the other hand, Cr containing coatings based on Ni may develop a very stable, protective thin Cr_2O_3 layer. In addition, in both Fe and Ni based coatings, the formation of a thin protective Cr rich oxide is affected by other elements present in the material. Finally, on Al containing coatings, such as Fe aluminides and FeCrAls, Al_2O_3 forms under steam at 650º C. Provided that a critical content of Al is maintained underneath the scale, Al_2O_3 is very stable, surpassing 40,000 h under steam at 650º C, without evidence of spallation. In turn, the critical Al content depends on the coating's Cr content, as it happens when oxidation takes place at temperatures of 900º C or higher, under air. However, under steam, alumina phases formation and transformations are different, as at 650º C χ-Al_2O_3 forms initially, slowly transforming into α-Al_2O_3. General considerations regarding the stability of protective oxides formed under steam as a function of the composition of the subjacent material will be provided.

3:30pm **A1-2-7 Investigation of the Anti-adhesion Effect of Nano- and Micro-structured Surfaces**, ***M. Juez Lorenzo*** *(maria.juez-lorenzo@ict.fraunhofer.de), V. Kolarik, R. Roussel, V. Kuchenreuther*, Fraunhofer ICT, Germany, *F. Velasco*, Universidad Carlos III-Madrid, Spain, *S. Guzman*, Universidad Carlos III- Madrid, Spain, *F. Pedraza*, Université de la Rochelle, France

The reduction of adhesion of corrosive deposits on high temperature material surfaces bears a considerable potential to reduce damage by corrosion. The effect of nano- and micro-structuring the surface by coating with spherical Al particles was studied in the frame of the European project PARTICOAT. These coatings form with an appropriate heat treatment a surface with nano- or microstructures similar to the Lotus leaf structure. Alloy 321 and IN738 were coated with Al particles with a size between 1 and 20 µm and a heat treatment between 650°C and 950°C was applied, yielding surfaces with needle-like structures. A salt with 40% Na_2SO_4 and 60% V_2O_5, molten and solidified prior to the experiment, was deposited on

the coated surface. The samples were then heated in air from room temperature to 675°C with a heating rate of 10°C/min. The sample surface was observed in situ with a video camera revealing the melting of the salt and its interaction with the surface. The analysis of the sample surface as well as the cross-section was performed by optical microscopy, SEM and EDX. The surface region of the coating is infiltrated by the molten salt. In the case of Alloy 321, the infiltrated coating layer is partially detached from the remaining un-affected coating, which may provide a predetermined delamination section for the salt drop. Contact with the metal surface was not observed within the experimentation times. Surface structures with fine long filaments with a thickness of approximately 110 nm showed the lowest infiltration depth of the salt into the coating.

3:50pm **A1-2-8 Chloride Induced High Temperature Corrosion in Waste and Biomass Fired Boilers – Degradation Mechanisms and Mitigation Measures**, ***T. Jonsson*** *(tj@chalmers.se), J. Liske, J.E. Svensson, L.G. Johansson*, Chalmers University of Technology, Sweden

The fireside environment in power boilers may be quite corrosive, especially in boilers firing biomass and waste, where the fireside environment is characterized by a combination of high levels of reactive alkali (NaCl and KCl), HCl and relatively low SO_2 concentrations. The corrosion problems shorten the lifetime of the waterwall and the steam superheater, limiting the maximum steam temperature. This paper presents new results on the mechanism behind the accelerated high temperature corrosion suffered by stainless steel and low alloyed steel in the presence of alkali chlorides, O_2 and H_2O. We also discuss different measures to mitigate the corrosion problems in real boilers. Thus, sulphur can be added to the fuel in order to convert the alkali chlorides to the corresponding alkali sulphates, which are far less corrosive. Another opportunity to increase the lifetime of the boiler is to apply coatings or use alloys that are optimized with respect to chloride-induced corrosion. This work is mainly based on laboratory investigations of corrosion but will also make comparisons with corrosion experiments in real boilers.

4:10pm **A1-2-9 Properties and Performance of Al/Al_2O_3 Coatings on 304 Steel in Metal Dusting Environments**, *E. Uribe*, EGIC, Mexico, ***O. Salas*** *(osalas@itesm.mx), J. Oseguera, D. Melo-Maximo*, ITESM-CEM, Mexico, *C. Lepienski*, UFPR, Brazil, *R. Torres*, PUCPR, Brazil, *R. De Souza*, Usp, Brazil

Al/Al_2O_3 thin films were produced by reactive magnetron sputtering on 304 stainless steel substrates to investigate the effect of various deposition parameters on the structural evolution and properties of the films and their performance as protective coatings in metal dusting environments. Selected deposition parameters included: level of oxygen flow, rate of oxygen feeding and application of bias voltage to the substrate. The resulting films were characterized by optical microscopy, scanning electron microscopy + energy dispersive analysis, and x-ray diffraction, and their adhesion by scratch testing. The coatings were then subjected to a carburizing atmosphere at high temperature in a thermobalance to evaluate their response to metal dusting. The results indicate that the coatings present good adhesion and density which are desirable for their present application.

4:30pm **A1-2-10 Microstructural Evolution of Cr/Cr_2O_3 coatings during exposure to Metal Dusting conditions**, ***L. Melo-Maximo***, Instituto Politécnico Nacional, Mexico, *O. Salas (osalas@itesm.mx)*, ITESM-CEM, Mexico, *V.M. Lopez-Hirata*, Instituto Politécnico Nacional, Mexico, *D. Melo-Maximo, J. Oseguera*, ITESM-CEM, Mexico, *R. Torres*, PUCPR, Brazil, *R. De Souza*, Usp, Brazil

An extensive microstructural characterization of Cr/Cr_2O_3 thin films deposited on 304 substrates after exposure to highly carburizing conditions was carried out in order to investigate the role of these coatings in protection against metal dusting. The films were produced by reactive magnetron sputtering. The effect of bias voltage application as well as the partial pressure of oxygen on the structure and properties of the films was investigated. Promissing films as well as uncoated substrates were then exposed to a carburizing atmosphere at high temperature for various times to follow and compare the structural changes on the surface of the samples.

4:50pm **A1-2-11 High-temperature Oxidation Corrosion of Boiler Steel with Al Coating under Co-firing of Biomass Charcoal / Coal Deposits**, ***C.Y. Tung*** *(k_82276648@hotmail.com)*, National Taiwan University of Science and Technology, Taiwan, Republic of China, *C.J. Wang, S.P. Wen*, National Taiwan University of Science and Technology, Taiwan, Republic of China

The study the SA209-T1 and SA213-T22 boiler steel with Al coating, in different proportions 24-120 hours at 600 ° C by mixed burning biomass charcoal / coal in order to investigate the high-temperature corrosion of the fly ash deposition of sedimentary fuel. Not Al coating boiler steel Experimental results show that the deposition of co-firing biomass charcoal / coal for T1 and T22 steel materials of high-temperature corrosion mechanisms, the initial period of biomass charcoal or coal has not been released from combustion of sulfur, chlorine and other elements, for simple high-temperature oxidation behavior. The lack of chromium T1, of KCl impact occur the accelerated oxidation insignificant, but the overall corrosion is still better than chromium steel is sourced serious. With the growth of the time, its role in sulfur chlorine ingredients within the fuel consumed via reaction the more gentle, mainly late corrosion behavior of the two kinds of steel materials are based on high-temperature oxidation. This study is enhancing resistance to high temperature oxidation and corrosion by the Al coating boiler steel.

Hard Coatings and Vapor Deposition Technology
Room: Royal Palm 4-6 - Session B1-2

PVD Coatings and Technologies

Moderator: S. Fairchild, Air Force Research Laboratory, J.H. Huang, Department of Engineering and System Science National Tsing Hua University, S. Weiβmantel, University of Applied Sciences Mittweida

1:30pm **B1-2-1 Design and Metallurgy of High-performance Sputtering Target Materials**, ***P. Polcik*** *(peter.polcik@plansee.com)*, PLANSEE Composite Materials GmbH, Germany **INVITED**

Today, a large number of tools and components are protected by hard coatings deposited with physical vapor deposition methods. The continuous improvement of coatings takes place by introducing new coating architectures or through implementation of new compositions in thin films designed for special applications. Furthermore the leading coating equipment manufacturers work on cost and quality optimization for high volume implementation. Costs can be reduced, for example, by reducing process times. This generally requires higher power densities and may lead to new target dimensions and shapes. Concurrently, as new coatings and processes become widely accepted, the target manufacturers have to support the development and to deliver suitable solutions for each requirement.The targets used for hard coating applications are produced either by powder or by melting metallurgy processes. Targets manufactured by powder metallurgy must exhibit uniform microstructure, high density, as well as a homogeneous distribution of chemical elements. High-quality targets thus depend upon the manufacturing expertise as well as the quality of the powder ingredients used.Most ongoing developments of hard coatings are focused on the beneficial effects of altering standard compositions with selected elements to control the composition of the coating. The big challenge is to find a suitable technology that can produce targets of a sufficient purity containing all these elements on the one side and to insure performance of the final product on the other side. In order to support the efforts of equipment manufacturers and coating designers, new technologies have to be applied to produce targets in appropriate shape and dimensions. To deliver cost-optimized targets for high-volume applications, the whole process chain, including powder quality and standardization of raw materials, has to be considered. Other efforts, including the desire for higher target utilization, are strongly related to the increase in power density applied to the targets. Therefore, target suppliers must be concerned with strategies to lessen such impact, including the development of materials with high heat conductivity and thermal shock resistance.

2:10pm **B1-2-3 Synthesis of Very Thick, Sputter-Deposited, Iron and Tantalum Film-Based Targets for Laser Experiments to Understand High Pressure Behavior in Materials**, ***P. Mirkarimi*** *(Mirkarimi1@llnl.gov), K. Bettencourt, N. Teslich*, Lawrence Livermore National Laboratory, US

There is significant interest in the measurement of the equation of state and other parameters of bcc metals at high pressures and low temperatures. One example is Iron, where understanding its behavior at high pressures is useful for understanding planetary development. Targets are needed to perform these important measurements on large experimental platforms such as Omega (Rochester), The National Ignition Facility (Livermore) and the Z-machine (Albuquerque). Experimental design requirements have actually pushed the thickness of the "film" beyond that of the "substrate". We have sputter deposit very thick stepped Iron and Tantalum films on diamond substrates for experiments at NIF, with steps of ~10 mm and total thicknesses up to ~ 100 mm. The diamond substrates were only 40-80 mm thick for these films. These large thickness films/targets have been fabricated while maintaining other important properties, such as a reasonably sharp rolloff of the coating at the step edges and a reasonable roughness at the film surface.

We also have sputter deposited Tantalum films up to ~2,000 microns (2 mm!) thick on aluminum substrates, enabled through control of the film stress. The substrates were subsequently removed for use as targets for experiments at Z-machine. We believe this is by far a record thickness for sputter deposited Tantalum films.

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344. IM release number is: LLNL-ABS-492350

2:30pm **B1-2-4 Characterization of Al Sputter Process in Multiple Frequency Capacitively Coupled Plasmas (MFCCP)**, ***S. Bienholz*** *(bienholz@aept.ruhr-uni-bochum.de)*, *N. Bibinov*, *P. Awakowicz*, Ruhr University Bochum, Germany

In PVD technology various different arrangements of capacitively coupled plasmas mainly magnetically enhanced are available for Al based sputtering processes. Nevertheless most techniques do not allow separate control of ion flux and ion energy distribution at the target, which limits the control range of sputtering process. However, an MFCCP process provides access to a curtain control range of plasma density and ion flux towards the target by tuning the power of a very high frequency excitation. An additional low frequency excitation effectively adjusts the self bias voltage and therefore the ion energy distribution at the target.

In this contribution a complete plasma characterization including specially resolved electron density, electron temperature and gas temperature is performed by evaluating the optical emission detected with an absolute calibrated spectrometer. From this data, the ion flux on the Al target is calculated and used in a TRIDYN simulation, which provides the sputtered Al flux from the target as a result. A Monte Carlo model delineates the transport of sputtered material through the plasma towards the substrate, which allows a theoretical prediction of the deposition rate. Furthermore, the film growth is determined experimentally by weighing a silicon wafer before and after the deposition process using a analytical balance. A comparison of the measured and predicted deposition rate can lead in some cases to rather small sticking coefficients. For verification of those results, the density of sputtered Al atoms in the plasma is determined from the photo emission of Al atoms. The spacial density distribution also implies a low sticking coefficient of sputtered material at the substrate. The low sticking coefficient can possibly explained by high ion bombarding energies at the substrate resulting from comparably high plasma sheath voltages in front of the substrate.

The authors would like to acknowledge the funding provided by the "Deutsche Forschungsgemeinschaft" within the frame of the SFB-TR 87 and the "Ruhr University Bochum Research School".

2:50pm **B1-2-5 Influence of Magnetron Sputtering Conditions on WTi Thin Films**, ***A. Le Priol*** *(arnaud.le.priol@univ-poitiers.fr)*, *E. Le Bourhis*, *P.O. Renault*, Institut P' - Universite de Poitiers, France, *H. Sik*, *P. Muller*, SAGEM Défense Sécurité, France

This study reports on the influence of sputter-deposition conditions on the structural, electrical properties and chemical composition of a refractory alloy (WTi) thin films. WTi thin films have been deposited using a planar DC Magnetron sputtering apparatus from WTi alloyed target (70:30 At%) in pure Ar working gas, under working pressure ranged from 0.14 to 1.4 Pa, at constant power discharge, without substrate bias and external heating. Body-centered cubic W_XTi_{1-X} solid solution thin films have been obtained, with x in the range $0.75<x<0.81$. The films have a α-W structure with a strong {110} fiber texture. Ti depletion in WTi thin films have been observed by MEB-EDX analysis and attributed to atoms transport, re-sputtering at substrate level and disparity of W and Ti sputtering yields. For both ultra-thin (10 nm) and thin (180 nm) films a stress transition from tensile-to-compressive stress state has been observed as the working pressure increases by using Stoney and X-Ray Diffraction ex-situ methods. The stress transition has been shown to be similar for both thickness but less well defined for ultra-thin films. Preliminary in-situ stress measurements in the magnetron chamber have been performed by using Stoney method. For a low working pressure (0.5 Pa), in-situ stress state exhibits a change during deposition from tensile to compressive at a thickness of about 14 nm. For a high working pressure (1.1 Pa), a tensile stress state is observed all along the deposition whatever the thickness (up to 180 nm). Influence of thickness and working pressure on electrical properties has been revealed (range from 60 to 200 μΩ.cm). Thin films microstructure was highlighted by FIB-MET observations. WTi ultra-thin and thin films process-structure-property relations are studied and discussed in relation with the state of the art.

3:10pm **B1-2-6 Architectural Design of Al-rich Cubic Coating Materials within the AlN-CrN System**, ***C. Sabitzer*** *(corinna.sabitzer@tuwien.ac.at)*, Christian Doppler Laboratory for Application Oriented Coating Development at Montanuniversitat Leoben and Vienna University of Technology, Austria, *J. Paulitsch*, Vienna University of Technology and Montanuniversität Leoben, Austria, *P. Polcik*, PLANSEE Composite Materials GmbH, Germany, *M. Arndt*, *R. Rachbauer*, OC Oerlikon Balzers AG, Liechtenstein, *P.H. Mayrhofer*, Vienna University of Technology, Austria

Aluminum chromium nitride ($Al_xCr_{1-x}N$) coatings (within the AlN-CrN quasibinary system) are known for their excellent oxidation and wear resistance, thermal stability and high hardness. In general, these properties are correlated to their Al content, x. Recent studies indicated that by increasing x up to ~ 0.75 (hence, 75 at% Al of the metal sublattice), which corresponds to the *ab initio* suggested solubility limit within the cubic (NaCl type) structure, the film properties can be enhanced significantly. Exceeding this Al content, a cubic/hexagonal or a single phase hexagonal (wurtzite ZnS type) structure will be formed, resulting in decreased properties. However, stabilizing Al-rich $Al_xCr_{1-x}N$ coatings in a single phase cubic structure should result in a further increase in mechanical properties and thermal behavior. Therefore, monolithic as well as multilayered $Al_xCr_{1-x}N$ coatings were deposited by cathodic arc evaporation (in N_2 atmosphere) using powder metallurgically prepared Al_xCr_{1-x} targets with compositions of x = 0.7, 0.75, 0.85, and 0.9. X-ray diffraction studies clearly exhibit a single phase cubic structure for the monolithically grown nitride coatings using $Al_{0.7}Cr_{0.3}$ and $Al_{075}Cr_{0.25}$ targets, a mixed cubic/hexagonal structure for the coatings prepared from $Al_{0.85}Cr_{0.15}$ targets, and a single phase hexagonal structure when using $Al_{0.9}Cr_{0.1}$ targets, independent from the dc bias voltage applied to the substrates. Multilayer variations of the single phase cubic layers with the mixed cubic/hexagonal or hexagonal layers (by combining the individual targets during the preparation by an industrial plant) contain also a hexagonal phase fraction in addition to the cubic phases when applying low bias voltages of -40 V. However, when increasing the bias voltage up to -120 V, the hexagonal phase formation can be suppressed. This is even valid for the multilayer arrangements combining $Al_{0.75}Cr_{0.25}N$ layers with the highest Al containing layers prepared from $Al_{0.9}Cr_{0.1}$ targets. These multilayers ($Al_{0.75}Cr_{0.25}N/Al_{0.9}Cr_{0.1}N$) exhibit a pronounced hexagonal phase content when applying -40 V bias but a cubic structure for -120 V bias. The structural modification from pronounced hexagonal to cubic results in increased hardness values, from ~17 to 32 GPa, as well as increased thermal stability and oxidation resistance.

Our results highlight the importance of an architectural design in addition to the alloy development for optimized material properties and performance.

3:30pm **B1-2-7 Influence of Argon Flow on Growth Rates in Reactive Magnetron Sputtering of Oxides and Production of an Esthetic Coating for Dental Implants**, ***D. Muff***, *C. Pecnik*, *R. Spolenak* *(ralph.spolenak@mat.ethz.ch)*, ETH Zurich, Laboratory for Nanometallurgy, Switzerland

The production of stoichiometric oxide ceramics by reactive magnetron sputtering is usually only possible with low deposition rates. This is due to oxygen poisoning of the sputter source at high oxygen flow rates [1, 2]. This study investigates the influence of argon flow on the transition zone between metallic mode sputtering with high sputter rates and oxidic mode sputtering with significantly reduced sputter rates. The aim is to produce stoichiometric and, thus, transparent thin films of various oxides in metallic mode sputtering. Rutherford backscattering, ellipsometry and profilometry measurements confirm that high argon flow rates help to prevent unwanted reaction of the sputter source with the reactive gas and allow for fast deposition of optically transparent materials such as TiO_2, ZrO_2 and SiO_2.

The findings from the previous investigations are used for the production of a novel ceramic coating for dental implants. Due to its inherent dark grey color, titanium might cause undesired darkening of the peri-implant mucosa when used for transgingival dental implant screws [3]. Spectrophotometric measurements show that the presented coating significantly increases the lightness of the implant and prevents mucosal discolorations completely.

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3:50pm **B1-2-8 Investigations of Arc-evaporated $(Al_{0.7}Cr_{0.3})_2O_3$ Coatings from Al-Cr-Si and Al-Cr-Fe Targets**, ***J. Paulitsch*** *(joerg.paulitsch@tuwien.ac.at)*, Christian Doppler Laboratory for Application Oriented Coating Development at Montanuniversitat Leoben and Vienna University of Technology, Austria, *R. Rachbauer, J. Ramm*, OC Oerlikon Balzers AG, Liechtenstein, *P. Polcik*, PLANSEE Composite Materials GmbH, Germany, *P.H. Mayrhofer*, Vienna University of Technology, Austria

Corundum type $(Al_xCr_{1-x})_2O_3$ oxides are of major interest especially when synthesized using physical vapour deposition techniques at low temperatures around 500°C. First studies on cathodic arc-evaporated solid solution Al-Cr-O oxides showed promising results if the Al content is not exceeding 50 at%. However, detailed investigations demonstrated that not only the increased tendency of droplet formation due to oxide island formation on the target surface, but also the development of an fcc-structure is limiting the quality of these films.

Recent studies showed that using $Al_xCr_{1-x-y}Si_y$ targets reduces the oxide island formation on the target surface and influences the structure and morphology of the oxide formed. Furthermore, oxidation tests of Al-Cr-Fe-N indicated that the FeO_2 oxide is promoting the Cr_2O_3 formation, which is needed to stabilize a corundum-type α-alumina in the solid solution oxide. Therefore powder metallurgical $Al_xCr_{1-x-y}Si_y$ targets, with Si contents y of 0.01, 0.02, 0.05 and 0.1 (1, 2, 5 and 10 at.%) as well as $(Al_xCr_{1-x})_zFe_{1-z}$ targets with Fe contents z of 0.01, 0.02 and 0.05 (1, 2 and 5 at%) were studied in detail on their arc-evaporation behaviour and their suitability to prepare corundum-type $(Al_xCr_{1-x})_2O_3$ oxide coatings.

4:10pm **B1-2-9 Synthesis of Al-Ti-O-N Thin Flms by Reactive Magnetron Sputtering**, *J.F.T. Simonet Fotso, R. Daniel,* ***C. Mitterer*** *(christian.mitterer@unileoben.ac.at)*, Montanuniversität Leoben, Austria

Recently, huge interest has arisen in the synthesis of transition metal oxynitride thin films, due to their excellent mechanical and optical properties as well as chemical stability. Within this work, we explored the evolution of structure and properties of Al-Ti-O-N films over a wide composition range from the nitride to the oxide side. Films were grown on silicon wafers in a laboratory-scale pulsed d.c. unbalanced magnetron sputtering system from powder metallurgical TiAl targets with an Al/Ti atomic ratio of 60/40, using either a constant level of nitrogen with rising oxygen partial pressure or vice versa. Coating composition and structure were investigated by energy- and wavelength-dispersive X-ray spectroscopy, scanning electron microscopy, atomic force microscopy, X-ray photo-electron microscopy, Raman spectroscopy and X-ray diffraction. Furthermore, hardness and elastic modulus were evaluated by nanoindendation. At constant nitrogen partial pressure, oxygen concentrations of up to 55 at.-% within the films could be established. In contrast, nitrogen incorporation at constant oxygen partial pressure is significantly hindered, resulting in nitrogen concentrations not exceeding a few percent. While oxygen-free coatings show a single-phase face-centered cubic phase, oxide coatings without nitrogen addition are based on the rutile TiO_2 structure. Low nitrogen or oxygen contents, respectively, result in the additional formation of a face-centered cubic TiAlON phase, whereas for high oxygen and nitrogen concentrations amorphous structures are formed.

4:30pm **B1-2-10 The Optimization of the Deposition Parameters to Prepare the $ZnSnO_3$ and Cd_2SnO_4 by RF Magnetron Sputtering from Powder Targets**, ***Y.W. Zhou*** *(zhouyanwen@yahoo.com)*, *P.F. Zhu, S.L. Li*, University of Science and Technology Liaoning, China

Transparent conductive oxide (TCO) ZnSnO3 and Cd2SnO4 films were prepared by RF magnetron sputtering from the powder targets mixed from zinc, tin and cadmium oxide powders according to the ratios of Zn:Sn=1:1 and Cd:Sn=7:3. In order to achieve the combined optimum electrical and optical properties of ZnSnO3 and Cd2SnO4, Taguchi experimental arrays for deposition parameters, i.e. deposition power, pressure and the separation between target and substrate, were designed and performed. New phrases were formed and the main preferred orientations of ZnSnO3 and Cd2SnO4 films were (220) and (200), respectively. The morphological structures of the films were columnar in the grain sizes over 100nm. The domains of nano-crystals in the columnar grains were about 10nm. The average transmittance of the ZnSnO3 and Cd2SnO4 films within the visible wavelength were over 90% and 85%. The concentrations of electrons of these n-type ZnSnO3 and Cd2SnO4 films were in the order of 1020 and 1021 cm-3, average mobilities, 20 and 40 cm2.V-1.s-1, and resistivies about 10-4 and 10-5Ω•cm, respectively. The optimized deposition processes of the ZnSnO3 and Cd2SnO4 films were 400W-0.3Pa-130mm and 200W-0.3Pa-130mm, respectively.

4:50pm **B1-2-11 Structural and Mechanical Properties of Cr-Al-O-N Thin Films Grown by Cathodic Arc Deposition**, ***A. Khatibi*** *(alikh@ifm.liu.se)*, Linköping University, Sweden, *J. Sjölen*, Seco tools AB, Sweden, *G. Greczynski, J. Jensen, P. Eklund, L. Hultman*, Linköping University, Sweden

Coatings of $(Cr_xAl_{1-x})_\delta(O_yN_{1-y})_\xi$ with $0.33 \le x \le 0.96$, $0 \le y \le 1$, and $0.63 \le \delta/\xi \le 1.30$ were deposited using cathodic arc evaporation in N_2/O_2 reactive gas mixtures on 50 V negatively-biased WC-10 wt.% Co substrates from different Cr and Al alloys with three different Cr/Al compositional ratios. For N_2 less than 63 % of the total gas, ternary $(Cr,Al)_2O_3$ films containing <1 at. % of N forms; as determined by elastic recoil detection analysis. Increasing the N_2 fraction to 75 % and above result in formation of quaternary oxynitride films. Phase analyses of the films by x-ray diffraction, transmission electron microscopy, and x-ray photoelectron spectroscopy show the predominance of cubic Cr-Al-N and cubic-$(Cr,Al)_2O_3$ solid solutions and secondary hexagonal α-$(Cr,Al)_2O_3$ solid solution. High Cr and Al contents result in films with higher roughness while high N and O contents result in smoother surfaces. Nanoindentation hardness measurements showed that Al-rich oxide or nitride films have hardness values of 24-28 GPa whereas the oxynitride films have a hardness of ~ 30 GPa regardless of the Cr and Al contents. Metal cutting performance tests showed that the good wear properties are mainly correlated to the oxygen-rich coatings, regardless of the cubic or corundum fractions.This abstract is based on an artile published with the same title in Acta Materialia*.

Keywords

Physical vapor deposition (PVD); Solid solution; Face-centered cubic crystals; α-Al_2O_3; Oxynitride

* A. Khatibi, J. Sjölen, G. Greczynski, J. Jensen, P. Eklund, L. Hultman, Acta Mater (2012), http://dx.doi.org/10.1016/j.actamat.2012.08.010

Hard Coatings and Vapor Deposition Technology
Room: Royal Palm 1-3 - Session B5-2

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

1:30pm **B5-2-1 Texture Dependent Elastic Constants of Polycrystalline Zr—Al—N Predicted by *Ab Initio* Calculations**, ***D. Holec*** *(david.holec@unileoben.ac.at)*, *J. Keckes, P. Wagner*, Montanuniversität Leoben, Austria, *F. Tasnádi*, Linköping University, Sweden, *M. Friák*, Max-Planck-Institut für Eisenforschung, Germany, *P.H. Mayrhofer*, Vienna University of Technology, Austria

Protective hard coatings make use of the outstanding mechanical and thermal stability of early transition metal nitrides (TMN) and their alloys with Al. Modern applications require sophisticated designs of the protective thin films in which modelling aims to play an important role, in particular in predicting otherwise hardly accessible material properties. Quantum mechanical calculations of elastic constants of compounds as well as alloys have become a well established and widely used tool.

Voigt, Reuss, Hill and Hershey methods allow for calculation of the polycrystalline elastic constants. However, the commonly used formulae yield these estimates for isotropic aggregates of grains (i.e., all grain orientations are present with the same probability), which is hardly the case for highly orientated polycrystalline thin films. To overcome this shortcoming, we generated a wide range of orientation distribution functions (ODFs) representing various common textures, and performed the polycrystalline averaging with respect to these ODFs. The compositional dependence of single crystal elastic constants for the ternary $Zr_{1-x}Al_xN$ system is obtained from first principles calculations. This allows us to discuss the dependence of the elastic response on both, the composition and the particular texture at the same time.

1:50pm **B5-2-2 Influence of Zr on Structure and Properties of Ti-Al-N Coatings**, ***Y. Xu***, Central South University, China, *L. Chen (chenli_927@126.com)*, Zhuzhou Cemented Carbide Cutting Tools Co., Ltd., China, *B. Yang, Y. Peng, Y. Du*, Central South University, China

Ti-Al-N hard coatings have been applied in various fields, where hard and oxidation resistant materials are needed. Here, we study the effect of Zr addition on structure, mechanical and thermal properties of Ti-Al-N coatings with various bias from -50 to -150 V deposited by industrial cathodic arc evaporation system. The results show that Zr addition favors the growth of hexagonal phase, where $Ti_{0.48}Al_{0.52}N$ coatings have single phase cubic structure, and $Ti_{0.44}Al_{0.50}Zr_{0.06}N$ coat ings show a dual-phase structure with cubic and hexagonal phases. Incorporation of Zr slightly

increases the hardness value from ~31.2 GPa for Ti-Al-N to ~33.1 GPa for Ti-Al-Zr-N with the same bias of -100 V. Increasing of bias voltage during deposition of Ti-Al-Zr-N coatings promotes the formation of cubic phase, and also results in a hardness increase from ~25.6 GPa for -50 V to ~33.1 GPa for -100 V and ~37.9 GPa for -150 V. Oxidation experiments demonstrate Ti-Al-N coatings completely oxidized at 850 °C for 16 h, whereas Ti-Al-Zr-N coatings only forms of a layered oxide scale ~1.0 µm. Furthermore, alloyed with Zr improve the machining performance of coated inserts regardless of continuous turning and milling.

2:10pm **B5-2-3 Understanding Stress Development in Nanoscale Sputtered Thin Films from Real-Time Diagnostics**, ***G. Abadias*** *(gregory.abadias@univ-poitiers.fr)*, *A. Michel*, *A. Fillon*, *J. Colin*, *C. Jaouen*, Institut P' - Universite de Poitiers, France **INVITED**

Understanding the physical mechanisms controlling thin film growth is of vital importance to obtain the desired microstructures and related specific properties. Subtle structural changes may occur in the early growth stages, driven by surface/interface effects, epitaxy, chemical driving forces or energetic conditions intrinsic to PVD techniques like sputtering. Atomic-scale sensitive and real-time diagnostics are therefore required to address such issues.

In the present work, we demonstrate the unique potential offered by real-time stress diagnostics, combined with structural investigation, to understand not only the stress development during thin film growth but more generally to study dynamic microstructural evolution processes. It is shown that stress measurements using a multiple-beam optical stress sensor (MOSS) implemented in the deposition chamber offer an efficacious and accurate way to identify structural changes with sub-monolayer sensitivity.

The presentation will focus on case studies of low-mobility materials, including sputter-deposition of single metals (Mo, W, Ta) and binary alloys (Mo-Si). The importance of i) the surface stress variation in the first monolayers regime and ii) interface energy minimisation in governing nucleation conditions will be demonstrated. In particular, for the Mo-Si system, the amorphous-to-crystalline phase transition is accompanied by a stress signature at a critical thickness. The differences in film stress evolution during polycrystalline and epitaxial growth will be also addressed. Finally, the role of grain size on the mechanisms of atom incorporation, at the origin of compressive stress often encountered in low-mobility materials, will be discussed.

2:50pm **B5-2-5 Hard Zr-Al-O Films with Enhanced Resistance to Cracking in Bending**, ***J. Sklenka***, *J. Musil (musil@kfy.zcu.cz)*, *R. Cerstvy*, *R. Jilek*, University of West Bohemia, Czech Republic

The paper reports on structure, mechanical and optical properties of Zr-Al-O films with enhanced resistance to cracking in bending. The Zr-Al-O films with Zr/Al > 1 and Zr/Al < 1 were prepared by reactive sputtering using ac pulse dual magnetron. The magnetrons were equipped with a target composed of Al plate (ϕ = 50 mm) fixed to the magnetron cathode by a Zr fixing ring with inner diameter ϕ_{in}. The content of Al in the Zr-Al-O film was controlled by $\phi_{in.}$. This way it was possible to control the ratio of the crystalline ZrO_2 phase and the X-ray amorphous Al_2O_3 phase in the Zr-Al-O film and thereby its structure. The Zr-Al-O films were deposited on (i) Si(100) substrates for measurement of (a)the mechanical properties (hardness H, effective Young's modulus E^* and elastic recovery W_e) and (b) the film structure, (ii) glass substrate for measurement of the optical transparency of film and (iii) on the thin metallic strip for measurement of resistance of the film to cracking in bending. It was found that (i) the Zr-Al-O films with Zr/Al < 1 are X-ray amorphous and exhibit a low hardness (H ≤ 13 GPa), effective Young's modulus E^* satisfying a low $H/E^* < 0.1$ ratio and low elastic recovery $W_e \leq 60\%$, (ii) the Zr-Al-O films with Zr/Al > 1 are crystalline and exhibit a high hardness (H » 18 to 19 GPa), effective Young's modulus E^* satisfying a high $H/E^* \geq 0.1$ ratio and high W_e up to 75% and (iii) the highly elastic hard Zr-Al-O films with H » 18 -19 GPa, low Young's modulus E^* satisfying the ratio $H/E^* > 0.1$ and high value of elastic recovery $W_e \geq 70\%$ exhibit strongly enhanced resistance to cracking; here $E^* = E/(1-n^2)$, E is the Young's modulus and n is the Poisson's ratio. The last finding is the most important result of this investigation.

3:10pm **B5-2-6 AlN-based Optically Transparent Hard Nanocomposite Coatings: Going from Si to Sn**, *E. Lewin*, ***J. Patscheider*** *(joerg.patscheider@empa.ch)*, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland

Thin films with enhanced hardness based on Al-A-N with additions of A = Si, Ge or Sn are attractive candidate materials, as they can be prepared to be optically transparent. Using reactive unbalanced magnetron sputtering from elemental targets, series of films from Al-Si-N, Al-Ge-N and Al-Sn-N were deposited and characterized. Enhanced hardness of more than 30 GPa is observed in Al-Si-N coatings as a consequence of their nanostructure, but instead of a typically sharp hardness maximum observed in transition metal nitrides/silicon nitride nanocomposites, a broad hardness maximum exists as a function of the silicon content in the layers. The choice of the additional A element allows depositing highly transparent coatings for the case of Si and for the case of Ge and Sn the control of color in the range from yellow to red by the tuning of the UV absorption edge, which can be tuned in the range 200 to 500 nm (corresponding to optical band gaps of 6.2 to 2.5 eV). Also the index of refraction could be controlled in the range between 2.0 and 2.5. In these systems enhanced hardness can be obtained at certain concentrations of Si, Ge or Sn, respectively. Generally hardness values between 16 and 30 GPa were attained. Depending on the content of the third element AlN-based solid solutions phases and the formation of nanocomposites is observed. Trends in the materials' properties of these materials will be presented and discussed.

3:30pm **B5-2-7 Nanostructure of Plasma CVD Films Containing Nanoparticles**, ***M. Shiratani*** *(siratani@ed.kyushu-u.ac.jp)*, *K. Koga*, *G. Uchida*, *N. Itagaki*, *H. Seo*, *K. Kamataki*, Kyushu University, Japan **INVITED**

Contribution of nanoparticles nucleated homogenously in reactive plasmas to formation of film structure is commonly discarded, because flux of nanoparticles to film surface is low and heterogeneous reactions on film surfaces are believed to determine predominantly the film structure. Here we overview nanoparticle formation in low pressure reactive plasmas [1] and then we show three examples in which nanoparticle flux can modify significantly film structure and hence film properties. The first example is a-Si:H. A-Si:H p-i-n solar cells show a performance degradation under prolonged light illumination. It is widely accepted that this effect is related to the creation of metastable defects. We have succeeded in depositing highly stable a-Si:H films using a multi-hollow discharge plasma CVD method by which the volume fraction of amorphous Si nanoparticles in films deposited in the upstream region is significantly reduced by driving clusters towards the downstream region [2]. Conventional a-Si:H films contain a few % of amorphous Si nanoparticles in their volume, whereas our stable a-Si:H films contain less than 0.01%. The second example is mc-Si. A-Si:H films containing a few % of crystal Si nanoparticles in their volume show inverse conical crystal growth from the crystal Si nanoparticles, whereas films containing several tens % of crystal Si nanoparticles show columnar crystal growth leading to mc-Si films [3]. The third example is porous low-k film. We have succeeded in depositing porous films with relatively high young modulus by depositing "isolated nanoparticles" [4]. Nanoparticles can be employed as another tuning knob of film structure control.

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4:10pm **B5-2-9 Structure and Properties of TiAlSiN Nanocomposite Coatings Deposited by Deep Oscillation Magnetron Sputtering**, ***Y. Ou***, Dalian University of Technology, China, *J. Lin*, Colorado School of Mines, US, *W. Sproul*, Reactive Sputtering, Inc., US, *J. Moore*, Colorado School of Mines, US, *M. Lei (mklei@dlut.edu.cn)*, Dalian University of Technology, China

Deep oscillation magnetron sputtering (DOMS) is an alternative high power pulsed magnetron sputtering technique which offers virtually arc free deposition for reactively deposition of insulating films. TiAlSiN nanocomposite coatings have been deposited with different nitrogen flow rates (*f*N2) in a close field unbalance magnetron sputtering system by sputtering a Ti40Al50Si10 target using the DOMS technique. A -60 V substrate bias voltage was used during the depositions. The microstructure and properties of the TiAlSiN coatings were investigated by means of electron probe microanalysis, X-ray diffraction, transmission electron microscopy, nanoindentation, and ball-on-disc wear test. It was found that the TiAlSi coating possessed an fcc-TiAl structure with a (111) preferred orientation. As the *f*N2 was increased from 0% to 20%, the TiAlSiN coatings gradually transformed from nc-TiAl/*a*-Si3N4 nanocomposite structure to nc-AlN/*a*-Si3N4 nanocomposite structure. The coatings exhibited a dense, uniform and smooth surface. TiAlSi coating showed a low hardness of 10.9 GPa and a H/E ratio of 0.062, whereas the TiAlSiN coatings exhibited improved mechanical properties, wear resistance and oxidation resistance with the incorporation of N, in which the TiAlSiN coating deposited at a *f*N2 of 10 % exhibited the highest hardness of 25 GPa, a high H/E ratio of 0.95 and excellent wear and oxidation resistances.

Key words: Deep oscillation magnetron sputtering (DOMS), High power pulsed magnetron sputtering (HPPMS), TiAlSiN coating, Hardness, Wear resistance

4:30pm **B5-2-10 Multifunctional Amorphous and Nanocomposite Nb-Si-C Coatings Deposited by dc-magnetron Sputtering**, ***N. Nedfors*** *(nils.nedfors@kemi.uu.se)*, Uppsala University, Sweden, *O. Tengstrand*, *P. Eklund*, *L. Hultman*, Linköping University, Sweden, *U. Jansson*, Uppsala University, Sweden

Coatings of Me-Si-C (Me = early transition metal) are interesting due to their multifunctional properties. A general observation is that the Si content is strongly correlated to the microstructure and thereby the properties of the Me-Si-C coatings. Typically, an increased Si concentration leads to a reduction in carbide grain size and in many systems to completely X-ray amorphous coatings. However, the amount of Si required to form an amorphous structure is dependent on the Me type. These observations raise two questions: first, how is the tendency for amorphous growth varying with different Me? Secondly, is it possible to tune the properties of an amorphous material by the choice of Me? We have chosen to study the previously not investigated Nb-Si-C system. Critical Si concentrations for amorphous growth is determined and compared with Zr-Si-C to identify possible trends. The Nb-Si-C coatings have been deposited by dc-magnetron sputtering using elemental targets. Structure and composition of the coatings have been characterized with X-ray diffraction, X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM). Nano-indentation were used to determine the mechanical properties of the coatings while the electrical resistivity has been measured using the four point probe technique.

Our results show a transition from a nanocomposite (nc-NbC/a-SiC) structure to a X-ray amorphous structure when the Si content reaches above 25 at.% (15 at.% for Zr). Electron beam induced crystallization is observed during TEM analysis, obstructing the characterization of the amorphous structures. However, bonding structures analysed by XPS indicates an amorphous network structure for the Nb-Si-C coatings reminding of the one described by Kádas et al. for dc magnetron sputtered Zr-Si-C coatings [1]. The transition in microstructure is reflected in the properties of the coatings with an increase in electrical resistivity (from 211 μΩcm to 3215 μΩcm) and a change in the mechanical behavior of the coatings. Hardness values of 19 GPa are achieved both for coatings exhibiting a nanocomposite and an amorphous structure. Comparison with dc magnetron sputtered Zr-Si-C films indicates a direct dependency for the hardness to the amount of C-Si bonds rather than type of transition metal for these types of amorphous Me-Si-C films.

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4:50pm **B5-2-11 Nanocomposite Coatings as Protection Layer for PcBN Tools in Hard Machining**, *E. Uhlmann*, ***J.A. Oyanedel Fuentes*** *(fuentes@iwf.tu-berlin.de)*, *R. Gerstenberger*, Technical University Berlin, Germany, *H. Frank*, GFE Schmalkalden e.V., Germany

The cutting material polycrystalline cubic boron nitride (PcBN) is ideally suited for machining of difficult-to-cut materials. It exhibits properties such as high hardness and high temperature resistance. However, due to the occurrence of tribo-oxidation and abrasion during machining of hardened steels abrupt tool failure is common. The deposition of coatings offers a possibility to protect the PcBN substrate. Initial research results indicate that nanocomposite coated cutting tools show a significantly improved tool life and process behaviour. This paper describes the results of machining tests with regard to the tool life and wear form. The results of the experiments were compared with commonly used tool coatings and uncoated PcBN for hard machining. Additionally, the wear mechanisms abrasion and tribo-oxidation were investigated in model wear experiments. Furthermore, FEM cutting simulations were used to investigate the interaction between substrate and coating.

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

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

Moderator: M. Stack, University of Strathclyde, J. Geringer, Ecole Nationale Superieure des Mines, M. Mathew, Rush University Medical Center

1:30pm **D2-2-1 Evaluation of the Bio-tribocorrosion Processes of Colonized Ti6Al4V Implants in Presence of Organic and Cellular Material**, ***M. Runa*** *(runa@dem.uminho.pt)*, University of Minho, Portugal, *M. Mathew*, Rush University Medical Center, US, *M. Fernandes*, University of Porto, Portugal, *L. Rocha*, University of Minho, Portugal

In uncemented Ti-based implants, the tribochemical reactions occurring at the implant/bone interface were reported to be caused by a combined effect of mechanical load and a complex chemical-biological environment. These reactions are due to micromotion occurring at the implant/bone interface from daily activities of the patients, and they can lead to tissue inflammation, crack initiation and early fracture of the implant. The interplay between chemical-biological-mechanical parameters and in particular the influence of relevant proteins and osteoblastic cells, on the material degradation is of extreme clinical relevance and needs to be clarified.

The aim of this work is to evaluate the bio-tribocorrosion mechanisms of etched Ti6Al4V alloys colonized with MG63 osteoblastic-like cells. The colonized materials and control groups were characterized through cell viability/proliferation and alkaline phosphatase activity. Tribocorrosion tests were performed under a reciprocating sliding configuration at different electrochemical potentials (-0.1V and +0.5V/SCE), using a simulated body fluid and the culture medium as the electrolyte. An alumina ball was used as counterbody. Normal loads between 0.05N and 1N, were applied (153MPa and 415MPa initial contact Hertzian pressure) which allowed more detailed information on the destruction pathways of the top surface layers of the material (adsorbed proteins, passive film, etc.) to be followed. All tests were performed at a controlled temperature of 37ºC.

The results obtained demonstrated the capability of the oxide film to re-grow (repassivation) after mechanical damage. The electrochemical behavior of the alloy was shown to depend on the stage of the passive film formed on top of the material. The interaction of biological material, present in the simulated body fluid, with the surface of the Ti6Al4V alloy was found to improve the resistance of the passive layer. The total weight loss (Kwc) and synergistic ratio between chemical and mechanical wear loss (Kc/Kw) were estimated to identify the mechanistic transitions in the wear-corrosion process, which ranged from 0.4 to 3.5, depending on the stage of the passive film. Also, the materials colonized with osteoblastic-like cells showed an important influence on the chemical and tribological response of this alloys, leading to valuable findings for long-term metallic implant applications.

1:50pm **D2-2-2 Tribocorrosion Evaluation of nc-TiN/a-Si_3N_4 Deposited on Ti6Al4V in Sliding Contact in Physiological Saline Solution**, ***J. Garcia*** *(jegarcia@up.edu.mx)*, *M. Flores*, Universidad de Guadalajara, Mexico, *O. Jimenez*, Universidad de Guadadalajara, Mexico, *E. Andrade*, Universidad Nacional Autónoma de México, Mexico

Several studies have been carried out using nc-TiN/a-Si_3N_4 deposited on Ti6Al4V substrates using DC and RF reactive dual magnetron sputtering in order to understand the behavior of this material when applied in human joint replacement. Characterization, mechanical and corrosive tests were conducted, including: XRD, XPS and RBS techniques to analyze the structure and composition of coatings, profilometry to analyze the topography of substrate, coating and wore Surfaces, scratch test to evaluate film adhesion and electrochemical technique as well as a reciprocating tribocorrosion test in physiological saline solution, to evaluate the corrosion susceptibility under static and reciprocating conditions respectively. All the results are analyzed and discussed.

2:10pm **D2-2-3 Nanotube Surface Modifications For Biomedical Applications**, ***T. Shokuhfar*** *(tshokuhf@mtu.edu)*, Michigan Technological University, US **INVITED**

Engineered-nanotubular structures offer exciting progress toward the design of multifunctional medical implants. To bring this to reality, the mechanical, physical, biocompatibility, and interfacial properties of such structures should be optimized. The mechanics of nanotubes is important from mechanotransduction points of view. We have observed that the fabrication of TiO_2 nanotubes with elastic modulus close to actual bone

promotes osteoblast growth. In order to investigate the effect of nanotubes on behavior of osteoblast cells, series of novel experiments on measuring the mechanical properties of individual TiO_2 nanotubes followed by in-vitro cell culture tests were conducted. The nanotubes were tested in the chamber of transmission electron microscope using an in-situ atomic force microscopy stage with force resolutions better than 1 nN. Thin and thick nanotubes were tested to check if there are variations of mechanical properties as a function of size. It was shown that the nanotubular characteristics of the surface improve cell proliferation, attachment and spreading of osteoblast cells. We have developed a novel cell/surface interfacial characteristic method using focused ion beam milling (FIB) and scanning transmission electron microscopy (SEM) techniques. With this novel approach it was possible to cut through sections of cells and the underlying substrate and directly observe the biophysical interactions of osteoblasts with TiO_2 nanotubes. The results of this approach show a tight interface where TiO_2 nanotubes act as anchoring sites for osteoblasts to attach and even grow inside the hollow section of nanotubes. This tight interaction would eventually result in enhance bon-implant interlock. Based on these findings, it is possible to speculated that surface modification of Ti implants by a TiO_2 nanotube layer with elastic behavior close to the actual bone can be promising to overcome stress-shielding, a common reason for implant failures.

2:50pm **D2-2-5 Predicting Thickness of Passive Films in Order to Prevent Degradations of Implants**, ***J. Geringer*** *(geringer@emse.fr)*, Ecole Nationale Superieure des Mines, France, *M. Taylor, D. Macdonald*, Penn State University, US

Every year, one in every 30 Americans has a hip prosthesis implanted, i.e. 250,000 every year implants in the US market. Health issues with regard to patient mobility, which in turn reflects an aging population, are of increasing concern,but we also see a trend toward younger and younger patients. Younger, first time recipients of hip prostheses are of concern, because of the high probability that they will be recipients of multiple prostheses replacements over their lifetimes, since some implants have approximate lifetimes of 15 years. The femoral stem, for example, should be made of 316L/316LN stainless steel, in order to optimize lifetime. Fretting corrosion, friction under small displacements, between stainless steel and bone, for instance, occurs during human gait, due to repeated loadings and un-loadings,. Some experimental investigations of fretting corrosion have been reported. As is well known, metallic alloys and especially stainless steels are covered with a passive film that inhibits corrosion and hence degradation when implanted within the body. This passive layer of few nanometers in thickness at ambient temperature, is the key of our reactive metals-based civilization according to some authors. This work is dedicated to predicting the passive layer thicknesses of stainless steel under fretting corrosion conditions, with specific emphasis on the role of proteins. The analysis is based on the Point Defect Model (PDM, micro scale) and an update of the model on the friction process (micro-macro scale) to yield the Fretting Model (FM). A genetic algorithm was used to optimize the fretting model on the experimental data, in order to derive values for important model parameters. The major results are, as expected from experimental results, albumin inhibits corrosive degradation of the steel; an incubation time is necessary for degradation of the passive film; under fretting corrosion and in the presence of a high concentration of chloride ion, passivity of the steel is also inhibited. These factors are identified as those that determine the ultimate lifetime of the prosthesis.

3:10pm **D2-2-6 Electrochemical Behavior of Esthetic Dental Coatings Tested in Sodium Chloride Solution and Artificial Saliva**, ***C. Pecnik***, *D. Muff, R. Spolenak (ralph.spolenak@mat.ethz.ch)*, ETH Zurich, Laboratory for Nanometallurgy, Switzerland

Commercially pure titanium and titanium alloys are predominantly used for dental implants, since these materials have excellent physical and chemical properties [1]. However, in certain cases a gray discoloration of the soft tissue can be observed using titanium implants, resulting in an undesired esthetic outcome [2, 3]. Therefore, a new coating system which combines the mechanical properties of metals with the good optical properties of ceramics would enhance the esthetics of dental implants. Above all, clinical success of dental implant systems depends strongly on their reliability. The coating should not only be esthetically pleasing and mechanically durable, but it should also withstand the corrosive environment below soft tissue.

In this study, ceramic and metallic thin films were deposited on commercially pure titanium substrates by reactive sputtering. Their color is formed by light interference phenomena. In order to characterize the corrosion properties of these systems, electrochemical impedance spectroscopy and potentiodynamic measurements were carried out using a three-electrode setup. Four coating systems (n = 3) were tested in 0.9 wt% NaCl solution and in artificial saliva (modified recipe of Fusayama et al. [4]) under different pH and temperature conditions. After the measurements, the samples were examined using a scanning electron microscope (SEM) and energy-dispersive X-ray (EDX) detector.

The roughness of the substrate not only influences the color of the investigated samples here, but also their corrosion behavior. Special focus has been given to the corrosion resistance of samples immersed in artificial saliva in order to establish a life-time model for the future application.

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3:30pm **D2-2-7 Submicroporous Ta_2O_5 Coating Enhanced the Initial Biological Responses to Ti Surface**, ***Y.S. Sun***, *H.H. Huang (hhhuang@ym.edu.tw)*, National Yang-Ming University, Taiwan

An amorphous tantalum pentoxide (Ta_2O_5) coating with submicroporous topography was prepared on titanium (Ti) using a simple hydrolysis-condensation process at room temperature to enhance the initial biological responses to Ti. Surface characteristics of the test specimens were analyzed using Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy, glancing angle X-ray diffractometry, field emission scanning electron microscopy and t ransmission electron microscopy . The corrosion resistance was evaluated by 5-day ion release measurement in simulated blood plasma (SBP). The cytotoxicity of the materials was determined according to ISO 10993-5 specification. The biological responses, including initial fibronectin adsorption and human bone marrow mesenchymal stem cells responses, were evaluated. Results showed that the non-cytotoxic amorphous Ta_2O_5 coating with submicroporous topography was deposited on the Ti surface using a simple hydrolysis-condensation process. This Ta_2O_5 layer significantly decreased the ion release from Ti surface in SBP, and enhanced the initial fibronectin adsorption and cell proliferation. We conclude that the presence of an amorphous Ta_2O_5 coating with submicroporous topography on the Ti surface decreased the ion release and enhanced initial biological responses.

3:50pm **D2-2-8 Scanning Electrochemical Microscopy (SECM) Investigation of Tribolayer Formation on a MoM Hip Implant**, *J. Meyer*, Chicago State University, US, *C. Nagelli*, ***M. Mathew***, *M. Wimmer, J. Jacobs*, Rush University Medical Center, US, *R. LeSuer (rlesuer@csu.edu)*, Chicago State University, US

Currently metal-on-metal (MoM) hip implants are facing serious challenges. Corrosion remains one of the major concerns that limit biocompatibility and longevity of metals employed for the joint prostheses. It can lead to implant weakening from release of metal debris causing damage to cells, tissues, and host organs, eliciting potentially dangerous immune and inflammatory responses. Many electrochemical methods are available to monitor and measure the corrosion processes, however each one has its own specific application and limitations. Recent studies reported the presence of metallo-organic mixture in the form of a film or layer at the contact zone of the metal joints. The mechanical and chemical beneficial factors of such tribolayer were also reported. However, the non homogeneous structure and distribution of the layer presents problems when trying to improve the performance of the hip implant system.

In this study, scanning electrochemical microscopy (SECM) is employed to indentify the reactivity of tribolayer coated surfaces, providing insight into the corrosion protection provided by the thin film. The substrate used in this work is a low-carbon (LC) CoCrMo alloy under two different surface conditions: (1) Polished- new implant surface and (2) tribolayer coated surfaced-retrieved implant surface.

The obtained SECM images indicate that the mechanically polished surface is heterogeneous with needle-like features (50 x 10 µm) displaying increased electrochemical activity and kinetics. The presence of the tribolayer provides some corrosion resistance although there appears to be some residual surface activity possibly due to incomplete surface coverage. The knowledge about the distribution of tribolayer is essential to determine the efficiency of the tribolayer formation on implant surface. Further studies are required to generate a clear understanding the underlying mechanisms that promote the tribolayer formation

4:10pm **D2-2-9 Enhancements in Corrosion Resistance and Biocompatibility of Biomedical Ti-25Nb-25Zr Alloy Using Electrochemical Anodization Treatment**, ***H.H. Huang***, *C.P. Wu*, National Yang-Ming University, Taiwan, *T.H. Lee (biomaterials@hotmail.com)*, Chung Shan Medical University, Taiwan

The biocompatibility of an implant material is determined by its surface characteristics. This study investigated the application of a fast and simple electrochemical anodization surface treatment to improve both the corrosion resistance and biocompatibility of β-type Ti-25Nb-25Zr alloy with lower elastic modulus for implant applications. The electrochemical anodization treatment produced a thin (< 100 nm) oxide layer with nanoscale porosity (pore size < 50 nm) on the Ti-25Nb-25Zr alloy surface. The surface topography and microstructure of Ti-25Nb-25Zr alloy were analyzed. The corrosion resistance was investigated using potentiodynamic polarization curve measurements in simulated body fluid (SBF). The cell adhesion and proliferation of human bone marrow mesenchymal stem cells on test specimens were evaluated using various biological analysis techniques. Results showed that the presence of a nanoporous oxide layer on the anodized Ti-25Nb-25Zr alloy surface increased the corrosion resistance (*i.e.*, decreased both the corrosion rate and the passive current) in SBF solution compared with the untreated Ti-25Nb-25Zr alloy. Surface nanotopography enhanced the cell adhesion and proliferation on the anodized Ti-25Nb-25Zr alloy. We conclude that a fast and simple electrochemical anodization surface treatment improves the corrosion resistance and biocompatibility of β-type Ti-25Nb-25Zr alloy with lower elastic modulus for implant applications.

4:30pm **D2-2-10 Anti-fish Bacterial Pathogen Effect of Immobilized TiO_2/Fe_3O_4 Powder on Glass**, ***T.C. Cheng*** *(cheng.tachih@gmail.com)*, National Pingtung University of Science and Technology, Taiwan, Taiwan, Republic of China, *Y.C. Lee*, National Pingtung Univeristy of Science and Technology, Taiwan, Republic of China, *H.C. Hsu*, National Pingtung University of Science and Technology, Taiwan, Republic of China

For the application of visible light responsive TiO_2/Fe_3O_4 powders in disinfection of fish pathogens is hindered by the recovery of the powder from water. The TiO_2 sol-gel is evaluated to immobilize TiO_2/Fe_3O_4 powder on glass using spin coating. TiO_2/Fe_3O_4 powders are synthesized at various molar ratios of TiO_2 to Fe_3O_4. The 1.5μm thickness film with rough and cracked surface is formed. It contains 30 nm diameter particles, anatase TiO_2 and Fe_3O_4 after analysis using SEM and XRD. According to indigo carmine dye degradation assay using visible light, the optimal percentage of TiO_2 sol-gel to TiO_2/Fe_3O_4 powder is 0.4 g/ml. The efficiencies of anti-fish bacterial pathogens are 50% for *E. tarda* and 20% for *A. hydrophila* meanwhile deformed bacteria or damaged bacterial cell membranes are observed at 3 hours visible light irradiation. These results indicate the feasibility of coating TiO_2/Fe_3O_4 on aquarium glass for reducing the fish pathogen concentration and minimizing the disease prevalence in aquarium without using UV light.

4:50pm **D2-2-11 Novel Functionalization of Anodized Ti6Al4V Nanotubes through Thermal Oxidation Approach**, ***S. Patel***, *C. Takoudis (takoudis@uic.edu)*, University of Illinois at Chicago, US

Biocompatible metal implants for retaining normal functionality have been given special attention in the field of dentistry and orthopaedics. Ti-V alloy has shown to extend the life span of implants due to its high biocompatibility, high mechanical resistance, low density, high corrosion resistance, and atoxicity. Implants' success rate also depends on osseointegration. Material properties such as wettability, roughness, surface energy and composition are key factors that affect osseointegration. In addition to micro and nano-roughening techniques such as sandblasting/acid etching and anodization, other techniques such as thermal oxidation, atomic layer deposition and chemical vapor deposition have been introduced to generate TiO_2 coatings for improved surface properties. TiO_2 has also been shown to improve and accelerate osseointegration through bone morphogenic protein signaling, apatite formation, and up-regulation of collagen II, osteocalcin, biglycan, collagen I, osteopontin and TGF-β1. TiO_2 layers protect the bulk Ti-V from dissociating cytotoxic aluminum and vanadium ions into the biological environment. Furthermore, TiO_2 is known to readily react with water to form hydroxyl groups on its surface, increasing surface energy and promoting cellular attachment. Recently, anodized TiO_2 nanotubes (TNTs) have shown to enhance cellular response of human mesenchymal stem cells due to increased surface area for cellular adhesion. TNTs 50 nm in diameter was formed by electrochemically anodizing Ti-V in 0.2 wt.% ammonium fluoride (NH_4F, 48% aqueous solution) in ethylene glycol with an applied voltage of 60 V DC for 3 hours. Anatase TNTs are preferred over amorphous or rutile as it resembles the crystalline structure of hydroxyapatite, which plays a key role in bone repair. Optimal parameters for forming anatase TNTs can be obtained by calcinating TNTs at 300, 450, 600 and 700 °C for two different durations, 3 and 6 hours. Annealing TiO_2 at 300 °C is known to convert amorphous into anatase TiO_2. Annealing at 450 °C is reported to promote anatase, while at 600 °C a majority of rutile with little anatase is formed. Finally, at 700 °C the rutile structure is anticipated to form. Advancing this project further will be discussed by performing surface characterizations including goniometry, scanning electron microscopy and other techniques that provide information regarding hydrophilicity, surface topography and surface composition of treated TNTs. Cellular growth is known to be more efficient on surfaces with higher hydrophilicity and higher anatase TiO_2 content rather than on surfaces which are hydrophobic, amorphous or rutile.

5:10pm **D2-2-12 A Tribocorrosive Investigation of Commonly Used Implant Alloys**, ***D. Royhman*** *(droyhman@gmail.com)*, Rush University Medical Center, USA, *M. Mathew*, Rush University Medical Center, US, *J. Yuan*, University of Illinois at Chicago, College of Dentistry, US, *M. Wimmer*, Rush University Medical Center, US, *C. Sukotjo*, University of Illinois at Chicago, College of Dentistry, US

Background: Commonly an implant is made of titanium alloy (Ti6Al4V; Ti alloy), cobalt-chromium-molybdenum alloy (CoCrMo; CoCrMo alloy). In the body, these implant metals are exposed to extremely complex and variable conditions, which can lead to degradation of the material and subsequent adverse biological reactions. Such conditions include intermittent mechanical events (mastication) and varying chemical conditions (synovial fluid, infection, and immune response). A recent multi-disciplinary approach, known as "*Tribocorrosion*" combines the study of mechanical degradation (tribology) with the study of chemical degradation (electrochemistry).

Objective: The objective of this study was to investigate the tribocorrosive nature of the two most commonly used implant metals (Ti6Al4V alloy and CoCrMo alloy) using simulated in-vivo environmental conditions.

Hypothesis: CoCrMo alloy offers superior tribocorrosive resistance than Ti6Al4V alloy under tested conditions for bioimplant applications.

Methods: 18 Ti6Al4V and 18 CoCrMo alloy discs, were divided into 12 groups (n=3) as a function of material (Ti6AL4V and CoCrMo), pH (3.0 and 7.6), and testing parameters (Open circuit potential, potentiostatic scan, and potentiodynamic scan). Sliding duration (1800 cycles), frequency (1.0 Hz) and load (16 N) parameters mimicked the daily mastication process. Bovine Calf Serum, (BCS) with variable pH levels was used to mimic the chemical environment. Electrochemical impedance spectroscopy was conducted before and after tribocorrosion to compare the changes in corrosion kinetics as a function of mastication. Surface morphology was characterized using white-light-interferometry and scanning electron microscopy. Finally, total weight loss and roughness values were calculated.

Results: The results of this study show that CoCrMo alloy shows superior tribo-corrosion behavior compared to Ti6Al4V alloy under sliding conditions, CoCrMo alloy offers superior wear resistance, and that synovial fluid components can affect the electrochemical nature of the metal/electrolyte interface as a function of pH

Conclusion: In general, CoCrMo alloy offers superior biomaterial properties for implantation under tested loading conditions compared to Ti6Al4V alloy. Further studies are required to understand mechanistic transition under synergistic behavior wear and corrosion.

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

Friction, Wear, and Lubrication; Effects & Modeling

Moderator: V. Fridrici, Ecole Centrale de lyon, O. Eryilmaz, Argonne National Laboratory, US, S.M. Aouadi, University of North Texas

1:30pm **E1-1-1 Tribological Comparison Between a Commercial DLC and an Experimental TaSiN Thin Films**, ***M. Figueroa*** *(mafguadarrama@hotmail.com)*, *E. García*, SEPI, ESIME-Zacatenco, Instituto Politécnico Nacional, Mexico, *G. Ramírez*, Instituto de Investigaciones en Materiales,, *S. Muhl*, *S. Rodil*, Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de Mexico, México, *A. Cavaleiro*, *A. Ramalho*, University of Coimbra, Portugal

The aim of this work is to compare the tribological properties, friction coefficient and wear rate, of a commercial DLC thin film and a nanocomposite thin film of tantalum nitride (TaN) nanocrystals embedded in an amorphous silicon nitride (SiNx) phase, both coating were deposited on a cp-titanium substrates polished to roughness of 70 nm.

The structure and hardness of the thin films were evaluated by x-ray diffraction and nanoindentation. The adhesion of the film to the substrate was evaluated using scratch testing, using a 100Cr6 steel ball from 0 to 80 N along 8 mm of scratch. The friction coefficient of both coatings was studied in a CETR reciprocating ball-on-flat tribometer using a 10 mm diameter polycrystalline alumina ball as the counter-body, with a 2 N normal load and a stroke of 10 mm at 5 Hz. The wear properties were studied by micro-scale abrasive ball cratering using a 25.4 mm diameter 100Cr6 steels ball, a constant velocity of 75 RPM and applying two different loads 0.1 and 0.05 N and a wide range of sliding distances from 3 to 300 laps. For all the tests a controlled flow of slurry of 8.4 µm diameter SiC micro particles at 10% wt. concentration in distilled water was used. The wear scars were analyzed by profilometry, optical microscope and scanning electron microscopy to understand the wear mechanisms involved.

The results indicated that the hardness of TaSiN was higher than the DLC thin film. We observed considerable variation in the different critical loads for each coating and testing conditions. In terms of friction coefficient the DLC thin film had a lower value than the TaSiN thin film, but the TaSiN had a significantly better wear resistance than the DLC samples. Finally, we report the details of the wear mechanisms that occur for the two types of thin film.

1:50pm **E1-1-2 Tribological Behavior of DLC Films with Various sp^3/sp^2 Ratios Deposited by Pulsed Laser Ablation and Lubricated by Base Oils**, ***C. Choumad-Ould*** *(could.hefrd@hef.fr)*, HEF, LaHC, LTDS, France, *C. Héau*, HEF, France, *T. Tite*, Laboratoire Hubert Curien, UMR 5516, Université de Lyon, Université Jean Monnet, France, *A.S. Loir*, *C. Donnet*, *F. Garrelie*, LAHC, France

The tribological behavior of Diamond-Like Carbon (DLC) films is critical in various applications [1]. Indeed, the friction level determines both the loss of energy and the stress within the structure, and the wear resistance determines the durability of the coating, allowing the stability of the coefficient of friction by keeping the contact surfaces unchanged. Such behavior depends on the chemical composition (absence or presence of hydrogen, doping with metal or non-metal elements), carbon hybridization (sp^3/sp^2 Ratio) and nanostructure (disorder of the network) of the DLC film. A significant difference in behavior was in particular observed between ta-C and a-C:H films and whose understanding requires further investigation [2]. For this purpose, DLC films with a high sp^3/sp^2 ratio can be considered as a model DLC. Nanosecond pulsed laser deposition (ns-PLD) is of particular interest to reach such high sp^3 contents, up to ~ 80% [3]. In this study, we explore the influence of the composition and the sp^3/sp^2 ratio of DLC coatings on their tribological behavior. Hydrogenated DLC films deposited by conventional PECVD with various levels of hydrogen and unhydrogenated DLC films deposited by PLD either in the nanosecond mode (ns-PLD), either in the femtosecond mode (fs-PLD), thus allowing to reach various sp^3/sp^2 ratios confirmed by Multiwavelength Raman spectrometry, are tested and compared. The tests are performed on a ball-on-flat device. The coatings are deposited on the ball for better evaluation of the level of wear. Tests with DLC coatings deposited on both the ball and the flat are also carried out to evaluate the influence of the coating of the two contact partners on the tribological behavior. **Keywords**: Tribological properties; DLC coating; Pulsed laser deposition; sp^3/sp^2 ratio; Hydrogen ratio **References**: [1] Héau C., DLC Films in Mechanical and Manufacturing Industry, p. 469-483, Tribology of Diamond-Like Carbon Films, Springer (2008). [2] Héau C, Ould C, Maurin-Perrier P, Tribological Behavior Analysis of Hydrogenated and Non-hydrogenated DLC Lubricated by Oils with and without Additives, (proposed for publication). [3] Sikora A, Garrelie F, Donnet C, et al. Structure of diamondlike carbon films deposited by femtosecond and nanosecond pulsed laser ablation, J. Appl. Phys., 2010, 108: 1-9.

2:10pm **E1-1-3 In-situ Synthesis of DLC Boundary Films From Base Lubricating Oils at Sliding Tribological Interfaces**, ***A. Erdemir*** *(erdemir@anl.gov)*, *O. Eryilmaz*, Argonne National Laboratory, US **INVITED**

Nanocomposite coatings are made of nano-scale multilayers and/or composite architectures that make them very hard, resilient, and tough. These properties are much desired in most tribological applications since they often insure longer durability and better performance even under very stringent operating conditions. In this study, we explored the possibility of further functionalizing such nanocomposite coatings by making them catalytically very active so that they can also derive or extract their own carbon-based boundary films in-situ from the base lubricating oils (including mineral, synthetic, or vegetable base oils). In our nanocomposite coating architectures, we identified and combined a variety of catalytically active hard (nitrides, carbides, or oxides of Mo, W, V, Re, etc.) and soft phases (such as Ag, Ni, Pd, Au, Cu, etc.) at some optimum concentrations so that when tested under lubricated sliding conditions, they would be able to crack base oil molecules (mainly long-chain hydrocarbons) into dimers and trimers and then deposit them as protective boundary films on sliding contact surfaces. Using UV Raman and a variety of other surface and structure analytical techniques, we elucidated the structural chemistry of these boundary films and confirmed that they were similar to those diamonlike carbon (DLC) films that are typically produced by CVD and PVD methods. Under the very severe contact conditions of our tribological test systems, these DLC boundary films were able to afford friction coefficients of as low as 0.02 and provide some of the highest resistance to wear and scuffing. In this paper, we will concentrate on the structural and chemical nature of these DLC boundary films and ascertain fundamental mechanisms that are responsible for their impressive tribological behaviors.

2:50pm **E1-1-5 Critical Role of Tribofilm in the Performance of Electrical Contacts Involving Cu-DLC Nanocomposite Coating**, ***R. Hombo***, Denso Corporation, Japan, *T. TAKENO*, Tohoku University, Japan, *J. Fontaine (julien.fontaine@ec-lyon.fr)*, LTDS, France, *H. MIKI*, Tohoku University, Japan, *N. KATO*, *T. NOZU*, *N. INAYOSHI*, Denso Corporation, Japan, *M. BELIN*, Ecole Centrale de Lyon, France

Metal containing diamond-like carbon coatings have unique tribological characteristics that depend on various factors such as combination of materials, sliding conditions, environments and so on. In this study, electrical and tribological properties of a copper containing diamond-like carbon (Cu-DLC) nanocomposite coating deposited on copper-based substrates were investigated. A hybrid deposition process composed of plasma enhanced chemical vapor deposition and DC magnetron co-sputtering of copper target was used for the deposition. The tribological behavior was investigated by using a ball-on-flat reciprocating tribometer, up to 2000 sliding cycles. The counterpart of the Cu-DLC plate was a ball of copper alloy. The four-terminal method was used for the measurement of the electrical contact resistance between the ball and the Cu-DLC plate during the tribo-test. While initial value of the electrical contact resistance was hundreds of milliohms, it gradually decreased with increasing number of sliding cycles, reaching about 4 to 6 milliohms after 200 cycles. The friction coefficient was approximately 0.25, one third of the one for an uncoated substrate, and was stable from the beginning of the test to 2000 cycles. A tribofilm was built up on the sliding surface of the ball as the sliding cycle increased, consisting mainly of copper according to energy dispersive X-ray spectroscopy. Surprisingly, the Cu-DLC coating on the plate was almost worn out after less than 200 cycles, without detrimental effects neither on the coefficient of friction nor on the electrical contact resistance. The good electrical and tribological characteristics of the contact were thus provided by the tribofilm on the ball. The unique structure and properties of the tribofilm, resulting from a selective transfer process of nano-sized copper grains, will be discussed.

3:10pm **E1-1-6 Influence of the Coating Structure of a-C:H-W Coatings on their Wear-performance: a Theoretical Approach and its Practical Confirmation**, ***A. Gies*** *(astrid.gies@oerlikon.com)*, OC Oerlikon Balzers AG, Liechtenstein, *T. Chudoba*, ASMEC GmbH, Germany, *N. Schwarzer*, Saxonian Institute of Surface Mechancis, Germany, *J. Becker*, Oerlikon Balzers Coating Germany GmbH, Germany

Diamond-like Carbon – coatings are widely used in the automotive industry due to their extraordinary wear and friction reducing properties which can mainly be attributed to their high hardness, low affinity to metals and very low coefficients of friction. Depending on the application, DLC-coated surfaces might experience severe mechanical interactions with the counterpart which determine the lifetime and reliability of the coated surface and therefore the entire tribological system. In order to well adapt a DLC-coating to a tribological system, it is necessary to know the stress- and strain-fields arising in the coating-substrate system under mechanical loads.

A few years ago, a theoretical approach was proposed with the aim of modelling contact problems in order to optimize the coating properties in a way to avoid any plastic deformation or fracture of the coating-substrate system for a given load range [1]. As a result, it was shown that the use of a layered coating structure with a gradual transition of the Young's modulus from the substrate to the coating surface might protect both, substrate and coating plus the often rather sensitive interface area from plastic deformation. In addition, a final top layer with a lower modulus or a gradient with decreasing Young's modulus should avoid any coating fracture due to tensile stresses.

In this work, a graduated a-C:H-W coating was deposited on a steel substrate according to the above described optimized layer system. The mechanical properties of this graduated coating system were determined using nanoindentation. In addition, a multiaxial, 3-dimensional nanoindentation test (reciprocating wear test with nanometre resolution) was carried out in order to analyse the wear-performance of the graduated coating system. By comparing the wear-performance of the graduated coating system to a non-graduated one we were able to confirm the above described theoretical approach predicting a better wear-performance for a graduated coating system.

[1] N. Schwarzer: "Coating Design due to Analytical Modelling of Mechanical Contact Problems on Multilayer Systems", Surface and Coatings Technology 133 –134 (2000) 397 - 402

3:30pm **E1-1-7 From Predictive Modelling via Optimized Testing to Applied Coating Development: DLC Coatings Durability under Nano-fretting Conditions**, *T. Liskiewicz (t.liskiewicz@leeds.ac.uk)*, Leeds University, UK, *B Beake*, Micro Materials Ltd., UK, *N. Schwarzer*, Saxonian Institute of Surface Mechanics, Germany, ***M. Davies***, Micro Materials Ltd, UK

Improved integration of measurement data obtained from mechanical testing is required to provide reliable inputs for predictive wear models. In this work, a new global increment nano-fretting wear model based on the effective indenter concept has been used and the results were compared with experimental data. A series of DLC coatings with varied mechanical properties was deposited using industrial scale PECVD system and characterised on low-drift nano-indentation platform. Successive nano-scale fretting measurements have been performed with a variety of probes at different contact loads in order to examine the effect of different contact conditions on coating wear. A physical analysis of the nanoindentation test allowed us not only to extract the true coating Young's Modulus (E) but also the coating yield strength (Y). In comparison to the hardness (H) this is the basis for a more generic understanding of the mechanical coating behavior. This allowed direct examination of the influence of the variation of Y/E in the coatings on the observed nano-fretting wear. Correlation with H/E, evaluation of the stress field evolution during the test and the extraction of wear and fretting parameters now gives us the opportunity to actually discuss the effects possibly being dominant within the performed nano-tribo-tests. The model does not only allow to analyze nano-fretting tribological experiments but also to forward simulate such tests and it gives hints for better component life-time predictions.

3:50pm **E1-1-8 Microwear Investigations of DLC Coatings with Nanometer Resolution in Normal and Lateral Direction**, *T. Chudoba*, ***K. Mayekar*** *(k.mayekar@asmec.de)*, ASMEC Advanced Surface Mechanics GmbH, Radeberg, Germany

In the last years several techniques have been developed to investigate the wear of surfaces with nanometer resolution. This mainly includes the Atomic Force Microscopy (AFM) in the lowest force range. However, measurement techniques to determine the displacement with nanometer resolution in the higher force range, approximately between 1mN and 1N, hardly exist. On the other hand it is interesting to investigate single asperity contacts with contact radii between 0.5µm and 50µm and to understand the dominating wear mechanisms in this load range. This is now possible with the Universal Nanomechanical Tester of ASMEC which has both in normal and lateral direction nanometer and micro-newton resolution during reciprocating wear experiments. The instrument was used for wear measurements on diamond like carbon coatings (DLC) of different hardness, produced by chemical and physical vapor deposition (CVD/PVD) methods. Two conical diamond indenters with a tip radius of 6µm and 70µm and a hard metal sphere with 100µm radius have been applied. For the lateral displacement, 80µm oscillation length at 0.17Hz oscillation frequency was set for every cycle of 6s. A s uitable applied force range was selected for each indenter type to study the wear behavior. Additionally some of these samples were measured in an oil bath to study the influence on the friction coefficient. The average friction coefficient and the average normal displacement per cycle were calculated for both conditions. The values of force and contact pressure limit were detected when the wear process begins. Additionally it was analyzed how the wear rate per cycle develops. The results showed that for the lower pressures less than one atomic layer was removed per slide and no correlation was found between the friction and the wear rate.

4:10pm **E1-1-9 Failure Mechanisms of DLC and TiN Biomedical Coatings on SS316L and M2 Substrates under Cyclic Impact-sliding Loads**, ***Y. Chen***, *X. Nie (xnie@uwindsor.ca)*, University of Windsor, Canada, *J. Housden*, Tecvac, Ltd., UK, *A. Matthews*, University of Sheffield, UK

Owing to the superior tribological and mechanical properties with corrosion resistance, biocompatibility and hemocompatibility, a-Si:H DLC and TiN coatings have emerged as promising materials for biomedical (implant) applications. A cyclic inclined impact-sliding test was utilized in dry and Hank's balanced salt solution (HBSS) conditions to study the fatigue wear behaviors of DLC and TiN coatings and the supporting capability of different substrates—soft SS316L and hardened M2. Effects of substrate hardness on the coating failure mechanisms were studied. This test simulates the reciprocal combined impact-sliding motion by using a steel counterface. In each impact-sliding cycle, the forces comprised a dynamic impact load, Fi, and a pressing load, Fp, (Fi/Fp=120 N/300 N). It was found that HBSS didn't cause corrosion degradation because dense Si (for DLC) and Ti (for TiN) interfaces dominated the corrosion behaviors. Instead, the solution provided a lubricate effect and enhanced coating durability. The main coating failure mechanisms under very high contact stress in this test were fatigue cracking, chipping and peeling. Softer substrate exhibited energy absorption against impacts and caused less failure percentage on coating surface. But hard substrate provided a better loading support to the coating which altered the coating failure evaluation procedure.

4:30pm **E1-1-10 Tribological Behavior of the Superhard Coatings of Ta-N-Si and Nb-N-Si**, ***G. Ramirez*** *(enggiova@hotmail.com)*, Argonne National Laboratory, US, *S. Rodil*, Universidad Nacional Autónoma de México - Instituto de Investigaciones en Materiales, Mexico, *A. Erdemir*, *O. Eryilmaz*, Argonne National Laboratory, US, *S. Muhl*, Universidad Nacional Autónoma de México - Instituto de Investigaciones en Materiales, Mexico

In this work, two different superhard coatings were prepared; Nb-N-Si and Ta-N-Si. The coatings were deposited using a reactive dual magnetron sputtering system, using two targets, one metallic target (Nb or Ta) and a silicon target, in a reactive mixture of gases (argon and nitrogen). By changing the power in the silicon target, the amount of incorporated Si could be changed from 0 to about 15 at%. For the tribological tests, the films presenting the maximum hardness were chosen, which correspond to Si contents about 5 at% for both films. The films were grown on M2 high speed steel to evaluate the tribological behavior.

The microstructural properties, measured using X-ray diffraction, showed the growth of crystalline coatings presenting the FCC phase of the metallic nitrides (NbN or TaN). The composition of the films was measured using X-ray photoelectron spectroscopy (XPS). The mechanical properties were obtained using the nanoindentation technique and were ~35 GPa for the $Nb_{46}N_{44}Si_5$, and ~40 GPa for the $Ta_{45}N_{44}Si_5$.

The tribological behavior was evaluated using two techniques, Ball on Disk (BoD) to evaluate the behavior in boundary lubricated sliding conditions, and High Frequency Reciprocating Rig (HFRR) to evaluate the behavior in the mixture of hydrodynamic and boundary condition regimes. The tests were made in two conditions: air to evaluate the coating as solid lubricant, and in engine oils to evaluate the performance of the coatings to application in the automotive industry.

The BoD tests were carried out in air, base oil (PAO 4), and fully formulated 5W30 grade full synthetic engine oil. The results of the test in air showed an improvement of the wear resistance of the coated steel for both coatings. The coefficient of friction of the Ta-N-Si coating was lower than for the bare substrate, while the Nb-N-Si did not present any significant reduction. Similarly, the tests on engine oils showed that the Nb-N-Si coatings were inert and did not improve the tribological behavior in comparison to the M2 steel. Meanwhile, a reduction in the CoF was observed for the Ta-N-Si.

The HFRR test results showed a similar trend to those obtained using BoD. The Raman technique was used to understand the mechanism that improved the tribological behavior of the coatings.

Acknowledgements: S.E. Rodil and G. Ramirez wish to acknowledge the financial support from DGAPA-UNAM IN103910.

4:50pm **E1-1-11 Friction Reduction by Thermal Post-deposition Treatment of Arc Evaporated TiAlTaN Coatings in Methane**, ***N. Schalk*** *(nina.schalk@mcl.at)*, Materials Center Leoben Forschung GmbH, Austria, *C. Mitterer*, Montanuniversität Leoben, Austria, *C. Czettl*, CERATIZIT Austria GmbH, Austria, *B. Sartory*, Materials Center Leoben Forschung GmbH, Austria, *M. Penoy*, *C. Michotte*, CERATIZIT Luxembourg S.àr.l., Luxembourg

For severe cutting applications, the reduction of friction between work piece and coated tool surface is of vital importance to limit the thermal load. In the last decade, several low friction coatings like diamond like carbon and MoS_2 have been suggested. Within this work, the surface of arc evaporated TiAlTaN coatings was modified by thermal treatment in methane. The modified coatings were investigated with respect to their gain in weight, composition and structure by a precision balance, GDOES, SEM-FIB, and TEM. The determined gain in weight could be attributed to an up to ~200 nm thick discontinuous carbon layer on the coating surface. This carbon layer was identified as graphite using Raman spectroscopy. SEM and TEM revealed a few nm thick carbon diffusion zone in the TiAlTaN coating. The friction coefficient determined by ball-on-disc tests was reduced from 0.66 for the as-deposited coating to 0.25 after the treatment in methane, where the low friction behaviour is stable over 1000 m.

5:10pm **E1-1-12 Dangling Bonds Induced Cross-linking Model in Nanoscratched Graphene Layers**, *Q. Zhang*, Key Laboratory of Education Ministry for Modern Design and Rotor-Bearing System, School of Mechanical Engineering, Xi'an Jiaotong University, China, *D.F. Diao (dfdiao@mail.xjtu.edu.cn)*, Shenzhen University and Key Lab. Of Ed. Ministry for Modern Design and Rotor-Bearing Sys., Xi'an Jiaotong Univ., China, ***L. Yang***, Key Laboratory of Education Ministry for Modern Design and Rotor-Bearing System, School of Mechanical Engineering, Xi'an Jiaotong University, China

Dangling bonds induced cross-linking between interlayer graphene during nanoscratch is simulated by molecular dynamics method. The normal stress over 74 GPa leads to broken of the hexagonal ring of intralayer graphene, producing unstable dangling bonds which easily make up sp2 or sp3 with neighbor layers. The cross-linking density increases with the scratching depth, causing higher scratch hardness and reaching the peak of 90 GPa. The cross-linking is reversible after scratch when the normal stress is less than 90 GPa, beyond which the atoms from different graphene layers will be mixed together forming amorphous, making the scratch hardness decrease sharply. Keywords: Dangling Bonds; Cross-linking; Graphene Layers; Scratch Hardness

Applications, Manufacturing, and Equipment
Room: California - Session G4-2+E

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

Moderator: M. Arndt, OC Oerlikon Balzers AG, X. Nie, University of Windsor

1:30pm **G4-2+E-1 Facing Challenge of Stamping Advanced High Strength Steels**, ***B.J. Janoss*** *(bernie.janoss@ionbond.com)*, Ionbond, US **INVITED**

PVD, CVD, and TD coatings have been successfully used for years to enhance the productivity of many forming tools. The wide variety of products available in the marketplace have enabled users to select an option based upon its own preferences and objectives because virtually all the available products provided enhanced performance when used in applications forming low carbon steel materials.

However the rapidly increasing trend of increased use advanced high strength steel materials (AHSS), has resulted in greater challenges for coatings to produce acceptable levels of productivity in these new, demanding applications. These AHSS materials, with common tensile strength levels of 780 MPa to 980 MPa and soon to be 1180 MPa, produce forming conditions containing high mechanical fatigue forces, severe work hardening conditions, and high levels of friction between the workpiece and the coated tool surface. Some AHSS alloys are hot formed and quenched to produce the desired mechanical properties, and these applications present thermal challenges for potential coating solutions along with chemical reactivity with an aluminum coating on the strip aimed protecting the steel from oxidation.

This paper will provide an overview of the challenges presented for potential coating solutions by the increasing use of AHSS materials, both by cold forming and hot stamping. Guidelines will be provided regarding the characteristics of potential coating solutions require in order to successfully perform in AHSS forming applications. Common existing coating solutions will be compared in terms of these key characteristics. Further, recommendations will be made for what would make the optimum coating solution. Case study results will also be provided.

2:10pm **G4-2+E-3 Substrate Effects on Failure Behavior of Hard Coatings Under Inclined Cyclical Loading Conditions**, ***J.F. Su***, *X. Nie (xnie@uwindsor.ca), H. Hu*, University of Windsor, Canada, *D. Young*, FORD Motor Company, US, *D. Adamski*, General Motors, US, *D.J. Zhou*, Chrysler Corporation, US, *E. McCarty*, Materials Technology Consulting, US

Due to the increasing use of advanced high strength steels (AHSS), die wear prevention has become an important issue in the stamping of automotive parts. Since physical vapor deposition (PVD) coatings usually has a much higher hardness and resistance of wear than electroplated or electroless coatings and nitrided steels, PVD coatings have been considered as necessary top layers on dies surface to battle the wear problems. In this project, three steel substrates were coated using a PVD CrN + plasma nitriding duplex treatment. Effects of the substrates' hardness, elastic modulus and microstructural morphology on coating failure behaviour were studied under inclined cyclic loading test conditions with intention to simulate coating failures in stamping operation . The coating wear tracks after the tests were observed using a scanning electron microscope (SEM) at both top view and cross section view. The result showed that coated sample with more uniform and homogeneous steel substrates Toolox and NAAMS S2333 performed better than samples with D2 and S0050A substrates.

2:30pm **G4-2+E-4 Manufacturing of Metal-based Microparts: Fabrication Strategies and Application of Coatings to Engineering of Tool Surfaces**, *Y. Mu, K. Chen, B. Lu,* ***W.J. Meng*** *(wmeng1@lsu.edu)*, Louisiana State University, US, *G.L. Doll*, University of Akron, US **INVITED**

A wide range of industrial applications, current and anticipated, drive the process of miniaturization of thermal and chemical devices. In a range of applications, metal-based microsystems enjoy advantages of performance, cost, or both, over silicon-based counterparts. Examples include microchannel heat exchangers, miniature gas chromatograph sensors, and others. The critical bottleneck restricting the use of metal-based microsystems in actual applications has often been the lack of effective and economical manufacturing methods for metal-based microparts. In this talk, our activities in manufacturing of metal-based microparts through several microscale replication strategies, such as compression molding, roll molding, etc., will be summarized. Our efforts in engineering surfaces of fabrication tools through conformal coating deposition will be illustrated. Our recent attempts to test for coating/substrate interfacial failures will be described.

3:10pm **G4-2+E-6 Effects of Thin Film Metallic Glass Coating on Sharpness Improvements of Cutting Tools**, *C.L. Li, T.Y. Liu,* ***J.P. Chu*** *(jpchu@mail.ntust.edu.tw)*, National Taiwan University of Science and Technology (NTUST), Taiwan, Republic of China, *J.-W. Lee*, Ming Chi University of Technology, Taiwan, Republic of China, *J.S.C. Jang*, National Central University, Taiwan, Republic of China, *M.J. Chen, S.H. Chang*, Mackay Memorial Hospital Tamsui Campus, Taiwan, Republic of China

The presence of microscopic roughness in surface and cutting edge may lead to deterioration in the sharpness and durability of commercial cutting tools. Thin film metallic glasses (TFMGs) have been reported to have some unique properties such as smooth surface. In this work, a novel thin film metallic glass was deposited on stainless steels cutting tool for sharpness improvements. For comparison studies, conventional hard coatings including diamond-like carbon and metal nitride coatings were also prepared. These coated cutting tools were analyzed with various material characterizations and evaluated by the blade sharpness index test. The characterization results of sharpness and durability of these coated cutting tools will be discussed in present talk.

3:30pm **G4-2+E-7 Decomposition of Ti-Cr-Al-N/Ti-Cr-N Multilayer Coatings**, ***R. Forsén*** *(rikfo@ifm.liu.se)*, Linköping University, IFM, Thin Film Physics Division, Sweden, *M. Johansson*, Seco Tools AB, Sweden, *N. Ghafoor*, Linköping University, Sweden, *M. Odén*, Linköping University, IFM, Nanostructured Materials, Sweden

The hardness of protective tool coatings is an important factor for high speed metal machining during which the temperature may exceed 1000 ºC at the cutting edge. Coatings that can retain their hardness at elevated temperatures is therefore of high interest. Ti-Al-N coatings exhibit a hardness increase at ~900 ºC due to spinodal decomposition into coherent nanometer-sized cubic (*c*)-AlN and *c*-TiN domains. We have shown that by adding Cr to this material system metastable monolithic *c*-$Ti_{0.31}Cr_{0.07}Al_{0.62}N$ coatings exhibit an age hardening process between 850 and 1000 ºC due to spinodal decomposition into coherent Ti- and Al-rich *c*-Ti-Cr-Al-N domains. At higher temperatures the domain size increases to around 20-40 nm where Cr relocates to Ti-rich domains whereupon the Al-enriched *c*-Ti-Cr-Al-N domains become Cr-depleted and consequently *c*-Al-N transforms into hexagonal (*h*)-Al-N. The hardness decrease associated with this transformation was less pronounced compared to ternary Ti-Al-N. The reason is a lowered driving force for relaxation of the coherent domain boundaries allowing the coatings to stay in a semi-coherent stressed state at higher temperatures. Another successful measure to enhance the hardness at elevated temperatures of Ti-Al-N has been reported through a Ti-Al-N/Ti-N multilayer growth concept where the coating architecture affects the decomposition. Our study is based on a combination of these two approaches. Theoretical results based on first principle calculations of the free energy in *c*-Ti-Cr-Al-N is coupled to experimental results obtained with nanoindentation, X-ray diffraction, analytical transmission electron microscopy and differential scanning calorimetry.

In a multilayer structure where coherent *c*-$Ti_{0.31}Cr_{0.07}Al_{0.62}N$ and *c*-$Ti_xCr_{1-x}N$ layers are sequentially deposited with a period of ~10 nm, the decomposition and the hardness increase at elevated temperatures is altered depending on x. The largest lattice mismatch between the layers occurs for x=1 (pure Ti-N) resulting in the highest hardness increase at elevated

temperatures. First principal calculations predict a minimum in the mixing enthalpy of *c*-$Ti_xCr_{1-x}N$ for x=~0.1. Thus, for this composition the layer is stable inhibiting Cr relocation into this layer from the surrounding *c*-$Ti_{0.31}Cr_{0.07}Al_{0.62}N$ layer. This can lead to an increased thermal stability of the cubic structure and a preservation of the coherent domains boundaries with a retained hardness up to 1200 ºC.

3:50pm **G4-2+E-8 The Characteristics of Titanium Nitride Thin Films deposited by Reactive Plasma Deposition System and their Dependence on the Output Power of Plasma Gun**, ***K. Tanaka*** *(tanak@mmc.co.jp), M. TAKAHASHI, Y. TANAKA, A. OSADA*, Mitsubishi Materials Corporation, Japan

Reactive Plasma Deposition (RPD) is a new method which enables to coat various types of thin films such as metal oxides as functional coatings and nitrides as hard coatings without metal particles. Furthermore, RPD system compared to conventional sputtering or cathodic arc technique is expected to have highly ionized and excited plasma. The kinetic energies of the atoms, radicals and ions in chamber and the ionization ratio in the plasma are expected to change as a function of the output power of plasma gun, and the control of these factors is important to grasp the characteristics of the deposition of the films.

To investigate the characteristics of the deposition of the films by RPD method and their dependence on the output power of the plasma gun, we deposited titanium nitride (TiN) thin films onto cemented carbides by changing the output power and target-substrate distance (TSD). The crystallographic properties were characterized by X-ray diffraction pattern (XRD) and the cross-sectional morphologies were observed by Scanning Electron Microscope (SEM).

Each TiN film showed NaCl-type structure in several deposition rates. However, compressive stresses in the films were increased and (111) peak of XRD patterns were broadened by increasing the output power of plasma gun. The cross-sectional morphologies changed from columnar structure to granular as the output power increased. The ratio of ion current per deposition rate at each TSD decreased as the output power increased.

Even with the same deposition rate without bias voltage, the film characteristics changed into granular structure with lower crystallinity and compressive stresses in the films were increased. Energetic condition of the plasma was shifted in higher level as drawn in the structure zone diagram reported by A. Anders[1]. In RPD method, the increase of the output power of plasma gun led to the increase of joule flux into anode-crucible from the cathode. The kinetic energies of evaporated atoms, radicals and ions became higher by thermal excitation. From the result of the measurement of the ion current, the ionization ratio was decreased as the output power increased.

In RPD method, by increasing the output power, the structures of the films became granular with lower crystallinity and the compressive stresses in the films were increased. The kinetic energies of the evaporated atoms, radicals and ions were one of the main factors of the characteristics changes. The ionization ratio, as another important factor, was decreased conversely.

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4:10pm **G4-2+E-9 Influence of PVD (Cr,Al)N Coatings and Surface Topography on Adhesion Behaviour towards PMMA**, *K. Bobzin, N. Bagcivan, R.H. Brugnara,* ***T. Münstermann*** *(muenstermann@iot.rwth-aachen.de),* Surface Engineering Institute - RWTH Aachen University, Germany

Direct production by injection molding of microstructured optical parts made from plastic offers the possibility to improve the functionality of optical components with a shorter process chain and lower production costs. Due to high deforming forces and tool wear new material concepts have to be developed for injection die molding processes. One possibility is to protect the molding die with a physical vapor deposition (PVD) coating. Beside protection against wear, PVD coating systems show a high potential to decrease deforming forces during production of microstructured optical parts. The present research work deals with the influence of different adhesion energies and surface topographies on adhesion behavior between (Cr,Al)N and polymethylmethacrylatan (PMMA). The adhesion energy was calculated using contact angle measurements of the substrate, the coatings and the PMMA. To evaluate the normalized adhesion force an experimental setup was developed, which enables application oriented adhesion measurements for different combinations of specimens and plastics. For the correlation between adhesion energy and normalized adhesion forces uncoated samples made of X42Cr13 (AISI: 420), which is typically used as material for molding dies, were compared with arc-PVD and magnetron sputter ion plating (MSIP)-PVD coated samples. The coating properties were further studied by nanoindentation regarding mechanical properties and by cross sectional SEM micrographs regarding morphology and coating thickness. The influence of surface topography was studied using microstructured specimens prepared with different pretreatments. The structures were generated by polishing and micro blasting using glass beads and SiC with different pressures and described by roughness parameters. Finally, the interaction of both influences, surface energy and topography towards the normalized adhesion forces was studied. The responsible mechanism for adhesion forces between microstructured surfaces and plastic were pointed out according to structure size. Afterwards, the results were confirmed by the use of coated and uncoated specimen prepared by laser structuring.

Topical Symposia
Room: Sunset - Session TS4-1

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

1:30pm **TS4-1-1 Self-Assembly of Two-Dimensional Nanosheets Induced by Interfacial Polyionic Complexation**, ***F. Kim*** *(kim-g@icems.kyoto-u.ac.jp), J. Zou*, Kyoto University, Japan **INVITED**

Significant progress has been made during the past decade in preparing nanosheets from a wide range of materials, which are actively pursued for various applications such as energy storage, catalysis, sensing, and membranes. One of the next critical challenges is developing a robust and versatile assembly method which allows the construction of the nanosheets into functional structures tailored for each specific purpose. An interesting characteristic of nanosheets is that they often behave as charged macromolecules, and thus can readily interact with an oppositely charged polyelectrolyte to form a stable complex. In this report, we demonstrate how such complexation process could be utilized for directing the self-assembly of nanosheets. By confining the nanosheet-polyelectrolyte complexation at air-liquid or liquid-liquid interfaces, the nanosheets are successfully assembled into various mesoscale architectures including fibers, capsules, and films. Furthermore, incorporation of additional components such as nanoparticles or small molecules can be easily achieved for further tailoring of material properties. This novel assembly method opens pathway to many useful nanosheets superstructures, and may be further extended to other types of nanomaterials in general.

2:10pm **TS4-1-3 Synthesis of Mono- to Few-layer Graphene on Cu-Ni Alloy for Transparent Conducting Electrodes**, ***L.Z. Huang***, *P.K. Nayak*, National Cheng Kung University, Taiwan, Republic of China, *S.C. Wang*, Southern Taiwan University of Science and Technology, Taiwan, Republic of China, *J.L. Huang (jlh888@mail.ncku.edu.tw)*, National Cheng Kung University, Taiwan, Republic of China

Transparent conducting films (TCFs) are used in many modern technological devices such as solar cells, displays and touch screens. The current most popular TCF is indium tin oxide (ITO). But due to the limited supply of Indium and high expenses, it is urgent need to look for a substitute material to replace ITO. Generally thin films of carbon based materials are regarded as a suitable alternative for this purpose. Out of all carbon based materials, recently developed graphene is a promising material for flexible TCF due to its high electrical conductivity and high optical transmittance. But, it is a very challenging task to prepare high quality large area graphene films using the existing methods such as mechanical exfoliation of graphite, Silicon carbide sublimation and chemical methods due to the existence of various defects during synthesis.

Recently, advances on chemical vapor deposition (CVD) growth of graphene on Ni and Cu polycrystalline films have been achieved, which have stimulated various applications owing to the scalability and transferability. Graphene films on Ni are grown as mixture of various layers and Cu has very low carbon solubility (i.e. <0.001 atom % at 1000 ℃). In this aspect, Cu-Ni alloy is the best choice for substrate to fabricate high-quality uniform graphene layers in compared to pure Ni and Cu because it exhibits moderate as well as controllable carbon solubility by tuning atomic fraction of Ni in Cu.

In the present work, we report the synthesis of mono-to few-layer graphene films on commercial Cu-Ni alloy foils (70:30 wt %) by varying various experimental parameters such as growth temperature, growth time and cooling rate during chemical vapor deposition. Such films were transferred to glass substrates after etching the metal substrate in an aqueous solution of $FeCl_3$. The quality and microstructure of graphene film were characterized by Raman spectroscopy, optical microscope (OM), field emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM). From the sheet resistance and transmittance measurements on the prepared graphene films, it is observed that such films are potentially useful

for transparent thin conducting electrodes. The details analysis of graphene films as transparent conducting electrodes will be presented in the paper.

2:30pm **TS4-1-4 Soft Materials with Hard Skin: Synthesis, Assembly and Applications**, ***F. Cavallo*** *(fcavallo@wisc.edu), M. Lagally*, University of Wisconsin-Madison, US **INVITED**

A recent and rapidly expanding research field is demonstrating, and exploiting, the fact that large-area (~0.03 to 3 cm), thin sheets (~5-500 nm) made up of materials of any class and any structure can be released from their original substrate and bonded to a new host. These new structural elements quickly came to be called *nanomembranes* (NMs). Especially of interest are crystalline semiconductor sheets. Nanomembranes are mechanically ultra-compliant, they are readily transferable to other hosts and conform and bond easily, they can take on a large range of shapes (including nanoribbons, micro-/nanotubes, and structures with combinable dimensions from 0D to 3D) via appropriate strain engineering and patterning, and, in planar geometry, they are stackable.

I have exploited the unique properties of Group IV semiconductor NMs to fabricate bi- or multi-material composites characterized by a large mismatch between the elastic moduli of an inherently stiff, but quite thin, top layer, such as Si or Ge, and a low-stiffness (*i.e.*, compliant) supporting substrate. Specifically I have developed a high-yield process to transfer and bond NMs onto a soft substrate, and have they form both into planar and wavy geometries.

In my talk, I will present detailed mechanical analysis showing that the exceptional compliance of NMs, and the possibility of mechanically engineering them in their 2D form allow matching the mechanical properties of cellular environments and hence achieving a successful bio-inorganic integration from a mechanical/electronic perspective.

Furthermore I will illustrate how NMs can be engineered to create novel device architectures, i.e., 3D devices integrating multiple functionalities, such as scaffolding for cell culture, electronics, optics, and fluidics. Finally I will present a few examples of 3D devices having potential application [#] [#] [#] in traditional and newly developed biomedical fields, such as electrophysiology, biomechanics, and optogenetics.

3:10pm **TS4-1-6 The Effects of Electron Irradiation Conditions on the Formation of Embedded Graphene Sheets During Carbon Film Deposition in ECR Plasma**, *C. Wang*, ***D.F. Diao*** *(dfdiao@mail.xjtu.edu.cn)*, Shenzhen University, Xi'an Jiaotong University, China

Graphene sheet is expected for broad applications since it has outstanding physical and mechanical properties. However, graphene based structures and devices are limited by its nature of two-dimensional atom network. It is of great significance to develop new carbon film with the properties similar to graphene and also thick enough for three dimensional processing. In this paper, a graphene sheets embedded carbon (GSEC) film is obtained by low energy electron irradiation in electron cyclotron resonance plasma. Embedded graphene sheets were observed by transmission electron microscopy (TEM). Raman analysis showed that the electron structure of the GSEC film is similar to that of bilayer graphene, and the structure is unlimited by the film thickness, which was controlled by film growth rate and deposition time. The effects of plasma density and electron irradiation energy on the growth rate of GSEC film were studied. The structures and electrical resistances of GSEC films prepared in different electron irradiation conditions were studied with TEM observation and four point measurement, respectively. The mechanism of graphene sheets formation under electron irradiation was elucidated, in which the inelastic scattering process between electron and carbon atom is considered as the main cause.

3:30pm **TS4-1-7 Intrinsic Wettability of Graphene**, ***H. Liu*** *(hliu@pitt.edu)*, University of Pittsburgh, US **INVITED**

Surface contamination of graphene is known to significantly degrade device performance. Although various ways to clean graphene has been reported, little is known about the nature and especially the source of the contamination. We find that that within 1 hour of exposure to ambient air, a clean graphene surface is contaminated with a thin layer of hydrocarbon. We show that contrary to the conventional wisdom that graphene is hydrophobic, a clean graphene is actually hydrophilic.

4:10pm **TS4-1-9 AFM Based Investigation of Organic Semiconductor Nanostructures Grown on Graphene Electrodes**, *M. Kratzer*, Institute of Physics, Montanuniversitaet Leoben, Austria, *B. Vasić, A. Matković, U. Ralević, R. Gajić,* Institute of Physics, University of Belgrade, Serbia, ***C. Teichert*** *(teichert@unileoben.ac.at)*, Montanuniversität Leoben, Austria

We have shown recently by in situ Low Energy Electron Microscopy experiments that the organic semiconductor para-sexiphenyl (6P) grows at low deposition temperatures on Ir(111) supported graphene in a layer-by-layer mode with the molecules lying on the substrate [1]. This molecular orientation is indeed desired for applications of the prepared films in organic light emitting diodes or solar cells for which the graphene acts as a transparent and flexible electrode. At substrate temperatures above room temperature, crystalline 6P needles form on a wetting layer composed of lying molecules [2].

Here, we changed our fabrication route to less expensive substrates and deposition techniques. 6P was grown on exfoliated graphene flakes transferred to silicon oxide [3] by hot-wall epitaxy. The substrate temperature ranged between 275 K and 400 K. The resulting film morphology was measured by ex situ atomic force microscopy (AFM). Whereas on silicon oxide terraced 6P mounds have been observed in the entire temperature range studied, there is on graphene a clear change in growth morphology with temperature. At low temperatures, terraced mounds coexist with short needles whereas above 360 K exclusively straight needles grow in selected directions. Such nanostructures offer the possibility to be studied by photoconductive AFM to probe their local response on irradiation with monochromatic light.

This work has been supported by the Austrian Science Fund project S9707-N20, and the Serbian Ministry of Science under project # OI171005.

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4:30pm **TS4-1-10 Large-Scale Synthesis of Graphene Films by Pulsed Laser Deposition**, ***T. Tite***, *A.S. Loir, C. Donnet, F. Bourquard, S. Reynaud, J.-Y. Michalon*, Laboratoire Hubert Curien, UMR 5516, Université de Lyon, Université Jean Monnet, France, *J.P. Chatelon*, Laboratoire Télécom Claude Chappe, EA 3523, France, *F. Garrelie (florence.garrelie@univ-st-etienne.fr)*, Laboratoire Hubert Curien, UMR 5516, Université de Lyon, Université Jean Monnet, France

Since its discovery in 2004, graphene has attracted tremendous interest due to its exceptional and advantageous physical properties [1]. However, to implement graphene as a leader material for future applications not only the challenges posed by the large scale growth need to be tackled but also a crystalline quality as comparable to mechanically exfoliated samples from graphite need to be obtained. Although, chemical vapor deposition (CVD) constitutes the mainstream among the large scale growth techniques [2], new routes still needed to be explored.

In the present study, we proposed to fabricate graphene by pulsed laser deposition (PLD) technique. PLD is a well-known technique for the deposition of amorphous carbon (a-C) such as DLC (Diamond-Like-Carbon) [3]. By ablating a graphite target, thin DLC films has been deposited by PLD under high vacuum condition either on catalytic metal (Ni, Cu) thin film or directly on the substrates (n-doped Si, fused silica) followed by a sputtered nickel metal thin capping layer. The growth process involves vacuum annealing of the ablated a-C layer and a natural cooling way. The dependence of graphene synthesis on process conditions, including the a-C thickness, temperature, setting time, and gas flow (Ar/H_2) were investigated. The quality of graphene is examined through Raman analysis, UV-VIS spectroscopy and microscopic studies (AFM, SEM…). SERS applications of the PLD-based graphene layer have also been demonstrated. Our method provides a new route to produce large scale graphene with good crystalline quality and good electrical properties, which is an important step for future applications.

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Coatings for Use at High Temperature
Room: San Diego - Session A2-1

Thermal and Environmental Barrier Coatings
Moderator: R. Trice, Purdue University, D. Litton, Pratt & Whitney, V. Maurel, Mines-ParisTech, France

8:00am **A2-1-1 Columnar Thermal Barrier Coatings (TBCs) by PS-PVD**, ***R. Vassen*** *(r.vassen@fz-juelich.de), G. Mauer, S. Rezanka,* Forschungszentrum Jülich GmbH, Germany **INVITED**

During the last years the Plasma Spray – Physical Vapor Deposition Process (PS-PVD) attracted a lot of interest due to its unique features. In this process plasma spraying is performed at reduced chamber pressures of 100 to 200 Pa. In combination with a high torch power a partial or complete vaporization of the used powderous feedstocks can be achieved. Correspondingly, the deposition mechanisms and the resulting coating microstructures differ from conventionally sprayed coatings. Thin and dense ceramic coatings can be obtained as well as columnar structured strain tolerant coatings with low thermal conductivity.

The paper will focus on strain tolerant zirconia based thermal barrier coatings. In contrast to the high roughness of bond coats used for atmospherically plasma sprayed TBCs the bond coating for the PS-PVD process has to be smooth to achieve sufficient bonding. In addition, the growth of the thermally grown oxide (TGO) on the bond coat as well as the growth rate of the TBC itself has to be adopted. For the optimized coatings excellent thermal cycling performance in burner rig facilities could be demonstrated. The coatings showed lifetime more than two times better than conventional APS TBCs. The reason for this excellent behavior will be discussed in detail.

Finally, an outlook for future applications of the flexible and powerful PS-PVD process especially in energy systems will be given.

8:40am **A2-1-3 PS-PVD - Deposition of Thermal Barrier Coatings**, ***M. Goral*** *(mgoral@prz.edu.pl), S. Kotowski, J. Sieniawski,* Rzeszów University of Technology, Poland

In the article the results of ceramic coating deposition by PS-PVD method will be presented. Plasma Spray Physical Vapour Deposition enables to obtain columnar structure of ceramic coatings (EB-PVD like). The Rene 80 nickel superallowy was used as a base material. The Zr-modified aluminide coating deposited by CVD method as well as MeCrAlY coating deposited by APS method were used as a bond coat. The LPPS-Thin Film system produced by Sulzer Metco on Research and Development Laboratory for Aerospace Materials was used for YSZ coting deposition. The Metco 6700 yttria-stabilized zirconia powder was used as a coating material. The 03CP plasma gun was used in research for ceramic powder evaporation. The power current, plasma gas flow and composition, pressure in process chamber, rotation speed of sample and powder feed rate were changed during experimental processes. The microstructural observation and chemical composition analysis was conducted using scanning electron microscope with EDS analyzer. The XRD phase analysis was conducted as well. The research showed that power current, pressure and powder feed rate had the stron influence on thickness, structure and composition of ceramic layer. The PS-PVD method is a alternative process for APS and EB-PVD technologies.

9:00am **A2-1-4 Development of Porous TBC Systems with Enhanced Durability using TriplexPro 210 Technology**, ***R. Dorfman***, *C. Dambra (Chris.Dambra@sulzer.com), J. Medrano, D. Chen, M. Nestler,* Sulzer Metco (US) Inc.

Over the last few years, there has been a great deal of R&D looking at alternative chemistries to traditional 7-8 wt% Yttria Stabilized Zirconium oxide (YSZ) coating systems. The main reason for this is that engine temperatures have been increasing and coating surface temperatures greater than 1200C for prolonged periods of time will result in: 1) accelerated phase destabilization, 2) increased surface sintering, and 3) cracking and spallation. However, many existing engines will see service temperatures that do not exceed 1200C. For these engines, legacy YSZ materials will still be used for cost reasons. This program has evaluated several different YSZ materials in developing a cost efficient, mechanically durable YSZ system using TriplexPro technology. Key areas studied include the effects of powder properties and spray paramters on coating microstructure and performance. This program also reviews application cost verses performance. Key testing included: 1) burner rig testing, 2) Furnace Cyclic Testing (FCT), 2) thermal Conductivity and 4) Metallographic analysis. Technical results showed that high purity agglomerated and sintered and/or HOSP YSZ powders can be manufactured and sprayed to produce poroous coatings with improved thermal cyclic performance.

9:20am **A2-1-5 Investigating CeO_2, TiO_2 Stabilized ZrO_2 for Application in Thermal Barrier Coatings (TBCs)**, ***C. Macauley*** *(cmacauley@umail.ucsb.edu),* University of California, Santa Barbara, *D. Lipkin,* General Electric (Global Research Center), US, *C. Levi,* University of California, Santa Barbara, US

As gas turbine operating temperatures are raised to reap the environmental and economic benefits of increased efficiency, the failure mechanisms that shorten the working life of TBCs are exacerbated and expanded. The current industry-standard TBC composition, yittria stabilized zirconia (YSZ), is inherently limited to reach the prospective goals of technology motivating the search for new compositions with improved capabilities. Zirconia co-doped with CeO_2 and TiO_2 has shown promise as an alternative 'next generation' TBC. Previous work showed a relatively large, non-transformable, single-phase tetragonal field stabilized at 1350°C . Compositions within this field have been manufactured into coatings by air-plasma spray. Phase and microstructural evolution of thermally sprayed freestanding TBCs upon isothermal aging are investigated as a function of time at 1316° C and 1427° C. Coating performance during thermal gradient tests and possible explanations for observed behavior will also be discussed.

9:40am **A2-1-6 Thermal Barrier Effect of Topcoats from Sintered Micro-sized Hollow Spherical Alumina Particles**, *R. Roussel*, ***V. Kolarik*** *(vladislav.kolarik@ict.fraunhofer.de), M. Juez-Lorenzo, H. Fietzek,* Fraunhofer ICT, Germany

Micro-sized spherical Al particles in the range of 1 to 20 µm, deposited according to the PARTICOAT concept (www.particoat.eu) as slurry by brushing or spraying on the surface of a Ni- or Fe-based alloy, oxidize at high temperatures 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. For investigating the thermal barrier effect of the topcoat, an experimental set-up using a radiation heater 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. Free standing samples of topcoats from sintered hollow alumina spheres, produced with Al particles in a size range of 1 to 20 µm, were prepared with various thicknesses. Samples from an industrial APS YSZ thermal barrier coating with the same thickness were used for comparison. Exposing 2 mm thick coatings to the heat radiation, the temperature of 850°C was measured on the exposed side. Without cooling, 300°C were measured on the backside for the hollow alumina particle based topcoat and 350°C for the commercial TBC. On both sides the temperatures remain without change until the end of the experiment after 3 h providing a stable temperature difference of 550°C and 500°C respectively. With airflow cooling, the backside temperature drops to 100°C with an exposed side temperature of 850°C for the hollow alumina particle based coating and to 120°C with an exposed side temperature of 880°C for the commercial YSZ. With a 300 µm thick alumina particle based topcoat a temperature difference of 356°C without and of 550°C with backside cooling was observed. The topcoat from sintered hollow alumina particles achieves a thermal barrier effect comparable to that of commercial YSZ and is capable to protect materials against temperature at low costs. Results from exposure experiments with coated IN738 and Alloy 321 confirm the impact of this novel coating system obtained by a heat treatment in one production step.

10:00am **A2-1-7 Multilayer Thermal Barrier Coatings: Interplay among coating design, processing and properties**, ***S. Sampath*** *(sanjay.sampath@stonybrook.edu),* Stony Brook University, *G. Dwivedi,* Stony Brook University, US, *V. Vishwanathan,* Stony Brook University, *Y. Chen,* Stony Brook University, US **INVITED**

The continued need for increments in gas turbine operating temperatures has necessitated developments in new thermal barrier materials and their processing. Of particular interest in recent years is the potential for Gadolinium Zirconate as a candidate TBCs to replace yttria stabilized zirconia. Gd_2Zr_2O7 in particular provide lower conductivity and resistant to environmental damage from ingested sand particles (categorized as CMAS for calcium magnesium alumino-silicate). Zirconates however, have several challenges including low fracture toughness, incompatibility with the thermally grown alumina and low erosion resistance. Multilayer concepts based on combinations of zirconia and zirconate have been developed to address the multifunctional requiremetns. This paper seeks advances in processing science and control for layer-by-layer optimization of coating

microstructure and properties so as to meet multifunctional obligations. The paper will demonstrate the advantages of plasma spray for such layered coating system along with identification of critical challenges.

10:40am **A2-1-9 Influence of Temperature on Phase Stability and Thermal Conductivity of Single- and Double-Ceramic-Layer EB-PVD TBC Top Coats consisting of 7YSZ, $Gd_2Zr_2O_7$ and $La_2Zr_2O_7$,** *K. Bobzin, N. Bagcivan, T. Brögelmann,* ***B. Yildirim*** *(yildirim@iot.rwth-aachen.de),* Surface Engineering Institute - RWTH Aachen University, Germany

More than 650 million tons per year of CO -emission is generated by air traffic. In order to meet the future demands like reducing the CO -emission and the fuel consumption of gas turbines, the increase of turbine inlet temperature (TET) is necessary. However, state-of-the-art coated superalloy materials might not stand a further increase of TET. Therefore the development of new top coats is necessary.

Yttria stabilized Zirconia (YSZ) is usually used as ceramic top coat for gas turbine parts of the first and the second stage of the gas turbine. Investigations have shown the accelerated phase transformation and the intensified sinter effects of the YSZ top coat at temperatures between 1,200 °C and 1,300 °C, leading to changes of microstructure. Such modifications of the microstructure lead to higher thermal stresses and consequently reduce the lifetime. Furthermore, thermal conductivity λ of the top coat increases. For this reason the pyrochlore zirconates lanthanum zirconate ($La_2Zr_2O_7$) and gadolinium zirconate ($Gd_2Zr_2O_7$) as top coat get into focus because of their promising material properties like both the phase stability up to their melting points and the lower thermal conductivity compared to YSZ.

Within this work single- (SCL) and double-ceramic-layer (DCL) top coats consisting of 7 wt. % yttria stabilized zirconia (7YSZ), $La_2Zr_2O_7$ or $Gd_2Zr_2O_7$ are deposited by means of Electron Beam-Physical Vapor Deposition (EB-PVD). Aim of this work is on the one hand the investigation of temperature-dependent phase behavior and change of thermal conductivity of SCL and DCL top coats. On the other hand the influence of different top coat materials and architectures on the growth of thermally grown oxide (TGO) between top coat and substrate is of key interest. In a first step morphology and coating thickness are determined using scanning electron microscopy (SEM). The SCL and DCL systems show a columnar microstructure with a coating thickness of about 150 µm. In a second step thermal conductivity of SCL and DCL systems is measured between 800 °C and 1,300 °C by means of laser flash technique. The third step is high-temperature X-ray diffraction measurements of SCL and DCL systems during heating and cooling between 800 °C and 1,300 °C at atmosphere. Finally, the TGO at the interface between top coat system and substrate is analyzed. Thickness of the TGO is determined by means of SEM, composition using chemical analysis and phases using X-ray diffraction. Thus, a correlation between morphology, architecture, coating material and the thickness of the TGO can give information about oxygen diffusion processes.

11:00am **A2-1-10 Experimental Determination of Mode II Fracture Toughness of TBC's**, *B. Zhang, S.J. Lockyer-Bratton, J. ElAwady,* ***K.J. Hemker*** *(hemker@jhu.edu),* Johns Hopkins University, US **INVITED**

Modern thermal and environmental protection systems have multiple layers and functionalities, and important phenomena governing the life of these systems occur in each layer and especially at the interfaces between the layers. Mechanical characterization of the ceramic topcoat is complicated by its brittle nature. Micro-scale bending experiments provide direct routes for characterizing the elastic response of EBPVD 7YSZ topcoats and for quantifying delamination toughness . A new experimental technique for measuring mode II delamination toughness, the compression edge delamination test, will also be presented, and results for commercial thermal barrier coatings for turbine engines will be presented. The insight gained in these experiments will be interpreted in context of the need for hierarchical models of layered protections systems.

Hard Coatings and Vapor Deposition Technology
Room: Royal Palm 4-6 - Session B1-3

PVD Coatings and Technologies

Moderator: S. Fairchild, Air Force Research Laboratory, J.H. Huang, Department of Engineering and System Science National Tsing Hua University, S. Weißmantel, University of Applied Sciences Mittweida

8:00am **B1-3-1 The Influence of Different Si-Contents of TiAlSiN PVD-Coatings on Mechanical and Tribological Properties at Elevated Temperatures**, ***T. Sprute*** *(tobias.sprute@tu-dortmund.de), W. Tillmann, F. Hoffmann,* Technische Universität Dortmund, Germany, *Y.Y. Chang,* National Formosa University, Taiwan, Republic of China, *Y.Y. Liou,* Mingdao University, Taiwan, Republic of China

TiN and CrN based binary or ternary layers have been used for many years in order to extend the service life of tools for machining. Increasing demands in the industrial use require more efficient layer systems. According to recent studies, silicon opened promising opportunities to influence the characteristics of thin titanium or chromium-based coatings for the better. So nanocomposites as TiAlSiN have an extremely high hardness and a fine grain structure . Furthermore, by the addition of silicon, the oxidation resistance as well as the tribological properties can be increased and improved.

Since these coatings are exposed to high temperatures used in machining processes, the influence of different silicon contents of the Ti/TiN/TiAlSiN multilayer system on mechanical and tribological behavior should be investigated at room temperature and elevated temperatures. In order to adjust different coating compositions and thus modify different silicon contents, various production parameters were systematically varied and tested their effects in detail . Within these studies, the hot working steel AISI H11 was used as the substrate . This steel substrate was previously plasma nitrided to raise the hardness and hence the supporting effect of the substrate opposite to the coating. The structure, the morphology and the different chemical compositions of the silicon-doped coating were investigated by means of scanning electron microscopy with additional device for energy dispersive X-ray spectroscopy. Scratch tests were also performed in order to characterize the quality of the adhesion between the substrate and the multilayer system. The mechanical and tribological properties such as hardness, Young´s modulus, friction and wear coefficient, which were determined using nanoindentation and ball-on-disk tests, as well as the thermal fatigue behavior, which was analyzed by means of an impact tester, were examined at elevated temperatures up to 500°C.

8:20am **B1-3-2 Compositional, Structural and Mechanical Evolution of Reactively and Non-reactively Sputtered Zr-Al-N Thin Films**, ***P.H. Mayrhofer*** *(paul.mayrhofer@tuwien.ac.at),* Vienna University of Technology, Austria, *D. Sonnleitner,* Montanuniversität Leoben, Austria, *J. Paulitsch,* Vienna University of Technology and and Montanuniversität Leoben, Austria, *D. Holec,* Montanuniversität Leoben, Austria

The compositional and structural evolution of $Zr_{1-x}Al_xN$ thin films as a function of the N_2-to-total pressure ratio (p_{N2}/p_T) during reactive magnetron sputtering is investigated in detail and compared with non-reactively prepared films. We therefore used powder-metallurgically (PM) prepared $Zr_{0.7}Al_{0.3}$, $Zr_{0.6}Al_{0.4}$ and $ZrN_{0.6}AlN_{0.4}$ targets (Plansee). Reactive sputtering was conducted with p_{N2}/p_T of 12, 25 and 50%. Based on these studies we can show that the Al incorporation to the prepared films as well as their crystalline structure is highly dominated by the N_2-to-total pressure ratio used. These findings are correlated with the resulting film structure, chemical composition, morphology and mechanical properties. For the coatings deposited with p_{N2}/p_T=12% a well-defined cubic (c) structure is obtained with high hardness values of 28-32 GPa . Annealing treatments lead to recovery effects and decomposition related processes of their super-saturated c-$Zr_{1-x}Al_xN$ phases. The hardness of the coating prepared from the $Zr_{0.7}Al_{0.3}$ target with p_{N2}/p_T=12% increases from ~32 to ~35 GPa upon annealing to 1100 °C . After annealing at 1500 °C the coatings are composed of their stable constituents c-ZrN and wurtzite structure w-AlN. When the coatings are prepared with higher N_2-to-total pressure ratios (e.g., p_{N2}/p_T=25 and 50%) their structure becomes nanocrystalline, most likely due to the competitive growth of cubic, hexagonal and amorphous phases, as suggested by X-ray diffraction (XRD). Due to the smaller supersaturated cubic phase content (as compared to the coating prepared with p_{N2}/p_T=12%), their hardness is only ~20 GPa. Annealing of these coatings leads to no significant changes in structure or hardness up to T_a ~1100 °C. This is supported by DSC, exhibiting only at temperatures above 1100 °C pronounced reactions, which are also connected with a pronounced N_2-release. Preparing the films non-reactively from $ZrN_{0.6}AlN_{0.4}$ targets lead to

well-defined crystalline single-phase c-$Zr_{0.68}Al_{0.32}N$ coatings with hardnesses of ~32 GPa. The hardness slightly increases to ~33 GPa for annealing at temperatures to 1200 °C. Up to this temperature no formation of w-AlN can be detected by XRD. The study highlights the importance of the particle energy delivered to the growing film material to prepare well-crystalline coatings with high thermal stability.

8:40am **B1-3-3 Mechanical and Antimicrobial Characteristics in Zr-based Thin Film Metallic Glasses at Various Processing Temperature**, ***J.H. Chu***, *H.W. Chen, J.G. Duh (jgd@mx.nthu.edu.tw)*, National Tsing Hua University, Taiwan, Republic of China, *J.-W. Lee*, Ming Chi University of Technology, Taiwan, Republic of China, *J.S.C. Jang*, National Central University, Taiwan, Republic of China

This study aims to investigate the effects of various deposition temperature on antimicrobial and mechanical properties in Zr-based thin film metallic glass (TFMG) fabricated by magnetron sputtering. The crystallography and chemical composition are analyzed by grazing incidence X-ray diffractometer (GIXRD) and electron probe micro-analyzer (EPMA), respectively. The microstructural features are observed through scanning electron microscope (SEM) and transition electron microscope (TEM). Enhanced hardness and modulus with temperature measured by nanoindentation are attributed to the shortening of average atomic distance and the increase of the short range ordered clusters. The antimicrobial performance of specimens is tested through inoculation and liquid culture methods. Antimicrobial activity is evaluated by copper ions released as well as plate count methods used against *Escherichia coli* and *Staphylococcus aureus.* The results show that the surface of 304 stainless steel substrate can be modified with deposited ZrCuNiAlSi TFMG, and their improved antimicrobial efficacy against those bacteria is attributed to their amorphous nature, hydrophobic properties and released copper ions. The TFMG developed in this study with adequate hardness and antimicrobial abilities can be used as a promising candidate to improve the surface properties of the medical appliances and also to reduce the possibility of nosocomial infection.

9:00am **B1-3-4 Incorporation of Nano-crystalline TiB_2 Layers in Zr-Cu-Ni-Al Thin Film Metallic Glasses for Improved Anti-wear Characteristics**, ***Y.C. Chan***, *H.W. Chen, J.G. Duh (jgd@mx.nthu.edu.tw)*, National Tsing Hua University, Taiwan, Republic of China, *J.-W. Lee*, Ming Chi University of Technology, Taiwan, Republic of China

To suppress the strain localization, inhomogeneous plastic deformation and brittle nature in thin film metallic glasses (TFMGs) is becoming highly valued. Accordingly, the current study attempts to provide a new strategy to attack this tough issue. Quaternary Zr-Cu-Ni-Al TFMGs/TiB_2 multilayer coatings with specially designed bilayer periods are deposited on silicon wafers and tool steels by r.f. reactive magnetron sputtering. Intrinsic hardness of multilayers obtained from nano-indenter is much higher than the average value calculated by rule-of-mixture. The SEM images of indents clearly verify that the shear bands are significantly distorted with incorporation of nano-crystalline TiB_2 layers. The multilayer configuration also shows a significant enhancement in tribological performance, as evaluated by nano-scratch and ball-on-disc tests. The improved mechanical properties mainly result from structure barrier effect and Hall-Petch relation, which effectively restrict the mutual propagation of shear bands and dislocations. Further microstructure and texture characterizations by TEM and corresponding dark-field images reveal the dependence for the thickness of TiB_2 layers on such a unique strengthening mechanism.

9:20am **B1-3-5 Corrosion Resistance of Amorphous, Nanocomposite, and Nanocrystalline Cr-C Films Deposited by Magnetron Sputtering**, ***K. Nygren*** *(kristian.nygren@kemi.uu.se), M. Andersson, J. Högström, W. Fredriksson, K. Edström, L. Nyholm, U. Jansson*, Uppsala University, Sweden

Crystalline chromium carbide (Cr-C) thin films are known to possess excellent corrosion resistance in acidic and saline media. Growth of crystalline Cr-C by sputtering typically requires a substrate temperature above 500 °C, which prevents hardened steels and other temperature-sensitive substrates from being coated without adversities. We have observed that sputtered low-temperature films can be described as an amorphous nanocomposite with two non-crystalline phases: amorphous CrC_x and amorphous carbon (a-C). One interesting feature of amorphous Cr-C is the lack of grain boundaries which would eliminate grain boundary corrosion. On the other hand, large stable crystallites mean that corrosive attacks need to overcome a high energy threshold. The absence of carbide grains in amorphous films may therefore lower the overall corrosion resistance. The objective of this study is to investigate the influence of the deposition temperature and the composition on the microstructure of Cr-C films, as well as their corrosion resistance.

Cr-C thin films with 25-85 at% C were deposited at 20-700 °C by direct current magnetron sputtering from elemental targets under UHV conditions. XRD and TEM show that films deposited at 20–300 °C are amorphous. An increase of the temperature to 500 °C leads to a transformation from amorphous to nanocrystalline Cr_7C_3 or nanocomposite Cr-C/a-C films depending on composition. XPS shows that the amorphous CrC_x phase has a composition close to crystalline Cr_7C_3. There is no shift in the C1s core level binding energy between amorphous and crystalline Cr_7C_3 films, which indicates a similar short-range chemical order. XRD reflections from Cr_3C_2 were observed at 700 °C and this phase was accompanied by a positive shift in the C1s spectra. The corrosion resistance has been investigated by polarization curves, chronoamperometry, XPS, and SEM. The amorphous films are less oxidation resistant than the more crystalline films. Generally, higher deposition temperature results in lower accumulated charge in chronoamperometry. Films deposited at 500 °C have a 50% reduction in charge when compared to films deposited at 20 °C, and post-corrosion XPS shows a similar trend in the amount of surface oxides. More a-C phase also lowers the corrosion current. Raman spectroscopy shows that the hybridization of the a-C phase is predominantly sp^2, which contribute to a relatively low hardness around 7-10 GPa. Reactively sputtered nanocomposite films have previously been shown to yield a low coefficient of friction (0.13), which suggests that the studied films are candidates to enhance properties of steel in combined corrosive and tribological environments.

9:40am **B1-3-6 Corrosion Resistance and Tribological Properties of CrN, CrN/SiC, and CrN/DLC Coatings Grown by Cccelerated Plasma Arc Deposition**, ***D. Bell***, Phygen Coatings, Inc., US, *C. Mulligan (christopher.p.mulligan.civ@mail.mil), M. Senick*, US Army ARDEC, Benet Laboratories, US, *V. Khominich, Z. Gay*, Phygen Coatings, Inc., US

CrN monolayers along with CrN/SiC and CrN/DLC duplex layers up to 5 μm thick were grown by accelerated plasma arc deposition on 4340 steel substrates. The layers exhibit a dense and defect free microstructure. The tribological properties were evaluated with dry ball-on-disk sliding tests against an alumina counterface at room temperature. The CrN monolayer exhibits a coefficient of friction, $\mu = 0.28$, while CrN/SiC and CrN/DLC duplex exhibit much lower $\mu = 0.08$ and 0.06, respectively. The low friction is attributed to the top layers of amorphous SiC and DLC, respectively. The wear rates of the coatings were very low and measured as $5.3x10^{-7}$, $7.3x10^{-7}$, and $7.9x10^{-7}$ mm^3/Nm, respectively, for CrN, CrN/DLC, and CrN/SiC. Corrosion resistance was evaluated in both cyclical environmental testing as well as quantitatively via potentiodynamic corrosion tests in sodium chloride solution. The corrosion resistance in both cases is compared to standard electroless Ni and electroplated Cr coatings. The highest level of corrosion resistance was observed for the CrN monolayer and CrN/SiC duplex layer. Both exhibit improved corrosion resistance over electroplated Cr coatings and comparable corrosion resistance to electroless Ni coatings. This high level of corrosion resistance is remarkable for physical vapor deposited thin nitride layers. The accelerated plasma arc deposited materials show great promise for applications in which a combination of low friction, wear resistance, as well as corrosion resistance are required.

10:00am **B1-3-7 Comparative Study of Transition Metal Boronitride Hard Coatings Fabricated by Reactive Magnetron Sputtering Process**, ***J.-W. Lee*** *(jefflee@mail.mcut.edu.tw), L.W. Ho*, Ming Chi University of Technology, Taiwan, Republic of China, *W.S. Lai, C.J. Wang*, National Taiwan University of Science and Technology, Taiwan, Republic of China

INVITED

The boron containing transition metal nitride hard coatings have been studied by researchers and applied in industries intensively due to their high hardness, good wear, corrosion and oxidation resistance. In this work, the ternary and quaternary Cr-B-N, Cr-Ti-B-N, Ti-Cr-B-N and Ti-Zr-B-N coatings were co-deposited by magnetron sputtering of Cr plus CrB_2, Cr plus TiB_2, Ti plus CrB_2 and Ti plus ZrB_2 targets, respectively, in a reactively gaseous mixture. Comparative studies on microstructure, mechanical, adhesion, tribological properties and corrosion resistance of Cr-B-N, Cr-Ti-B-N, Ti-Cr-B-N, and Ti-Zr-B-N coatings with various Cr, Ti, Zr and B contents were conducted. The structure and phase composition of coatings were determined by X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR). The mechanical properties of the coatings were measured using nanoindentation, HRC-DB and scratch tests. The tribological properties were evaluated in air using conventional ball-on-disc tribometer. The electrochemical tests were performed in 3.5 wt.% NaCl medium. The maximum hardness reaching ~34 GPa was found for the Ti-Cr-B-N and Ti-Zr-B-N coatings. The nanocomposite structured transition metal boronitride coatings showed a better corrosion resistance than that of the coatings with columnar structures. The effects of boron and transition

metal contents on the hardness, microstructure and phase evolution of quaternary transition metal boronitride coatings were also discussed.

10:40am **B1-3-9 Using Filtered Vacuum-arc Plasma for PIII&D Process of Ti-Al-Y-N Coatings and their Abrasive and Cavitation Resistance**, *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

Deposition from the filtered vacuum arc plasma is the widely used effective method of manufacturing high quality protective wear resistant coatings. Ti-Al-Y-N coatings with small Y percentage have demonstrated high hardness and excellent oxidation resistance which provides their application for protection the machine parts which operate under extreme environmental conditions. In our recent work [1] we investigated structure and properties of such coatings prepared by the plasma immersion ion implantation and deposition (PIII&D) using filtered vacuum-arc plasma source.

A high-voltage pulsed bias applied to the substrate permits the deposition of thicker coatings with good adhesion and low residual stresses. I n the present work we examined the cavitation and abrasion resistance of PIII&D deposited Ti-Al-Y-N coatings doped with yttrium (≤ 1 at.%) and analyzed correlation between their properties and structure.

$Ti_{0.5-x}Al_{0.5}Y_x$ alloys (x = 0, 0.002, 0.004, 0.01) produced by vacuum-arc remelting were used as cathodes in the vacuum-arc plasma source. Ti-Al-Y-N coatings with thickness of 5-6 micron were deposited on the 302 stainless steel substrates from filtered vacuum-arc plasma at nitrogen pressure of 0.1 Pa.

The substrate potential was either DC (-150 V) or negative pulsed, the amplitude A_U varied in the range of 0-2.5 kV.

The erosion resistance of the coatings was evaluated on the measured mass loss during cavitation treatment in distilled water. The tests were continued until visually watched open-ended pores in the coating were formed. Abrasion wear was determined in the scheme substrate plane – rotating abrasion disk. Adhesion properties, friction coefficient and wear resistance were determined using equipment by CSM Instruments.

The substrate potential during deposition process and Y content in the coatings were found to be important factors influencing the rate and character of their cavitation damage. The coating deposited at A_U=0 was subjected to pitting erosion. Long cracks prevailed on the surface of the cavitation treated coating deposited at DC (-150 V) potential. High voltage pulsed substrate potential contributed to decrease by 3-5 times in the rate of the mass loss under cavitation, quantity of the erosion defects on the treated surface diminishes sharply. Increase of Y content resulted in improvement of wear durability. Mean rates of cavitation and abrasion wear of (Ti,Al)N+1at.%Y were several times lower than that of (Ti,Al)N and TiN.

[1] V.A. Belous et al. Surf. Coat. Technol. 206 (2011) 1720.

11:00am **B1-3-10 Nanocomposite Mo-Ag-N Self-lubricating Hard Coatings Fabricated by Magnetron Sputtering**, ***J.F. Yang*** *(jfyang@issp.ac.cn)*, Institute of Solid State Physics, Chinese Academy of Sciences, China

Mo-Ag-N nanocomposite coatings were prepared by d.c. magnetron sputtering technique from a Mo target with embedded Ag pellets onto Si substrates, followed by vacuum annealing at temperature of 425, 500, and 600 ºC for 1hour. SEM, EDS, XRD, nanoindenter, and micro-macro tribometer were used to investigate the influence of Ag content and annealing temperature on microstructure, surface morphology and mechanical properties. As-deposited Mo-Ag-N coatings consisted of fcc γ-Mo_2N phase and fcc Ag phase where Ag uniformly distributed into Mo-N matrix. The hardness of Mo-Ag-N coatings initially increased to maximum value of 32 GPa for coatings containing 6 at.% Ag and then decreased with the further increase of Ag, whereas friction coefficient decreased monotonously with the increase of Ag content. With the increase of annealing temperature hardness, friction coefficient, and wear resistance decreased due to accumulation of a large amount of Ag particles or agglomerations onto surface resulted from high temperature intriguing phase segregation or diffusion.

Hard Coatings and Vapor Deposition Technology
Room: Royal Palm 1-3 - Session B6-1

Coating Design and Architectures
Moderator: R. Daniel, Montanuniversität Leoben, M. Stüber, Karlsruhe Institute of Technology

8:00am **B6-1-1 Flakey Stuff: Pushing the Limits of Engineering Coatings with Layered Atomic Structures**, ***C. Muratore*** *(cmuratore1@udayton.edu)*, Air Force Research Laboratory, Materials and Manufacturing Directorate, Nanoelectronic Materials Branch, US, *S.M. Aouadi*, Southern Illinois University, US, *J.J. Hu*, UDRI/Air Force Research Laboratory, Materials and Manufacturing Directorate, Nanoelectronic Materials Branch, US, *A. Voevodin*, Air Force Research Laboratory, Materials and Manufacturing Directorate, Nanoelectronic Materials Branch, US **INVITED**

For over 70 years, the sensitivity of solid lubricant materials to extreme ambient environments has limited aerospace capability. Solutions to this problem have taken decades to emerge because there is such a big difference between the operating environment in which the material needs to perform (e.g., at high temperature in air) and the environment in which structural and compositional analysis is conducted (e.g., ultra high vacuum at room temperature). I will talk about novel *in situ* techniques to examine the mechanical response of contact interfaces in extreme environments , and show how we have used these techniques to develop environmentally adaptive materials to overcome decades-old aerospace challenges. In the course of designing these materials, we have integrated features such as temperature-actuated self-healing and integrated wear sensors for automatic structural health monitoring. These features are built upon basic principles of thin film design. For example, all lubricant coating materials we have developed are nanocomposites. For the temperature-adaptive materials, a hard matrix surrounds nanoinclusions of the active lubricant materials to maximize crack resistance and hardness. The phases comprising these nanoinclusions, and their geometry and concentration are selected based on modeling results, so that complex phases providing low shear at specific temperatures are present in the friction contact. The thermal conductivity of the materials also adapts with temperature by almost an order of magnitude for an added measure of thermal protection for the substrate. Multilayers are also used to selectively inhibit or guide diffusion-based self-healing or lubricant delivery mechanisms. These diffusion barriers can give the coatings additional multifunctionality, such as wear sensing capability, where rare-earth dopants displaying distinctive luminescence spectra are integrated into the material to provide a high-intensity light-actuated response indicating the lifetime of the solid lubricant coating. All of these mechanisms can be combined in a single coating material to protect components from friction, wear and extreme temperatures over multiple environmental cycles with automatic health monitoring.

8:40am **B6-1-3** ***Ab Initio*** **and Experimental Study on the Effect of Si Additives on the Phase Stability of γ - and α-Al_2O_3**, ***F. Nahif*** *(nahif@mch.rwth-aachen.de)*, *D. Music, S. Mráz, M. to Baben, J. Schneider*, RWTH Aachen University, Germany

Using density functional theory and filtered cathodic arc deposition experiments the effect of Si addition on the stability and electronic structure of γ- and α-Al_2O_3 has been investigated. The concentration range from 0 to 5 at.-% was probed and the additives were positioned at different substitutional sites in the γ-phase. The calculations for $(Al,Si)_2O_3$ predict a trend towards spontaneous decomposition into α-/γ-Al_2O_3 and SiO_2. Therefore, the formation of the metastable γ-$(Al,Si)_2O_3$ phase can only be expected during non-equilibrium processing where the decomposition is kinetically hindered. The Si induced changes in stability of the metastable solid solution may be understood based on the electronic structure. Si additions clearly shift the relative stability towards the γ-phase which can be understood based on strong silicon-oxygen bonds in γ-$(Al,Si)_2O_3$. These predictions were critically appraised by diffraction experiments of as deposited and annealed Si-Al-O coatings deposited by filtered cathodic arc. The effect of Si additives on the amorphous to γ- and the γ- to α-phase transition temperatures was determined. It was found that the addition of Si significantly increases the amorphous to γ- and the γ- to α-transition temperatures in comparison to unalloyed Al_2O_3.

9:00am **B6-1-4 A Combinatorial Approach to the Synthesis of Cr-Zr Oxynitride Thin Films by Reactive r.f. Magnetron Sputter Deposition**, ***S. Spitz***, *M. Stüber (michael.stueber@kit.edu), H. Leiste, S. Ulrich*, Karlsruhe Institute of Technology, Germany

Cr-Zr-O-N thin films were deposited by reactive r.f. magnetron sputtering at 500 °C substrate temperature onto cemented carbide and silicon substrates. The depositions were realised by an experimental combinatorial

approach: the samples were placed in a row below a segmented Cr-Zr target so that the coatings exhibit different elemental compositions (from Cr-rich to Zr-rich according to the position in relation to the target) and constitution. In order to investigate the influence of oxygen and nitrogen contents on the films' structure, constitution and properties the O_2/N_2 gas flow ratios as well as the total reactive gas flows were varied systematically. The coatings were thoroughly characterised by electron probe micro analysis (EPMA), X-ray diffraction (XRD), transmission electron microscopy (TEM) and by microindentation.

A single-phase corundum-type structure was observed for Cr-rich coatings. The coatings` hardness could be increased up to 23.5 GPa by increasing the nitrogen flow while keeping the Ar and O_2 flows constant (i.e. total pressure increase). Up to 5.2 at% nitrogen could be incorporated in these corundum-type coatings. By keeping the total pressure constant and varying the O_2/N_2 flow ratio, the increase in hardness was moderate; however, the deposition rate could be doubled. Up to 1.9 at% nitrogen could be incorporated into corundum type films. The conditions for the growth of single-phase corundum-type Cr-Zr-O-N coatings will be discussed in detail.

Furthermore, results of the Zr-rich coatings will be presented: a change in the microstructure with increasing N_2 flow (to single-phase cubic or tetragonal structures) and hardness values up to 20 Gpa could be observed.

9:20am **B6-1-5 Protective Coatings for Aerospace Applications: From Materials Architecture to Coating Removal**, ***J.E. Klemberg-Sapieha*** *(jsapieha@polymtl.ca)*, École Polytechnique de Montreal, Canada **INVITED**

Material damage caused by solid particle erosion remains a crucial problem in aeronautical engines. Different wear phenomena occur in various parts of the jet engine such as gas turbine components, compressor section, heat exchangers, pumps and piping systems. Good understanding of materials deterioration allows one to develop appropriate strategies to protect technologically relevant metal substrate materials. Advanced erosion-resistant coatings, ERC, call for an "ideal" combination of the mechanical elasto-plastic, tribological, corrosion, thermal and other characteristics that can only be satisfied by using specifically tailored coating architectures considering nanocomposite, nanolaminate, multilayer and graded layer systems.

In the first part of this presentation, we demonstrate that finite element modeling of the coating architecture, combined with the tailored mechanical properties of individual materials of the coating systems including appropriate stress management, opens new opportunities as a predictive tool for high performance ERCs. We then introduce and discuss the selection rules describing the overall film behaviour with respect to their microstructure and their basic elasto-plastic properties, namely their hardness, *H*, Young's modulus, *E*, elastic strain-to-failure, resilience, and resistance to plastic deformation, expressed, respectively, by the H/E, H^2/E, and H^3/E^2 ratios.

After many hours in service, certain areas of the ERCs may begin to deteriorate. Since the components of engine are generally very costly, it is desirable to remove the original coating, repair the parts if necessary, and then apply a new coating. In response to these needs, in the second part of this presentation, we will describe new processes for removing damaged ERCs including dry and wet chemical etching. Preliminary results will be discussed in relation to the technological, economic and environmental context in the field of surface engineering solutions for aerospace industry.

10:00am **B6-1-7 Transformation Toughening as Applied to Coatings**, *C. Wang*, Northwestern Polytechnical University, China, *J. Han*, Northwestern University, US, *J. Pureza*, Universidade do Estado de Santa Catarina, Brazil, ***Y.W. Chung*** *(ywchung@northwestern.edu)*, Northwestern University, US

The objective of this research is to explore new ways to synthesize hard and tough materials. In this work, we synthesized multilayer coatings consisting of alternating nanolayers of TiB_2 and $FeMn_x$. Nanocrystalline TiB_2 is hard but also quite brittle. At sufficiently large values of x, $FeMn_x$ has a metastable fcc structure at room temperature. In the presence of a microcrack, the stress field due to the microcrack can cause a phase transformation of $FeMn_x$ from fcc to bcc, resulting in a volume expansion and consequent arresting of the propagating crack. This phenomenon was explored by synthesizing TiB_2/ $FeMn_x$ multilayer coatings using a dc magnetron sputter-deposition system. Using x-ray diffraction, we proved that $FeMn_{0.35}$ films acquire the metastable FCC structure at room temperature. We used the method developed by Xia, Curtin, and Sheldon[1] to measure the fracture toughness of TiB_2/ $FeMn_{0.35}$ and TiB_2/Fe multilayer coatings. These measurements showed that replacement of bcc-Fe by fcc-$FeMn_{0.35}$ increases the fracture toughness by roughly a factor of two, thus substantiating the concept of using phase transformation for the toughening of hard coatings.

[1]Z. Xia, W. A. Curtin, B. W. Sheldon, Acta Materialia 52, 3507-3517 (2004)

10:20am **B6-1-8 Limits to the Preparation of Super- and Ultrahard Nanocomposites**, ***S. Veprek*** *(stan.veprek@lrz.tum.de)*, *M.G.J. Veprek-Heijman*, Technical University Munich, Germany

We shall discuss the conditions needed for achieving hardness in excess of 50 or even 80 to $\geq$ 100 GPa in nc-TiN/a-Si_3N_4 and related nanocomposites with high elastic limit, and high oxidation resistance at elevated temperatures. It will be shown that achieving such properties may be limited by several constraints, such as lack of long-term stability of quasi-ternary nc-TiN/a-Si_3N_4/$TiSi_2$ nanocomposites, too low deposition temperature and impurities, which hinder the diffusion and formation of strong nanostructure in the quasi-binary, long-term stable nc-TiN/a-Si_3N_4 system. Moreover, achieving super- and ultrahardness in other nc-TmN/a-Si_3N_4 nanocomposites (Tm=transition metal) can be further limited by absence of spinodal mechanism of the decomposition of the Tm-Si-N solid solution.

10:40am **B6-1-9 A Study of TiAl - powder Metallurgical Target Behaviour in Direct Current and High Power Impulse Magnetron Sputtering PVD Processes**, ***S. Kolozsvari*** *(szilard.kolozsvari@plansee.com)*, *P. Polcik*, PLANSEE Composite Materials GmbH, Germany

Aluminum-based coatings produced by means of physical vapour deposition (PVD) that provide improved functionality on machine tools are well investigated. There are many studies dealing with the characterization of these TiAl- or AlCr-based high wear and oxidation-resistant thin films, deposited by both magnetron sputtering and cathodic arc-evaporation. Quality and cost optimization issues in machining drive the need to improve coating properties by, for example, alloying transition metals to standard compositions, as well as to develop targets with longer life time. In the present work we concentrate on the manufacturing of high performance sputtering targets and the relationship to the coatings produced by them. Two different target types - segmented and powder metallurgical - and thus two different manufacturing processes are compared. The performance of these will be examined using direct current (d.c.) and high power impulse magnetrons sputtering processes (HiPIMS) with the aim to achieve a defined TiAlN coating. The mechanical properties of the coatings - hardness, elastic modulus, adhesion, crystal orientation and chemical composition – will be examined with respect to the physical behaviour of the targets, e.g., voltage/current characteristics as the targets erode. These characteristics will be examined for a range of operating parameters (bias voltage, gas ratios, etc.) as well as at different power densities. The connection between coating quality, manufacturing costs and target functionality will always be a critical concern to those in the industry. The selection of a proper target and quality allows the coating manufacturer to decrease costs while simultaneously increasing the target and coating performance.

11:00am **B6-1-10 The Effect of Droplets in Arc Evaporated Hard Coatings on the Wear Behavior**, ***M. Tkadletz*** *(michael.tkadletz@mcl.at)*, Materials Center Leoben Forschung GmbH, Austria, *C. Mitterer*, Montanuniversität Leoben, Austria, *B. Sartory*, Materials Center Leoben Forschung GmbH, Austria, *C. Michotte*, CERATIZIT Luxembourg S.àr.l., Luxembourg

Hard coatings deposited by cathodic arc evaporation are often characterized by droplets, affecting their surface roughness and oxidation resistance. Within this work, the mechanical damage imposed by these droplets on the coating was investigated for dry sliding contacts. Ball-on-disk tests were done on TiAlN based coated cemented carbide discs at room temperature and 700°C. Surface as well as cross-sections of the wear tracks were investigated by scanning electron microscopy and focused ion beam (FIB) techniques. In wear tracks on areas without droplets, only evidence for mild abrasive wear of the coating could be found. The effects caused by droplets were examined by conventional FIB cuts as well as cut and slice techniques, energy dispersive X-ray spectroscopy mappings and transmission electron microscopy. While the area above these droplets is gradually worn away, tensile cracks are formed on the coating surface, tangentially surrounding the droplet in the area opposite to the sliding direction. In contrast, shear cracks are found in sliding direction, initiating at the droplet and propagating into the coating.

11:20am **B6-1-11 In-situ Micro-fracture-test Investigations in the Influence of Structure and Phase Transformation of CrN/AlN Multilayer Coatings**, ***M. Schloegl*** *(manfred.schloegl@tuwien.ac.at),* Montanuniversität Leoben and Vienna university of Technology, Austria, *J. Paulitsch,* Vienna University of Technology, Austria, *J. Keckes, C. Kirchlechner, M.J. Chordill,* Montanuniversität Leoben, Austria, *P.H. Mayrhofer,* Vienna University of Technology, Austria

Ceramic-like coatings are widely used for various industrial applications because of their outstanding properties like high thermal stability, oxidation resistance and abrasion resistance. However, the brittleness of such ceramic coatings often negatively influences their performance especially when used in conditions with an increased need for crack resistance. Therefore, this work is devoted to the study on fracture mechanisms of CrN based thin films with the aid of in-situ scanning electron microscopy (SEM) microbending, microcompression and microtension tests. The small test-specimens are prepared by focused ion beam milling. As generally monolithic coatings with their columnar structure provide low resistance against crack formation and propagation we perform our studies for CrN thin films and CrN/AlN multilayers. The latter offer alternating elastic constants and additional interfaces influencing crack propagation. Adjusting the AlN layer-thicknesses to ~3 and ~10 nm allows studying the impact of a cubic stabilized c-AlN layer and an AlN layer composed of cubic, amorphous and hexagonal fractions (for simplicity abbreviated with w-AlN) being sensitive to strain fields as suggested by ab initio calculations. The microtests clearly demonstrate that the monolithically grown CrN as well as the CrN/w-AlN multilayer coating with ~10 nm thin AlN layers (and hence a mixture of cubic, amorphous and hexagonal AlN phases) fail as soon as small cracks are initiated. Contrary, the CrN/c-AlN multilayer coatings composed of ~3 nm thin c-AlN layers are able to provide resistance against crack propagation. Hence, they allow for significantly higher loads during the tests. In-situ cross sectional scanning electron microscopy investigations during loading of our coatings clearly show the deflection of cracks within the CrN/c-AlN layers whereas no crack-deflection can be observed for the other coatings. Furthermore, in-situ micro-tensile-test investigations of coated polymer substrates exhibit the formation of a dense network of fine cracks within the CrN/c-AlN coatings. The other coatings exhibit fewer but more-open cracks. Consequently, the crack-propagation within the CrN/c-AlN coatings is more inhibited than within the CrN/w-AlN coatings. Additional studies on the structure and phase development of the CrN/c-AlN and CrN/w-AlN coatings ex-situ are conducted by HR-TEM studies. The study shows extensive in-situ fracture tests in a micro-scaled range providing necessary information on the fracture behavior of hard coatings.

Fundamentals and Technology of Multifunctional Thin Films: Towards Optoelectronic Device Applications
Room: Sunset - Session C2-1

Fundamentals of Thin Films towards Optoelectronics Devices
Moderator: T. Terasako, Graduate School of Science and Engineering, Ehime University, Japan, J.A. Zapien, City University of Hong Kong, Hong Kong Special Administrative Region of China

8:00am **C2-1-1 Carrier Transport and Photoluminescence Properties of Ga-Doped ZnO Films Grown by Ion-Plating and by Atmospheric-Pressure CVD**, ***T. Terasako*** *(terasako.tomoaki.mz@ehime-u.ac.jp), Y. Ogura, S. Fujimoto,* Graduate School of Science and Engineering, Ehime University, Japan, *H. Song, H. Makino,* Kochi University of Technology, Japan, *M. Yagi,* Kagawa National College of Technology, Japan, *S. Shirakata,* Graduate School of Science and Engineering, Ehime University, Japan, *T. Yamamoto,* Kochi University of Technology, Japan

Polycrystalline Ga-doped zinc oxide (GZO) films have high visible transmission compared with ITO (Sn-doped In_2O_3) films widely used for transparent electrodes in optoelectronic devices. We have had an issue to be resolved for GZO films: their electrical resistivity (ρ) is higher than that of ITO films. In this study, we have investigated what determines electrical properties of GZO films. In our previous work, for GZO films with carrier concentration (n) from 3×10^{18} to 1×10^{21}cm^{-3} deposited by ion plating with dc-arc discharge (IP), we reported that the grain boundary scattering mechanism plays a minor role in carrier transport. Temperature (T)-dependent Hall mobility (μ) measurements of the GZO films showed a continuous transition in dominant scattering mechanisms in intra grain from ionized impurity scattering mechanism (from non-degenerate ($3\times10^{18}<n<4\times10^{19}$cm^{-3}) to degenerate ($4\times10^{19}<n<3\times10^{20}$cm^{-3})) to thermal lattice vibration scattering mechanism ($n>3\times10^{20}$cm^{-3})) with increasing n.

In this study, to address routes toward better understanding of factors limiting carrier transport of GZO films, a comparison of effects of Ga-doping on electrical characteristics between GZO films deposited by IP (IP-GZO) and those grown by atmospheric-pressure CVD (AP-CVD GZO) has been made. 200-nm-thick IP-GZO films were deposited on glass substrates at a substrate temperature (T_S) of 200 ºC. GZO films with the thicknesses of 1-5 μm were prepared on r-plane sapphire substrates at T_S =550-750 °C by the AP-CVD using Zn, H_2O and $GaCl_3$.

T-dependent Hall-effect measurements showed that the dominant scattering mechanism in intra grain, which depends on n, of AP-CVD GZO is same as that of IP-GZO. Note that the gradient of T-μ curve ($\Delta\mu/\Delta T$) for AP-CVD GZO with $n=1\times10^{21}$cm^{-3} was a negative value of -0.045, which is about two times of that of IP-GZO with the same n.

PL measurements at 10 K for the AP-CVD GZO films revealed the shift of the dominant near-band-edge (NBE) emission from 3.368 eV at $n\sim2\times10^{18}$ cm^{-3} to 3.376 eV at $n=4.4\times10^{20}$ cm^{-3} accompanied with its asymmetric broadening. This behavior is probably due to a decrease in the exciton binding energy for Ga-related bound exciton line due to the screening of the Coulomb interaction caused by an increase in n. On the other hand, the dominant NBE emission of the IP-GZO film shifted from 3.347 eV at $n=3\times10^{18}$ cm^{-3} to 3.365 eV at $n=8\times10^{19}$ cm^{-3}. With further increasing n, it seems that the dominant NBE emission of IP-GZO approach that of AP-CVD GZO. We will discuss a comprehensive picture what caused the difference in the photon energy at any given n between IP-GZO and AP-CVD GZO.

8:20am **C2-1-2 Materials Smart Design of Wide Bandgap ZnO: Function Core**, ***T. Yamamoto*** *(yamamoto.tetsuya@kochi-tech.ac.jp), H. Makino, H. Song,* Kochi University of Technology, Japan **INVITED**

We propose a materials smart design of wide bandgap ZnO films with functional cores for their wide applications including optoelectronic devices such as flat display panels, thin film solar cells and short-wavelength light emitting diodes. Very recently, we reported a successful fabrication of 20-inch liquid crystal display (LCD) TVs mounted with indium-free Ga-doped-ZnO (GZO)-based common electrodes on RGBY(Red, Green, Blue, Yellow) color filters [1]. The most important feature of the LCD TVs is high luminosity compared with conventional LCD TVs utilizing ITO (Indium Tin Oxide)-based common electrodes. In addition, we have established flexible plastic substrates with low-resistivity GZO films for flexible electronics substrates [2]. In this work, we will discuss what a key ingredient in the recipe for success is. Nevertheless, the issue about the factors limiting carrier transport of polycrystalline n-type GZO films as well as Al-doped ZnO (AZO) is still open and is an object of theoretical and experimental investigations [3]. A resolution to the issue can provide us with a novel science & technology to achieve not only highly durable ZnO-based transparent conductive films but also p-type ZnO films. We will propose the materials smart design in terms of a codoping method introducing functional core into host materials to realize moisture resistant n-type ZnO for use in gas sensors and to achieve p-type ZnO [4].

[1] N. Yamamoto, H. Makino, S. Osone, A. Ujihara, T. Ito, H. Hokari, T. Maruyama and T. Yamamoto, Thin Solid Films, 520 (2012) pp. 4131–4138.

[2] K. Nagamoto, K. Kato, S. Naganawa, T. Kondo, Y. Sato, H. Makino, N. Yamamoto and T. Yamamoto, Thin Solid Films, 520 (2011) pp. 1411-1415.

[3] T. Yamamoto, H. Song, H. Makino and N. Yamamoto, ECS Transactions, 45 (2012) pp.401-410.

[4] T. Yamamoto, physica status solidi (a) 193, No.3 (2002) 423-433; Thin Solid Films, 420-421 (2002) 100-106; Jpn. J. Appl. Phys. Vol. 42 (2003) pp. L514-L516.

9:00am **C2-1-4 Electrical Properties of the ZnO Thin Films Grown on a-plane Sapphire Substrates using Catalytically Generated High-energy H_2O**, *N. Yamaguchi, T. Takeuchi, E. Nagatomi, T. Kato,* Nagaoka University of Technology, Japan, *H. Umemoto,* Shizuoka University, Japan, ***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. Although CVD methods has many advantages for industrial applications, deposition of high-quality ZnO thin films by conventional CVD methods consume a lot of electric power for the reaction of source gases and for increasing the substrate temperature. In order to save energy and resources, a more efficient reaction of the oxygen and metalorganic source gases during film growth is highly desired. In a previous paper, we reported a new growth method for preparing ZnO films by reacting dimethylzinc and high-energy H_2O generated from the Pt-catalyzed exothermic H_2 and O_2 reaction [1]. It was also reported that ZnO films with excellent crystallinity and optical properties, as well as large electron mobility (m_H) were grown on a-plane (11-20) sapphire (a-Al_2O_3) substrates. However, from the dependence of the

electrical properties on the film thickness, these ZnO films are considered to consist of an interfacial layer with a high defect density (degenerate layer), generated due to the large lattice mismatch between ZnO and Al_2O_3 substrates, and an upper layer with a low defect density. In this paper, the electrical properties of the ZnO films are reported and analyzed according to a two-layer Hall-effect model and a two-donor model [2].

The ZnO epitaxial films were directly grown on a-Al_2O_3 substrates at temperatures of 773-873 K without any buffer layer. The film thickness was between 0.1-4.5 mm. The m_H at room temperature (RT) increased from 30 to 190 $cm^2V^{-1}s^{-1}$ with increasing film thickness to approximately 3 mm. From the temperature dependence of the m_H, the m_H increased significantly with decreasing temperature to approximately 100-150 K, but decreased at temperatures less than 100 K for films greater than 500 nm in thickness. The m_H of the ZnO film (190 $cm^2V^{-1}s^{-1}$) at RT increased to 660 $cm^2V^{-1}s^{-1}$ at 100 K, but decreased at less than 100 K. In contrast, the m_H hardly changed with temperature for films lesser than 500 nm in thickness. The m_H and electron concentration of the upper layer were corrected based on the above results, assuming that the degenerate layer was 100 nm in thickness. Hydrogen and boron atoms were detected on the order of 10^{18} cm^{-3} and 10^{17} cm^{-3}, respectively, by secondary ion mass spectroscopy. These atoms are considered to be donor impurities in ZnO. Therefore, temperature dependence of the electron concentrations of the ZnO films was analyzed using the two-donor model.

[1] K. Yasui et al., MRS Proc. (2011), Vol. 1315, pp. 21-26.

[2] D. C. Look et al., Phys. Rev. Lett., 82, No. 12 (1999) 2552.

9:20am **C2-1-5 PEDOT:PSS Film having High Catalytic Activity for use as a Counter Electrode in Dye-sensitized Solar Cell**, ***C.C. Chang***, *L.C. Chen, D. Mishra, J.M. Ting (jting@mail.ncku.edu.tw)*, National Cheng Kung University, Taiwan

The replacement of Pt coated indium tin oxide (ITO) by poly-(3, 4-ethylenedioxythiophene):poly-(styrenesulfonic acid) (PEDOT: PSS) has been investigated. Commercial PEDOT:PSS was used as the starting material. Triton X-100 which was used as a surfactant were added to the PEDOT:PSS at different percentages, ranging from 0 to 10 wt%. The resulting films were characterized by Raman spectroscopy and UV-vis-NIR optical spectroscopy for the structure and optical absorption, respectively. Cyclic voltametry was also performed to determine the catalytic activity. The hole concentration and mobility were determined using Hall measurement. We show for the first time that the addition of Triton increases the catalytic activity, which was found to peak 5 wt%. The resulting films were also used as counter electrodes in rigid and flexible dye-sensitized solar cells (DSCs). The cells were evaluated using electrochemical impedance spectroscopy, solar simulator, and incident photon-to-electron conversion efficiency. The results also peak at 5 wt%. The Triton-added PEDOT:PSS counter electrode shows low series resistance and low charge-transfer resistance which approach that of plantium. We demonstrate that DSC with 5% Triton-added PEDOT:PSS counter electrode exhibits an efficiency of 4.62%, which is higher than that the DSC with Pt/ITO counter electrode.

9:40am **C2-1-6 Formation and Characterization of CIS Thin Films by Co-sputtering Using $CuSe_2$ and $InSe_2$ Targets**, ***E. Bleza***, *J. Jeon, W. Lee (wslee@chosun.ac.kr), N. Kim*, Chosun University, Korea

Chalcopyrite $CuInSe_2$ (CIS) thin films have been used as the absorber layer in the heterostructured thin film solar cell applications owing to their high absorption coefficient and the appropriate band gap energy of 1.04 eV. CIS thin films were generally prepared by using co-evaporation which should require the high-costly equipments for selenization process with hardness to control the accuracy in deposition rate for each element source. Non-selenization process was proposed and demonstrated for preparing CIS thin films without any Se- / S-containing gas in our previous study; the sputtering method was employed for the multilevel stack-structures by using In and $CuSe_2$ alloy targets followed by rapid thermal annealing (RTA) in the N_2 ambient. However, the chemical composition ratio of Se was lower than that of the required value for the high-efficiency photovoltaic devices. In this study, the co-sputtering method was used for the accurate control of chemical composition ratio by using $CuSe_2$ and $InSe_2$ selenide-targets as the starting materials to prepare the CIS thin films. The structural studies were examined by using some analytical techniques such as X-ray diffraction (XRD) and Raman scattering to confirm the CIS chalcopyrite phases in the RTA-treated thin films. UV-visible spectrophotometer and Hall Effect measurement system were employed to analyze the optical and electrical properties of CIS thin films fabricated by this non-selenization process with the co-sputtering method. The change of chemical composition in the RTA-treated CIS thin films was analyzed by using the secondary ion mass spectroscopy (SIMS) and Auger electron spectroscopy (AES) with a change of the sputtering power to $InSe_2$ target to verify the relationship between sputtering power to $InSe_2$ target and stoichiometry of CIS thin films by analyzing the chemical composition ratios of In / Cu and Se / Cu. The optimum sputtering power to $InSe_2$ target was obtained by considering the structural, chemical, optical, and electrical properties of CIS thin films.

10:00am **C2-1-7 Optical Properties of Sputter-Deposited Germanium Oxide (GeO_2) Films**, ***C. Ramana*** *(rvchintalapalle@utep.edu)*, University of Texas at El Paso, US, *N. Murphy, L. Sun, J. Jones, R. Jakubiak*, Air Force Research Laboratory, Materials and Manufacturing Directorate, US

Germanium oxide (GeO_2) exhibits many interesting physical, chemical and electronic properties for applications in a wide range of optical, electronic and optoelectronic devices. GeO_2 is a photoluminescence and dielectric material. It exhibits high values of dielectric constant, refractive index, thermal stability and mechanical strength. Due to these fascinating optical and electronic properties, GeO_2 has been considered as a promising material for optical waveguides and nano-connections in optoelectronic communications. Synthesis and optimization of a particular phase and compositional stability of GeO_2 is very important as this material exhibits several polymorphs. Additionally, the optical, photochemical and optoelectronic properties of metal oxide films are sensitive to the processing conditions such as base pressure, growth temperature, reactive pressure (if any), deposition rate and annealing conditions. Therefore, the controlled growth and manipulation of specific crystal structures of GeO_2 at the nanoscale dimensions has important technological implications. In the present work, GeO_x films were grown by the direct-current (DC) magnetron sputter-deposition employing Ge target for reactive deposition. The effect of oxygen gas flow rate on the structure and optical properties has been investigated. The deposition was made under the reactive atmosphere of argon (Ar) and oxygen (O_2) at a constant pressure of 5 mTorr. The Ar and O_2 were controlled using as MKS mass flow meters. While the total gas flow rate is 20 sccm, O_2 flow rate is varied from 0 to 20 sccm balance Ar. The deposition was carried out to obtain a ~100 nm thick GeO_x film. The grazing incidence X-ray diffraction and scanning electron microscopy analyses confirm that the GeO_x films grown were amorphous. The chemistry of Ge ions exhibit an evolution from pure Ge films to Ge+GeO_2 mixed phase and then finally to GeO_2 composition with increasing oxygen gas flow rate from 0 to 20 sccm. The optical properties primarily probed by the spectroscopic ellipsometry indicate that the effect of oxygen gas flow rate is significant on the optical constants of GeO_x films. The measured index of refraction (n) at λ=550 nm is 4.67 for films grown without any oxygen indicating the characteristic behavior of Ge semiconductor films. For O_2 flow rate of 5 sccm, mixed Ge+GeO_2 films exhibit a decrease in n value to 2.62. Finally n drops to 1.60 for oxygen flow rates of 10-20 sccm, where the films characterizing by the fully oxidized state of Ge. The results and detailed analysis will be presented.

10:20am **C2-1-8 Experimental and Theoretical Analysis of Solar Absorbing Mo-SiO_2 Cermet Coating**, ***Z. Tan*** *(zhuopeng@gmail.com), J. Zhou*, Tsinghua University, China, *D. He, f. Zhou, J. Yi*, Camda Institute of New Energy Technology, China

Solar spectrally selective absorbing Mo-SiO_2 metal-dielectric (cermet) coatings with a four layer structure were fabricated by using a sputtering technique. It consists two Mo-SiO_2 cermet layers on top of a pure Mo layer and one SiO_2 layer on top of the cermet layers. A method combined theoretical simulations and experiments were proved to be efficient and effective on identifying candidate film structures. Effects of film thickness, compositions and substrate surface roughness on film optical properties were studied. Both cermet layer thickness and compositions have large effects on the film absorptance and emission over the other factors. For the substrate surface roughness, it was found that the smoother it was, the less emittance the film would have. Method of thermal shock for temperatures ranging from 473 K to 773 K was employed to test the thermal stability under pressure of 0.1 Pa of the selected structure. Based on the experimental results, the selected cermet coating has solar absorptance over 0.94 and keeps stable after thermal shock for over one thousand cycles.

10:40am **C2-1-9 Effect of Nitrogen Incorporation on the Optical, Structural and Electrical Properties of Indium Zinc Oxide.**, ***J. Ortega*** *(jjosila@hotmail.com)*, Universidad Autónoma de San Luis Potosí, Mexico, *M. Aguilar-Frutis*, Instituto Politécnico Nacional, Mexico, *C. Falcony*, Instituto Politecnico Nacional, Mexico, *V. Méndez-García*, Universidad Autónoma de San Luis Potosí, Mexico, *J. Araiza*, Universidad Autónoma de Zacatecas, Mexico

Transparent IZO thin films were deposited on Si(100) substrates by RF reactive magnetron sputtering at room temperature under different nitrogen concentration in the plasma and reactive atmosphere. As precursor, an IZO target (In_2O_3-ZnO, 90-10 wt%) with a purity of 99.99% was used. The effect of the incorporation of nitrogen on the structural, electrical and optical properties was amply studied. Energy Dispersive Spectroscopy (EDS) confirms the presence of In, Zn, O and N in all the deposited films. The IZO:N films maintained the amorphous structure even after a gas flow

ratio of 15 sccm N_2/5 sccm Ar. The electrical resistivity, mobility and carrier concentrations were determined from Hall Effect measurements using the Van der Pauw configuration. The lowest resistivity obtained was $3.8x10^{-4}$ Ω·cm with a mobility of 31.9 $cm^2/V·s$, and carrier concentration of $5.1x10^{20}cm^{-3}$. By measurement of absorption and transmission Uv-vis spectroscopy in conjunction with the characterization by spectral ellipsometry (SE), the optical properties were analyzed according to the deposition conditions. For SE analysis were used two dispersion models, the Classical and Adachi models. The optical parameters obtained using both dispersion models presents a notable increase in the optical parameters, refractive index and extinction coefficient, related to the increment of nitrogen in the film. The band gap ($E_{g)}$) of the films depends strongly on the nitrogen incorporation and as a direct result, E_g presents a narrowing from 3.5 to 2.5 eV, associated with the Burstein-Moss effect as well as band gap renormalization due to the interaction electron-electron and electron-impurity.

Coatings for Biomedical and Healthcare Applications
Room: Sunrise - Session D1-1

Surface Functionalization, Drug Delivery, and Anti-microbial Coatings

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

8:00am **D1-1-1 Fabrication and Characterizations of ZnO Nanorods/ Ag Nanoparticle Composite on the Electropolished Ti Substrate.**, ***H. Chen*** *(hchen@ncnu.edu.tw)*, National Chi-Nan University, Taiwan, Republic of China, *Y.M. Yeh*, *S.M. Liu*, WuFeng University, Taiwan, *B.Y. Huang*, *J.Z. Chen*, National Chi-Nan University, Taiwan, Republic of China

ZnO and Ag nanoparticle nanocomposite functioning as anti-bacterial film been fabricated. ZnO nanorods on the electro-polished Ti substrate using electrochemical-hydrothermal methods. The titanium substrate was first electro-polished to remove the oxide and obtain an ideal flat surface. ZnO nanorods of two types of morphologies have been grown with $ZnCl_2$ and $Zn(NO_3)_2$ aqueous solutions. Subsequently, Ag nanoparticles of different size have dripped on top of the ZnO nanorods to form the ZnO nanorod/Ag nanoparticle nanocompoiste. To examine the material and optical properties of the nanocompoiste film, scanning electron microscopy (SEM), X-ray diffraction (XRD) analysis, and photoluminescence (PL) under a microscope were used to measure the film morphology, crystalline structure, and optical characteristics. Nanocomposites with various growth conditions of the ZnO nanorods and Ag nanoparticles of distinct sizes have been compared. To enhance antibacterial properties of the film, larger surface area of the nanocomposite is preferable. The films with well-crystallized nanorods with appropriate nanoparticles incorporation have been formed by examining the multiple analyses. The nanocomposite is promising for future biomedical applications.

8:20am **D1-1-2 Evaluations of Biocompatibility and Antibacterial Property: Effects of Various Coatings**, *T.Y. Kao*, *J.P. Chu (jpchu@mail.ntust.edu.tw)*, ***C.L. Li***, National Taiwan University of Science and Technology (NTUST), Taiwan, Republic of China, *Y.J. Chang*, National Taipei Municipal University of Education, Taiwan, Republic of China, *J.-W. Lee*, Ming Chi University of Technology, Taiwan, Republic of China, *M.J. Chen*, *S.H. Chang*, Mackay Memorial Hospital Tamsui Campus, Taiwan, Republic of China, *J.C. Lin*, Mackay Memorial Hospital Tamsui Campus, Taiwan, Republicof China

Various coatings are evaluated for biocompatibility and antibacterial property. These coatings for evaluations are such as TiN, DLC and thin film metallic glasses (TFMGs). TiN and DLC are commonly known as the hard coatings, while TFMGs have a great potential owing to their unique properties, such as high strength, high hardness, smooth surface, thermal plastic forming and antibacterial properties. In this study, Zr-based TFMGs and conventional hard coatings were deposited by magnetron sputtering. The effects of these coatings on microstructures, surface roughness, amorphization of TFMG, mechanical, antibacterial properties and cell adhesion behavior are explored, and the results will be presented in this talk.

8:40am **D1-1-3 Diamond-like Carbon for Articulation in Joint Replacements - Remaining Issues**, ***G. Thorwarth*** *(thorwarth.goetz@synthes.com)*, DePuy Synthes Companies, Switzerland, *K. Thorwarth*, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland, *D. Bernoulli*, *A. Wyss*, ETH Zürich, Switzerland, *U. Mueller*, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland, *R. Spolenak*, ETH Zürich, Switzerland, *R. Hauert*, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland **INVITED**

Being a proven excellent choice for bearing and rolling applications, diamond-like carbon (DLC) materials have found widespread use in industry, but are only beginning to enter the implant field. It is known that the main problems but also some key benefits with DLC originate from its high intrinsic stress. A successful long-lasting DLC implant coating must balance the key properties of DLC with a careful interface design and awareness of the substrate material capabilities. Failure to do so has in the past led to unexpected implant failure, causing numerous in-vivo revisions.

The presentation gives an overview of the in-vivo conditions and requirements to a DLC coated articulating surface and highlights identified failure mechanisms. It is shown that the human body environment presents critical conditions for otherwise established material choices. Strategies to avoid these failure mechanisms are discussed. Approaches for further functionalization of DLC coatings including antimicrobial doping are presented and their advantages and disadvantages are elucidated.

9:20am **D1-1-5 Bacterial Adhesion and Corrosion Studies on TiO_2 and ZrO_2 Coatings**, *R. Galicia*, Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Mexico, ***P. Silva-Bermudez*** *(suriel21@yahoo.com)*, Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de Mexico, México, *A. Almaguer-Flores*, Universidad Nacional Autónoma de México, Mexico, *S. Rodil*, Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de Mexico, Mexico

In the present work, quasi-amorphous (q-a) and polycrystalline (p-c) TiO_2 and ZrO_2 thin films were deposited on pure titanium (cp-Ti) substrates from pure metallic targets; using reactive Radio Frequency (RF) magnetron sputtering. An Ar/O_2, 8:2, atmosphere and a RF power of 200 W was used for the deposits. The q-a coatings were deposited with no substrate heating and using a deposition time of 1800 s. The p-c coatings were deposited at substrate temperature of 200°C and 250°C, for ZrO_2 and TiO_2, respectively; deposition time was 45 minutes for both coatings.For the corrosion studies, the cp-Ti substrates were prepared with SiC grits up to 1000 grade and then cleaned up using an ultrasonic bath immersing the substrates 15 minutes in acetone, isopropanol and deionized water, consecutively. For the bacterial adhesion studies, two cp-Ti substrates with different average roughness, 2 and 0.3 mm, were used, allowing the bacterial adhesion to be studied for different micro-roughness which was inherent from the substrate, nano-roughness since the q-a/p-c structure modified the roughness at the nano-level and chemical compositions; ZrO_2 and TiO_2. The film structure was characterized by X-ray diffraction, contact angle measurements to prove their wettability and X-ray photoelectron spectroscopy to obtain the composition, which was similar for the amorphous and crystalline phases. Finally, images of the surface topography were obtained by secondary electron microscopy (SEM).The investigation of the electrochemical behavior of the coatings was carried out in 0.89 wt% NaCl and phosphate buffer solution (PBS) solutions under no stirring conditions using a three electrode flat cell configuration. Potentiodynamic and Electrochemical Impedance Spectroscopy measurements were obtained using a Gamry Potentiostat. The results suggested that the four different coatings present an improved corrosion performance compared to that of the bare cp-Ti substrate.Bacterial adhesion experiments were done using *Escherichia Coli* and *Staphylococus Aureus*, two pathogen strains. The number of attached bacteria was obtained after 24 hours of incubation by the method of counting the number of colony forming units (CFU), which indirectly measures the number of viable cells that were initially attached to the surface. The attached cells were also observed directly on the coatings by SEM. The results suggested that the number of bacteria was larger for the p-c coatings. The correlation between these results and the surface properties is discussed.Acknowledgments to the financial funding and postdoctoral fellowship for P.S-B. under CONACyT project 152995 and to the CONACyT scholarship for R. G.

9:40am **D1-1-6 Surface Properties of Biomaterials and Their Application in Endogenous Tissue Engineering**, ***R. Olivares-Navarrete*** *(rene.olivares-navarrete@bme.gatech.edu)*, Georgia Institute of Technology, US **INVITED**

Biomaterials are used clinically to restore form and function to patients. When biomaterials are implanted into the body, they are first coated with proteins from blood, aiding in initial stem cell attachment to the material surface. In this way, stem cells can differentiate in cells that induce healing

and tissue formation. In this presentation I will focus mainly in biomaterials implanted in bone. In this application, stem cells attached to the implant surface differentiate into bone, forming a direct contact between bone and implant termed osseointegration. In dental and orthopaedic implants, osseointegration is crucial to maintain implant stability. However, if the stem cells that attach do not form bone, the implant will fail, requiring additional procedures. Therefore, it is important to design biomaterial surfaces to control stem cell fate once they are implanted. Previous studies have shown that material surface characteristics on which cells are grown influence their growth, development and differentiation, but these studies commonly use exogenous growth factors, hormones, and synthetic molecules. In this presentation, I will discuss the effect of biomaterial properties such as surface roughness, chemistry, and energy on stem cell fate and to explore the signaling pathways involved in osteoblastic differentiation of stem cells in response to these surface properties. Designing "smart" materials that control cellular activities or cell fate would translate to more efficient regenerative medicine and the abolishment of exogenous growth factors that can produce adverse effects.

10:20am **D1-1-8 Effect of Salivary Protein Adsorption in the Bacterial Adhesion on Microestructured Titanium Surfaces**, *M. Martínez-Hernández,* ***A. Almaguer-Flores*** *(argelia.almaguer@mac.com),* Universidad Nacional Autónoma de México -Facultad de Odontología, Mexico

It has been recognized that bacteria have affinities for different proteins that can be present in saliva. The aim of this study was to determine the effect of the adsorption of two salivary proteins and its effect on the adhesion of two bacterial strains on different microestructured titanium (Ti) samples with different surface properties. To evaluate the protein adsorption on the surfaces, Alpha-amylase, Cystatin-S and Histatin 5, were incubated during 2 hours on PT [pre-treatment (Ra<0.2µm)], A [acid-etched (Ra<0.8 µm)], and SLA [sand-blasted/acid-etched (Ra=4 µm)] Ti surfaces. The amount of proteins absorbed on each surface was measured by ELISA assay. To assess the bacterial adhesion, two oral microorganisms: *Streptococcus gordonii* and *Porphyromonas gingivalis* were incubatedindividually on the Ti surfaces previously coated with Alpha-amylase, Cystatin-S or Histatin 5. After incubation time, bacteria were detached by sonication and the number of colony forming units (CFUs) was counted by direct observation. In addition, the surfaces were observed by fluorescence microscopy to determine the surface coverage of bacteria using the LIVE/DEAD® BacLightTM (Invitrogen) kit. Significant differences were determined using ANOVA test. Results show that Alpha-amylase was detected on PT, A and SLA surfaces (41.1 ng/mL, 41.1 ng/mL and 52.03 ng/mL, respectively) while Cystatin-S was adsorbed on the same surfaces at 27.2 ng/mL, 20.3 ng/mL and 25.1 ng/mL, respectively), finally Histatin 5 was detected on higher quantities on the PT, A and SLA surfaces (107.1 ng/mL, 100.8 ng/mL and 103.7 ng/mL, respectively). In general, higher bacterial counts were detected on the SLA surfaces. *P. gingivalis* was detected in higher counts comparing with *S. gordonii* in all substrates tested regardless previous protein adsorption. Alpha-amylase decreased the adhesion of *S. gordonii* while Histatin 5 decreased the adhesion of *P. gingivalis*. The protein adsorption was influenced by the physical properties of each substrate while the bacterial adhesion was influenced mainly by the surface topography but also by the previous adsorption of the proteins that were tested.

10:40am **D1-1-9 Cell Response to Amorphous-Crystalline TiO_2 Thin Films**, *P. Silva-Bermudez,* Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de Mexico, México, *A. Almaguer-Flores,* Facultad de Odontología, Universidad Nacional Autónoma de México, Mexico, *SL. Hyzy, R. Olivares-Navarrete,* Georgia Institute of Technology, US, ***S. Rodil*** *(ser42@iim.unam.mx),* Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de Mexico, México

In this work, we deposited amorphous and crystalline titanium oxide (TiO_2) films to study the effect of atomic ordering, and micro-nano roughness on the cell adhesion, proliferation and differentiation. The films were deposited from a metallic Ti target using a magnetron sputtering method, a reactive Ar/O_2 atmosphere (80:20) and 200 W RF-power. Amorphous films were deposited at room temperature and crystalline films at substrate temperatures of 250ºC. The films were deposited on pure Ti grade 2 (cp-Ti) substrates with 2 different micro-roughness; pre-treated PT [Ra=0.4 mm] and sand blasted-acid etched, SLA [Ra=3.2 mm]). Moreover, at the nanometric level, it was observed that the amorphous-crystalline structure induce also modifications in the nano-roughness. The films were characterized by X-ray diffraction, which confirmed the crystallinity, and X-ray photoelectron spectroscopy to obtain the composition, which was similar for the amorphous and crystalline phases. Images of the surface topography were obtained by both atomic force microscopy and secondary electron microscopy. To characterize the biological response, human mesenchymal stem cells (HMSC) were plated at 10000 cells/cm^2 on uncoated PT and SLA cp-Ti substrates, as well as on TiO2-coated substrates; amorphous TiO_2/PT (aPT), crystalline TiO_2/PT (cPT), amorphous TiO_2/SLA (aSLA) and crystalline TiO_2/SLA (cSLA). Tissue culture polystyrene (TCPS) was used as a control. Cells were cultured in Mesenchymal Stem Cell Growth Media (Lonza) at 37C, and media was changed every other day. Cells were cultured for 7 days. After the incubation period, cells were harvested for cell number and alkaline phosphatase specific activity. Meanwhile, the conditioned media was analyzed for osteocalcin. HMSC grown on SLA and cSLA surfaces decreased cell number and increased alkaline phosphatase activity in comparison to TCPS, PT, or cPT. HMSC grown on aPT and aSLA showed lower cell number in comparison to TCPS, but higher cell number when compared to PT, SLA, cPT, or cSLA. Osteocalcin levels were higher on SLA and cSLA compared to TCPS, PT, or cPT. However, amorphous modifications on PT and SLA had higher osteocalcin levels when compared to control group, or the crystalline modification. The results show that HMSC differentiation is sensitive to surface micro- and nano-features, as well as to the surface atomic ordering of the TiO_2 films.

Acknowledgements: CONACYT 152995

11:00am **D1-1-10 Effect of Dielectric Properties of Ceramic Surface on its Binding with Protein in Solvent**, ***R. Sabirianov*** *(rsabirianov@mail.unomaha.edu),* University of Nebraska at Omaha, US, *A. Rubinstein, F. Namavar,* University of Nebraska Medical Center, US

Surface properties influence adsorption of adhesive proteins and subsequent cell adhesion on orthopaedic implants and greatly affect its biocompatibility. The role dielectric permittivity of the implant coating in the protein adsorption is poorly understood. We calculated the contribution of electrostatic interactions to the free energy of binding between protein and dielectric surface as a function of its dielectric permittivity using non local electrostatic approach [1]. We show that the unfavorable desolvation effects expected in classical consideration are considerably reduced. The formation of complex of protein with the dielectric implant surface is assisted by electrostatic interaction if coatings have a moderate dielectric constant. This compensation for the unfavorable desolvation effects is due to the presence of an interfacial solvent layer with low dielectric constant. We show that the electrostatic binding energy of protein with the dielectric implant surface depends non-monotonically on the dielectric constant of the latter. It is strongest for a medium with the dielectric permittivity of ~4. Thus, ceramic implant coating of reduced dielectric permittivity may be beneficial to strengthen the electrostatic binding of the adhesive proteins to the implant. Because biocompatibility of CoCrMo and Ti implant can be modifies by nanocrystalline coating therefore we performed a comparative analyze of the electrostatic interactions of protein with typical ceramics coatings TiO2 (anatase and rutile), ZrO2, Ta2O5 and glass. The results correlate with the experimental findings of adhered cells counting determined by Alamar Blue Assay on respective substrates fabricated by ion-beam assisted deposition.[2]

1. A.Rubinstein, R. F. Sabirianov, W. N. Mei, F. Namavar and A. Khoynezhad. Effect of the ordered interfacial water layer in protein complex formation: a non-local electrostatic approach. Phys. Rev. E, 82, 021915(2010)

2. J. D. Jackson and J. G. Sharp, H. Haider, K. L. Garvin and F. Namavar, Preliminary analysis of attachment, survival, and growth of bone marrow stromal cells on nanocrystalline hard ceramic coatings, *Ceramics, Cells and Tissues: Materials for Scaffolding of Biologically Engineered Systems. Interfaces and Interactions on a Nanoscale* ed A Ravaglioli and A Krajewski (Rome: Consiglio Nazionale Delle Ricerche) p 109

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

Mechanical Properties and Adhesion
Moderator: M.T. Lin, National Chung Hsing University, Taiwan, R. Chromik, McGill University, D. Bahr, Washington State University

8:00am **E2-2-1 Effects of Copper on the Microstructural and Functional Properties of Sputter-Deposited Ni-Ti Thin Films**, ***M. Callisti*** *(mc3a09@soton.ac.uk), B.G. Mellor, T. Polcar,* University of Southampton, UK

Sputter-deposited NiTi thin films are known to exhibit unusual properties such as shape memory effect and superelasticity making them attractive materials for MEMS and biomedical applications. Furthermore, their

thermoelastic martensitic transformation is accompanied by reversible changes in surface roughness, which is an important factor in tribology. Thus, it might be possible with these films to control surface roughness and/or surface features during the sliding process through external heating with consequent reduction of friction and wear. The application of these films as smart surfaces for tribology requires detailed understanding of microstructural phenomena involved during the martensitic transformation; moreover, low hardness and wear resistance limit the use of these films.

In this study, Ni-Ti-(Cu) coatings deposited by plasma-assisted magnetron sputtering have been investigated. To obtain transformation temperatures higher than room temperature and improved mechanical properties, Ti-rich NiTi films were deposited and co-sputtered with copper, respectively. The coatings with a thickness of 1.5 µm were isothermally annealed at 500°C for 1 h in an argon atmosphere, with the aim to produce coherent precipitates (GP-zones) in the matrix. A scanning electron microscope (SEM) equipped with Energy-dispersive X-ray spectroscopy (EDS) was used to observe cross-section of the coatings and their chemical composition, respectively. Their structure was evaluated by X-ray diffraction (XRD) and the mechanical properties were measured by a depth sensing nanoindenation.

The Ti/Ni ratio in the deposited films was kept constant when a series of five Ni-Ti-Cu coatings was prepared with copper content increasing up to 15 at.%. After annealing of the as-deposited amorphous coatings, XRD analyses showed a dominant martensitic structure at room temperature for all investigated compositions and thus indicating prevalent shape memory behaviour. Doping with copper affected the microstructure, since different kinds and densities of precipitates (i.e. coherent plates and spherical semi-coherent precipitates with the matrix) were identified. Application of the Scherrer equation to the strong martensitic peaks suggested a decreasing crystalline size with increasing Cu content. Nanoindentation revealed the effect of Cu content on mechanical (hardness and Young's modulus) and functional properties, as well as their variation with change in transformation path, and thus in the native phase from B19' to B19, for Cu contents lower and higher than 10 at.%, respectively.

8:20am **E2-2-2 Mechanical Response of Nanotwinned Metallic Coatings**, ***X. Zhang*** *(zhangx@tamu.edu), D. Bufford, Y. Liu, H. Wang,* Texas A&M University, US **INVITED**

Nanotwinned metals have received increasing attention recently as high density nanotwins can lead to unique electric, thermal and mechanical behavior, which are largely different from nanocrystalline metals with high angle grain boundaries. Twin boundaries serve as barriers to the transmission of dislocations, and are effective sources and sinks for dislocations during plastic deformation. We will review recent studies on a variety of sputtered nanotwinned fcc coatings, including 330 stainless steel, Cu and Ag. Both coherent {111} and incoherent {112} twin boundaries are observed, and the average twin spacing, on the order of ~ 10 nm, can be achieved by varying deposition conditions. In situ nanoindentation studies reveal that twin boundaries are mobile during deformation. Numerous dislocation-twin boundary interaction mechanisms are discussed.

9:00am **E2-2-4 Structural and Mechanical Properties of Al-Cu-Fe Quasicrystalline Thin Films**, ***S. Olsson*** *(simol@ifm.liu.se), F. Eriksson, E. Broitman, M. Garbrecht, J. Birch,* Thin Film Physics Division, IFM, Linköping University, Sweden, *L. Hultman*, Thin Film Physics Division, IFM, Linköping University, Sweden

Multilayered Al-Cu-Fe thin films have been deposited by triple-target unbalanced high vacuum magnetron sputtering onto Si and Al_2O_3 substrates. Isothermal annealing was performed using both an in situ XRD furnace, where the phase evolution was monitored, and in a tube furnace at temperatures up to 700 °C and annealing times up to 100 h.

It was found that when using Al_2O_3 substrates the icosahedral quasicrystalline phase $Al_{62}Cu_{25.5}Fe_{12.5}$ was formed at about 500 °C which was improving in structural quality and orientation with increasing temperature, but with the addition of a secondary β-phase, $Al_{50}(CuFe)_{50}$. For a Si substrate, Si starts to diffuse into the thin film at temperatures above 300 °C, preventing the quasicrystalline phase from forming. Instead, the cubic $Al_{62.5-x}Si_xCu_{25}Fe_{12.5}$ approximant phase forms at 430 °C. With increasing annealing time at 600 °C the Si content increases from x=8.3 at.% after 4 h to x=12 at.% after 64 h.

To evaluate the mechanical properties of the thin films, the nanohardness, elasticity, friction, wear resistance, and toughness factor have been investigated using a Triboindenter TI-950 from Hysitron. For the quasicrystalline thin films the hardness increases from 10 GPa to 14 GPa with increasing crystal perfection. The hardness of the β-phase was 10 GPa. For the approximant thin films a hardness of 16 GPa was found, which was decreasing to about 10 GPa with increasing Si content. At the same time the mean reduced elastic modulus is decreasing from 220 GPa to 160 GPa. For all films, irrespective of the phase content and annealing procedure, a low friction coefficient against the diamond tip of 0.12±0.03 was measured. The mechanical properties are related to the film microstructure analyzed by X-ray diffraction and high resolution transmission electron microscopy.

9:20am **E2-2-5 The Microstructure and Mechanical Properties of Nitrogen and Boron Contained ZrCuAlNi Thin Film Metallic Glasses**, ***T.P. Hsiao***, National Taipei University of Technology, Taiwan, Republic of China, *J.-W. Lee (jefflee@mail.mcut.edu.tw),* Ming Chi University of Technology, Taiwan, Republic of China, *Y.C. Yang,* National Taipei University of Technology, Taiwan, Republic of China, *C.L. Li, J.P. Chu,* National Taiwan University of Science and Technology (NTUST), Taiwan, Republic of China

In this work, ZrCuAlNi thin film metallic glasses (TFMGs) were grown on Si wafer and AISI420 steels by magnetron sputtering system. Different amount of nitrogen flow rates were controlled by plasma emission monitoring (PEM) during sputtering. And boron element was doped to evaluate the influences on the mechanical properties and microstructure of TFMGs. The supercooled liquid region of TFMG was determined by the differential scanning calorimetry (DSC) analysis. The microstructure was analyzed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The phase structure was confirmed by using x-ray diffraction (XRD). The mechanical properties were measured by nanoindentation. The scratch tester and ball-on-disk wear tests were employed to evaluate the adhesion and tribological properties. The surface roughness was determined by atomic force microscopy (AFM). It was concluded that the glass-forming ability and hardness of TFMGs were strongly influenced by the nitrogen and boron contents. The proper nitrogen and boron concentrations for ZrCuAlNi TFMG were proposed in this work.

9:40am **E2-2-6 Comparison of Nanoindentation and Micro-tensile Measurements on the Strain-hardening Ability of Nano-scale Metallic Multilayers**, ***R. Schoeppner*** *(rschoepp@wsu.edu),* Washington State University, US, *D. Bahr*, Purdue University, US, *H. Zbib*, Washington State University, US

Nano-scale metallic multilayers (NMM) exhibit superior mechanical properties and a resistance to harsh environments due to the nature of their interfaces. Incoherent interfaces are generally stronger, acting as barriers to slip transmission, and are also dislocation and radiation-induced defect sinks. Coherent interfaces show more ductility and increased strength due to their ability to act as dislocation barriers between layers. Trimetallic systems, having a combination of coherent and incoherent interfaces, have been shown through both experimental and molecular-dynamic (MD) simulations, to possess superior properties of both types of interfaces; high strength and ductility, as well as a significant strain-hardening ability. Examination of pile-up after indentation can hint at a material's strain-hardening ability. Sharper tips create higher effective strains when compared to using a blunt Berkovich tip. At these high strains, a material with low strain-hardening ability will have large pile-up zones around the indent; whereas a material with high strain-hardening ability will have smaller pile-up at similar contact areas. Initial indentation experiments revealed a smaller amount of pile-up at similar contact areas in trilayers when compared to bilayer systems, suggesting these trilayer systems have a higher strain-hardening coefficient. Mechanical properties of trilayer mixed interface systems from micro-tensile experiments are compared to those obtained from different tip geometries used in nanoindentation to verify the observed strain-hardening relationship. By specifying the layer thickness and material selection of the multilayer films, both modulus and hardness can be tailored, making them useful as wear resistant coatings. However, with repetitive impact loading, the increased hardness and decreased ductility of the films due to the strain hardening should be considered. This work was supported by a grant to WSU from the U.S. Department of Energy, Office of Basic Energy Science, under Grant No. DE-FG02-07ER46435. This work is also partially supported by Sandia National Laboratories, a Lockheed Martin Company for the United States Department of Energy's National Nuclear Security Administration under Contract DE-AC04 94AL85000.

10:00am **E2-2-7 High Temperature Instrumented Indentation System: Characterization and Optimization**, ***M. Fajfrowski***, *V. Jardret (vincent.jardret@michalex.com),* Michalex, France

High temperature instrumented indentation tests results are presented on a silicate glass, alumina and Tungsten samples at various temperatures between Room Temperature and 1000oC using the HTIIS 1000. This data is used to analyzed the thermal stability of the instrument, characterize key parameters such as load frame stiffness and indenter geometry, and finally determine the elastic and plastic properties of the samples at each temperature. The thermal management concept used in the instrument is described in details. The results show that the thermal management of the instrument provides very good stability during the tests. Tests performed at different maximum loads enable a complete characterization of the

instrument and the sample at high temperatures. This work illustrates peculiar behavior of silicate glass compared to other materials, confirming previously published data.

10:20am **E2-2-8 High-temperature Mechanical Behaviour of TiAlN Coatings**, *C. Ciurea, V. Bhakhri (v.bhakhri@imperial.ac.uk),* Imperial College London - South Kensington Campus, UK, *P.H. Mayrhofer,* Vienna University of Technology, Austria, ***F. Giuliani***, Imperial College London - South Kensington Campus, UK

In this investigation, high-temperature nanoindentation testing was employed to investigate the difference between the deformation behaviour of standard bulk (001)TiN single crystal (SC-TiN) and $Ti_{1-x}Al_xN$ coatings system at 295K to 623K. TiAlN system comprised of two sets of coatings 1) Magnetron-sputtered (MS) $Ti_{1-x}Al_xN$ (x=0, 0.34, 0.52, 0.62at%) coatings on (001) MgO substrate s and 2) Cathodic Arc-evaporated (CA) $Ti_{1-x}Al_xN$ (x=0.44, 0.6, 0.7at%) coatings deposited on WC-6%Co substrate s . High temperature nanoindentation experiments were carried out at three different loading rates of 0.5, 1 and 10 mN/s. This enabled us to capture the indentation hardness data at three different strain-rates at the end of loading sections of these tests. Hardness values for SC-TiN dropped significantly from 21.4±0.4GPa at room-temperature to 13.7±0.5GPa at 623K. The addition of Aluminium (Al) in TiN increased the room temperature hardness for both MS and CA coatings. The temperature dependence of hardness of MS (x=0 and x=0.34at%) and all CA (x=0.44, 0.6, 0.7at%) coatings followed the similar decreasing trend as depicted by SC-TiN. On the other hand, hardness of MS-Ti0.44Al0.56N coating was quite stable in the measured temperature range, with 29.2±1.3 GPa at 295K and decreased slightly to 26.4±1.2 GPa at 573K. A similar stable hardness over temperature range trend was exhibited by MS (x=0.62%) coating, suggesting that increase in Al addition improved not only the hardness but also lead to stable hardness with increasing temperature. Deformation kinetics analyses, carried out on temperature and strain-rate dependence of hardness data, showed that Al addition increased the activation energy for slip from 0.77 eV for SC-TiN to 1.37 eV for MS (x=0.52at%) coating. This indicated that the resistance to plastic flow is higher for MS-Ti0.48Al0.52 N coating compared to bulk SC-TiN and deformation took place by lattice resistance controlled dislocation glide mechanism. These findings were attributed to the presence of cubic-AlN phase in TiAlN matrix, revealed by X-ray diffraction and TEM analyses, which results in a coherently strained lattice rendering mechanical stability to x=0.52 and 0.62at% coatings at elevated temperatures. The cubic-AlN phase was found to be stabilised during deposition process in MS (x=0.52 and x=0.62 at%) coatings, however was absent in remaining MS (x=0 and 34 at%) and all CA (x=0.44, 0.6, 0.7at%) coatings.

10:40am **E2-2-9 Magnetron Sputtered W-V-N Superhard Nanocomposite Coatings**, *H. Sharma,* ***D. Kaur*** *(dkaurfph@iitr.ernet.in),* Indian Institute of Technology Roorkee, India

In this report, we studied the effect of vanadium concentration on W-V-N superhard thin films deposited on Si(100) substrates at 700°C using reactive magnetron sputtering. The concentration of vanadium was varied in the range 0-21 at%. The resulting films microstructure, surface morphology, hardness, young modulus, fracture toughness and adhesion strength were studied by X-ray diffraction, atomic force microscopy, and nanoindentation, respectively. The Results showed that the W-V-N solid solution formed with preferred orientations (111) and (200) for all the W-V-N films. Nanoindentation hardness and young modulus of W-V-N films initially increased and then decrease with increasing vanadium content. The maximum values of hardness (~ 44 GPa) and young modulus (~ 420 GPa) were found for V content in the range of 8- 15 at %. The fracture toughness of ~ 5.22 MPa $m^{1/2}$ and adhesion strength of ~ 30-45 N was found in W-V-N with silicon substrate. A significant improvement in structural and mechanical properties of W-V-N superhard thin films would make them very useful protective coatings for machining tools.

11:00am **E2-2-10 Microstructure and Mechanical Properties of Copper-tin Shape Memory Alloy Deposited from an Ionic Liquid Electrolyte**, ***N. Moharrami*** *(noushin.moharrami@ncl.ac.uk), S. Ghosh, S. Roy, S Bull*, Newcastle University, UK

Shape memory alloys (SMA) are finding an increasing range of industrial applications owing to the fact that a change in shape produced by plastic deformation can be recovered by heating and the materials may show a superelastic effect (i.e. plastic deformation is recovered at even at very large strains). Such materials show great potential as actuators and there has been considerable interest in developing SMA coatings and assessing them using nanoindentation tests. Although most work has been done on NiTi and CuAlZn there remains an interest in developing cheaper, simpler to process materials for mass market applications. Copper-15%Sn shows the shape memory effect and may be deposited by electrodeposition on a range of substrates. Whereas it is difficult to get the correct chemical and phase composition by plating from aqueous electrolytes good results are obtained when plating from an ionic liquid. In this study the nanoindentation response of copper-tin (Cu-Sn) coatings deposited from a Room Temperature Ionic Liquid (RTIL) has been measured and compared to that of coatings deposited from an aqueous electrolyte.

Exhibition
Room: Town & Country - Session Ex

Exhibition Keynote Lecture

8:00am **Ex1 Atmospheric Pressure Plasmas for Inline Coatings: Status and Challenges**, ***Massines*** *(francoise.massines@univ-perp.fr),* CNRS, France **INVITED**

Plasma-enhanced chemical vapor deposition (PECVD) is a well-known, easy-to-implement solution for the development of thin-film materials. The method allows fine-tuning of their properties and has minimal environmental impact. Replacement of conventional low-pressure plasma systems by in-line atmospheric pressure (AP) would be a solution for the increasing demand for fabrication of products with improved functionality at low cost. Over the past ten years, the expansion of atmospheric pressure plasma solutions for surface treatment of materials has been remarkable. New plasma sources and new reactors have been developed. At the laboratory scale, dense, porous, nanostructured thin films have been realized. These materials can be used as barrier layers, superhydophobic or antifog coatings, antireflective and passivating layers for crystalline solar cells, and for bio applications. New plasma sources, suitable for linear configuration and thus allowing large-area surface treatment, will be described and compared with respect to growth rate and thin-film properties. Challenges related to industrial process upscaling will be addressed. Current developments such as co-injection of nano-powders with liquid or gas thin-film precursors for fabrication of nanocomposites will be discussed.

Applications, Manufacturing, and Equipment
Room: California - Session G1-1

Innovations in Surface Coatings and Treatments
Moderator: L. Bardos, Uppsala University, R. Cremer, KCS Europe GmbH, Germany

8:00am **G1-1-1 High Density Plasma Nitriding of Dualumn Alloys for Automotive Parts**, ***T.A. Zho*** *(taizawa@sic.shibaura-it.ac.jp), K.M. Matsubara,* Shibaura Institute of Technology, Japan, *Y.S. Sugita*, YS Electric Industry, Co. Ltd., Taiwan

Duralumin alloys have been utilized as structural components and parts for aircrafts, train-cars and so forth. Their high specific strength was attractive to those applications; however, their little corrosion resistance and low wearing endurance became a fatal demerit in practical applications. In order to overcome these issues of high strength aluminum alloys, various surface treatments and surface engineering have been proposed in the past. Among them, plasma nitriding is one of the most promising solutions, where the nitride layer by AlN precipitation into aluminum alloy matrix was formed with the significant thickness from the surface to increase the corrosion and wearing toughness.

In the present paper, high density plasma nitriding is proposed as an effective surface treatment for duralumin. This process has a capability to control the RF- and DC-plasmas independently for nitriding. Different from the conventional nitriding processes, the matching between input and output powers is automatically adjusted with the shorter response time less than 1 ms. This enables us to temporally control and describe the plasma state by in-situ plasma diagnosis.

First, this plasma diagnosis was instrumented to search for optimum processing condition to plasma nitriding the duralumin alloys of type A2011 as well as A2014 and A2017. RF-voltage, DC bias, carrier gas pressure and nitrogen-hydrogen gas flow ratio are determined to maximize the peak intensities of activated nitrogen atoms and NH radicals in the spectroscopic measurement. In the case of plasma nitriding where RF-voltage was 250 V, DC-bias, 400 V, pressure, 40 Pa and the gas flow-rate, 80 to 20 %, the surface hardness of A2011 alloy sample increased to 800 Hv even for 7.2 ks at 753 K. Both XRD and SEM were utilized to investigate the formation of nitrided layer with AlN precipitates. Micro-hardness testing was employed to describe the hardness distribution in the cross-section from sample surface to matrix hardness of 100 Hv. Nitriding

behavior was discussed on the basis of diffusion theory, assuming that formation of AlN should take place at the nitriding front. Furthermore, XPS was employed to investigate the nitrogen binding state and to discuss the unbound nitrogen atom concentration.

This nitriding process was applied to automotive parts; i.e. a heat sink. Wearing toughness and strength as well as high thermal conductivity were required for this part. After plasma-plasma nitrding for 14.4 ks at 753 K, fins of heat sink with the thickness of 1 mm and the height of 10 mm were homogeneously nitrided.

8:20am **G1-1-2 Indentation Recovery of Thin Film Metallic Glass: Effects of Annealing Conditions**, ***A. Tesfaye***, *J.P. Chu (jpchu@mail.ntust.edu.tw)*, National Taiwan University of Science and Technology (NTUST), Taiwan, Republic of China

Because of their unique properties, most recently, thin film metallic glasses (TFMGs) have been studied for various applications. In this study, a $Zr_{50.3}Cu_{28.1}Al_{14}Ni_{7.6}$ (in at. %) thin film metallic glass is grown by RF magnetron sputtering system on silicon substrate, followed by nanoindentation conducted at room temperature. It is found that indentation of TFMG creates deformation and stress under the indenter. However, the indented area is able to recover to some extents by heating to temperatures within the supercooled liquid region (SCLR) due to surface tension-driven viscous flow as well as thermally-induced structural relaxation. Accordingly, $Zr_{50.3}Cu_{28.1}Al_{14}Ni_{7.6}$ TFMG is annealed at different temperatures in SCLR and, by using the atomic force microscopy, the indentation depth recovery is evaluated and the results will be discussed in this presentation.

Key Words: Thin film metallic glass, Indentation depth recovery

8:40am **G1-1-3 Influence of Deposition Technology and Process Parameters on the Formation of Growth Defects in PVD Hard Coatings**, ***P. Panjan*** *(peter.panjan@ijs.si)*, Jožef Stefan Institute, Slovenia **INVITED**

Growth defects are inherently present in PVD coatings. In an ideal laboratory environment, the growth defect density can be greatly reduced if proper care is taken. First one has to assure that the deposition chamber is clean, without residues from previous depositions. As many defects originate from the substrate, careful substrate preparation suppresses the defect formation considerably. Yet another effective move is to run the deposition at low power, or modest conditions in general, to prevent arcing, overheating and other defect-contributing mechanisms.

In industrial deposition of PVD coatings on the other hand, these measures are limited by technical and economical constrains. Chamber cleaning procedures have to be reduced to an acceptable level. Substrate conditions are up to the customer, which the coater can only partly influence – the substrate material is defined, while the polishing technique is also optimized to an acceptable level. The deposition is conducted at full power thus a certain degree of arcing has to be taken into account.

In summary, the growth defects in industrial PVD coatings are a fact. They are known to deteriorate the corrosion resistance because they can act as shortcuts for the corrosive media to penetrate down to the substrate. The influence on the tribological properties is more dificult to evaluate, however, a ruptured nodular defect is likely to enable cracking and local delamination of the neighbouring coating. For these reasons there are relevant questions regarding growth defects: what is their size, their internal structure, their origin; and how these properties influence the coating lifetime.

While the growth defects are easily visible on SEM, or even on a better optical microscope, it is much more difficult to extract any information on the individual defect properties (except of its size). Cross-section SEM can help, but only if the fracture exactly passes the growth defect, which is quite improbable. In addition, only one slice through the defect – or more likely around the defect is visible. Therefore a targeted cross-sectioning technique is necessary. This aim is well fulfilled by the focused ion beam technique (FIB), which is typically integrated into a SEM. After examination of the coating surface, a suitable growth defect is selected. A slice accross the defect is then made, or a series of slices, followed by standard SEM observation. Another step is to use these SEM micrographs for a 3D reconstruction and visualization of the growth defect. This step will be the topic of the presentation.

9:20am **G1-1-5 Suppression of Intermetallic Compounds through Microstructural Tunability in DC-sputtered Ni under Bump Metallization**, ***Y.H. Wu***, *J.G. Duh (jgd@mx.nthu.edu.tw)*, National Tsing Hua University, Taiwan, Republic of China

Suppressing the brittle intermetallic compounds (IMCs) is quite critical in microelectronic packaging for improving the reliability of mobile devices. Recently, Ni metallization layer is often reflowed with lead-free solders owing to slower consumption rate as compared to that of Cu. This study aims to explore the effects of DC-sputtered Ni films with various intrinsic characteristics on the growth of IMCs in Sn-3.0Ag-0.5Cu (SAC305)/Ni solder joints. Through systematically controlling the process parameters, including target power density, substrate bias and deposition temperature, the structures of Ni films can be effectively tailored. The crystallographic and grain size of Ni metallization layer were obtained by XRD and high-resolution images of TEM. SEM and AFM were used to examine the morphology and surface roughness of Ni films, respectively. The residual stress was calculated through curvature measurement system. To probe the interfacial reaction of solder joints, SAC305 solders were jointed with as-deposited Ni films by the standard reflow process under N_2 atmosphere. Through the quantitative analysis by FE-EPMA, $(Cu, Ni)_6Sn_5$ and $(Ni, Cu)_3Sn_4$ at the interface of SAC305/Ni were verified. Furthermore, the thickness of IMCs decreased with grain size and surface roughness of Ni films, implying the diffusion path would affect the growth rate of IMCs. Reduced residual stress seemed to significantly inhibit the growth of IMCs. It's suggested that the formation of IMCs strongly depended on the diffusion path and the quantity of the stress field in Ni metallization layer. A promising Ni metallization layer with refined structures was thus developed, which was expected to achieve better reliability in microelectronic packaging.

9:40am **G1-1-6 Influence of the Application Technology on the Corrosion Resistance of DLC-Coatings**, ***J. Ellermeier*** *(ellermeier@mpa-ifw.tu-darmstadt.de)*, *U. Depner*, *M. Oechsner*, TU Darmstadt, Germany

In many applications, the coated components need beside wear resistance an effectual protection against corrosion load. These are for example applications in the chemical or in the off-shore industry, where a combination of wear (abrasion, erosion or fatigue), corrosion environments, and thermal loading can appear simultaneously. Therefore, coating systems are desired which are characterized by a good resistance against wear and corrosion. From a wear resistance perspective, Diamond-like-Carbon systems are prime candidates for those coating systems. However, (microscopic) defects in those coating systems often prevent the achievement of good corrosion resistance.

The aim of our research was to investigate the influence of different application technologies (PVD or/and PECVD) and process parameters (target voltage, middle frequency voltage, gas mixture, pressure) on the nucleation and rate of defects within DLC coatings.

The coatings have been characterized by means of nano-indentation a scratch testing to address hardness and wear resistance, respectively. This paper is limited to the results concerning corrosion. The corrosion resistance has been analyzed by salt spray testing. By means of metallographic investigations (light microscopy, SEM) the mechanism of the degradation process due to corrosion was investigated. Additional characterization has been performed to assess the ratio of sp^2 vs. sp^3 configuration of the carbon and thus to realize the influence to the corrosion resistance.

From our study is concluded that by combined PECVD and PVD processing, the best performance regarding corrosion resistance could be achieved.

10:00am **G1-1-7 Cold Shield Production for Optoelectronic Applications**, ***G. Demirci***, Aselsan Inc., Turkey, *İ. Karakaya, M. Erdoğan (metehan@metu.edu.tr), MS. Aras, B. Arslan, F. Ulu*, Middle East Technical University, Turkey

Cold shield is used to improve the image quality and determine the f number of QWIP (Quantum Well Infrared Photodetector) cooled infrared detectors. Cold shield reduces the absorption of photons hitting the highly reflective outer surface; on the other hand, it provides absorption of photons hitting the highly absorbing inner surface. Thus, photons coming from the object to be displayed are directly passed through the opening of the cold shield, placed over the detector; which prevents absorption of the undesirable photons. Cold shields are produced by electroforming method to minimize thermal mass. Production of a 70 µm thickness self-standing cold shield, with the bright gold plated outer surface was aimed in this study.

10:20am **G1-1-8 Silicides Coating for Fuel Cladding in Gen IV Nuclear Reactors**, *S. Mathieu (stephane.mathieu@ijl.nancy-universite.fr)*, ***N. Chaia***, Universite de Lorraine, France, *F. Rouillard*, CEA Saclay, France, *M. Vilasi*, Universite de Lorraine, France, *M. Leflem*, CEA, France

The vanadium alloy V-4Cr-4Ti is an attractive structural material for fuel cladding either in gas- or sodium-cooled fast reactors (GFR and SFR, respectively) in generation IV nuclear systems. However, the high affinity of vanadium alloys for oxygen coupled with non-protective oxidation products leads to a high oxidation rate at moderate temperature (500-600°C) and also in environments containing a relatively low oxygen content, such as GFR and SFR environments. In fact, the solubility of oxygen in

vanadium is so high (6-7% at. at 650 °C) that oxygen negatively affects the mechanical properties of alloys, causing embrittlement. Further developments involve the use of protective coatings that i) have the ability to isolate vanadium from oxygen, ii) exhibit a low growing oxide scale at low oxygen pressure, iii) are non-reactive with liquid sodium and (iv) are thermodynamically stable with the vanadium alloy at the operating temperature. These criteria lead us to consider coatings containing sufficient amounts of Cr, Al or Si in their subsurface. This study focuses on the development of new protective coatings for this vanadium-based alloy. Halide-activated pack-cementation (HAPC) technique was used to develop V_xSi_y multilayered diffusive silicide coatings. These compounds exhibited a very low oxidation rate at 650 °C, both in air and at a low oxygen pressure (He, 5 ppm O_2). This silicide developed a protective layer of silica at 650°C in air and was not susceptible to the pest phenomenon, unlike other refractory silicides ($MoSi_2$, $NbSi_2$). The coatings formed mainly of MSi_2 were largely unreactive to liquid sodium (<10 ppm O_2) during a 360 h compatibility test at 550 °C. Further details of the oxidation performances of these new materials will be given during the talk regarding the expected properties in conditions that would be close to those met during accidental situation.

10:40am **G1-1-9 Multiscale Characterization of Physico-chemical Properties of an AISI 304L Surface Melted with a Nanopulsed Laser: Application to the Enhancement of the Corrosion Resistance After Laser Surface Melting**, ***W. Pacquentin*** *(wilfried.pacquentin@cea.fr), N. Caron, C. Blanc, M. Tabarant, F. Miserque,* CEA, France, *R. Oltra*, CNRS, France

Very often, the attacks which materials undergo come directly from surface phenomena such as corrosion, wear or other tribological damages. Thus, instead of using very expensive materials or imagining brand new materials, it is interesting to modify the surface properties of materials while maintaining mechanical properties of the bulk.

Among the great number of existing surface treatments, laser surface melting is a current process that keeps on developing because of the recent progress in the technology of lasers. The originality of this process stems from the modification of the chemical composition through the thickness without any weak interfaces, as may be the case with coating processes requiring several powders to obtain material with gradient composition.

This treatment consists in focusing a nanopulsed laser beam on the surface of the material, leading to the rather immediate melting of the surface through a micron depth, immediately followed by an ultra-fast solidification occurring with cooling rate up to 10^{10} K/s.

The combination of these processes leads to:

-the elimination of surface defects

-the formation of metastable phases

-the chemical segregation mechanism

-a structural refinement.

The effect of surface melting treatment on the corrosion behaviour of a widespread AISI 304L stainless steel was explored using a nanopulsed laser with high frequency, contributing to the originality of this work. The main goal is to correlate the surface modifications with the laser beam overlap parameter in order to monitor the corrosion resistance of the material. Different techniques such as scanning electron microscopy, X-ray diffraction, glow discharge optical emission spectrometry, and profilometry were used to characterize the global laser-melted surface.

But the laser radius of the beam equals 70 µm and shows a Gaussian energy distribution. Consequently, we would expect a distribution of the physico-chemical properties at the scale of the laser beam. Consequently, the characterization and the study of the distribution of the physico-chemical properties at a micro, or nano-scale are indispensable for understanding the laser-matter interaction which is extremely local and brief. Thus, we chose to characterize physico-chemical modifications by more local investigations such as transmission electron microscopy, micro-raman and X-ray photoelectron spectroscopy.

The best treatment led to an increase of the pitting potential by more than 500 mV, corresponding to a great improvement of the corrosion resistance. It was correlated to chromium enrichment, to the extinction of martensite and ferrite peaks and to the reduction of harmful inclusion density.

11:00am **G1-1-10 Novel Preparation of Single-layer and Few-layer Mica Nanosheets**, *D.S. Kwak, Y.J. Kwon, H.Y. Cho, T.V. Khai,* ***H.W. Kim*** *(hyounwoo@hanyang.ac.kr)*, Hanyang University, Republic of Korea

Mica, which is chemically inert, insulating, dielectric, hydrophilic, light in weight, elastic/resilient/flexible, reflective, and refractive, is an extremely useful material. Its chemically inert nature facilities it use as an important substrate for epitaxial vapor deposition, including the growth of graphene [1]. Apart from a diverse applications including an antigen for γδ T cells, layered insulators, the space for the possible origin of life, due to its very thin structure, few-layer mica sheet will be used in electrical components, electronics, isinglass, and atomic force microscopy. Furthermore, with its larger surface-to-volume ratio, functionalizing their surface will greatly extend the range of applications. **Accordingly, the fabrication of 2D nanosheets with few mica layers will provide enormous interest to the world-wide scientists and engineers community.**

Since the thin 2D materials become thermodynamically unstable below a certain thickness, the possibility of preparation of free-standing atomic layers has been intensively disputed so far. Recently, Novoselov et al. have used the mechanical cleavage method to show the separation of single- or few-layered graphene. **In this work, we have demonstrated the fabrication of single-layered and few-layered mica [muscovite ($KAl_3Si_3O_{10}(OH)_2$)] nanosheets not only by means of the mechanical cleavage method, but also by the solvothermal method followed by microwave irradiation.** In the solvothermal method, tetrahydrofuran (THF) organic solvent containing potassium hydroxide (KOH) was used for convenient and efficient exfoliation process. Following this, the single-layer or few-layer mica sheets were obtained by the microwave irradiation, which facilitates mass production in a short time with little cost and energy. In addition, in order to reveal the structural/chemical changes upon the exfoliation, we have compared the X-ray diffraction, Raman, and X-ray photoelectron spectroscopy spectra of the expanded mica nanosheets with those of the unprocessed mica powders.

Coatings for Use at High Temperature
Room: San Diego - Session A2-2

Thermal and Environmental Barrier Coating
Moderator: D. Litton, Pratt & Whitney, R. Trice, Purdue University, V. Maurel, Mines-ParisTech, France

2:10pm **A2-2-1 Thermal Barrier Coating Lifetimes for High Temperature, Low Density Superalloys**, ***J. Nesbitt*** *(JNesbitt@nasa.gov), R. MacKay, K. Reamy*, NASA Glenn Research Center, US

Recent studies at the Glenn Research Center have shown that select low density, single-crystal (LDS) superalloys possess an ideal combination of high creep strength and high oxidation resistance with lower density than today's state of the art superalloys. There is a significant payoff in the use of these LDS alloys since a reduction in the turbine blade weight has a cascading effect throughout the entire rotor (e.g., disk, hub, and shaft) as well as to non-rotating support structures. As with traditional superalloys, taking full advantage of these LDS alloys in the hottest sections of the turbine requires environmental coatings (oxidation and thermal barrier coatings (TBC's)). The purpose of this work was to compare the TBC lifetime of an LDS alloy with that of the commercial superalloy CMSX-4. The LDS alloy was evaluated both with and without small additions of Hf (0.15 wt.%). A conventional Pt-modified aluminide bondcoat was used with these alloys. The effect of bond coat was also examined by comparing the TBC lifetime for the Pt-modified aluminide bondcoat with a Pt-only bondcoat on the LDS alloy. Conventional electron beam-physical vapor deposited (EB-PVD) top coats of ZrO_2-7wt.%Y_2O_3 were used with all alloys.

The TBC lifetimes were evaluated by testing triplicate samples for one-hour cycles at 1135°C. The small Hf addition to the LDS alloy significantly improved the TBC lifetime. The lifetime of the Pt-only bondcoat was intermediate to that of the LDS alloy with and without Hf but with the Pt-modified aluminide bondcoat. The lifetimes of the Hf-containing LDS alloy were similar to that of the CMSX-4 alloy, both with the same Pt-modified bondcoat. It is suspected that the Hf within the CMSX-4 alloy and in the Hf containing LDS alloy contributed to the high TBC lifetimes. This work showed that LDS alloys, when containing small Hf additions, have TBC lifetimes similar to current commercial superalloys.

2:30pm **A2-2-2 Ultra-Low Thermal Conductivity Yttria Stabilized Zirconia Thermal Barrier Coatings Using the Solution Precursor Plasma Spray Process**, ***M. Gell*** *(mgell@mail.ims.uconn.edu), E. Jordan, J. Roth, C. Jiang*, University of Connecticut

The Solution Precursor Plasma Spray (SPPS) process has the potential of providing more durable and low thermal conductivity thermal barrier coatings (TBCs). The increased durability derives from a highly strain-tolerant microstructure consisting of fine, through-coating-thickness cracks and an increased inter-splat crack resistance associated with ultra-fine splats (<2 microns). Low thermal conductivity SPPS TBCs are associated with unique planar arrays of nano- and micro-porosity that are referred to as inter-pass boundaries (IPBs). Success in this effort will extend the use of YSZ TBCs and minimize the use of rare-earth elements required in most alternate low thermal conductivity TBCs. An extensive series of plasma trials were conducted to produce inter-pass boundaries in the standard, porous SPPS microstructure containing vertical cracks. The key variables influencing the formation of IPBs were determined. A Taguchi Design of Experiments was conducted to optimize the IPB microstructure. The key metric employed throughout this effort was the thermal conductivity of the individual coating, determined initially by using the Object-Oriented-Finite (OOF) Element method and then later, with more accuracy, the Laser Flash Analysis (LFA) method. This presentation will present the results of these trials and show how YSZ thermal conductivity is affected by SPPS processing variables. It will be shown that the thermal conductivity of SPPS YSZ TBCs can be reduced by more than 50% to value of 0.5 watt/meter/oK.

2:50pm **A2-2-3 Observations of Ferroelastic Switching by Raman Spectroscopy**, ***M. Gentleman*** *(molly.gentleman@stonybrook.edu)*, SUNY - Stony Brook, US **INVITED**

Raman spectroscopy has been shown to be a successful tool in the characterization of ferroelastic switching in zirconia based thermal barrier materials. In this study, Raman spectroscopy is used to examine damage induced by erosion testing on EB-PVD thermal barrier coatings. Mapping of thermal barrier coatings has revealed varying degrees of switching depending on erodent angle and temperature. Other studies have also shown the relationship between composition and ferroelastic parameters.

3:30pm **A2-2-5 Impact of Superalloy Composition and Bond Coat Roughness on Plasma-Sprayed TBCs with HVOF NiCoCrAlX Bond Coatings**, ***J.A. Haynes*** *(z15@ornl.gov), K.A. Unocic, B.A. Pint*, Oak Ridge National Laboratory, US

Globally, there is increasing demand for land-based power generation gas turbines that can burn fuels with increasing ranges of impurity levels. Such turbine systems may require different structural materials strategies for the hot section components, as compared to engines designed to burn higher purity fuels. Modifying superalloy compositions to be more resistant to a wider variety of corrosion mechanisms may also impact the performance of standard protective coating systems, particularly over the longer-duration cycles and lifetimes of land-based turbine components. This study investigated the influence of superalloy substrate composition, bond coat surface roughness, cycle length, temperature and water vapor on the furnace thermal cycle lifetime of plasma-sprayed thermal barrier coatings (TBCs). The TBC systems evaluated consisted of air plasma-sprayed (APS), yttria-stabilized zirconia (YSZ) top coatings with high velocity oxy fuel (HVOF)-deposited NiCoCrAlYHfSi bond coatings. Bond coat roughness was increased in selected specimens by overlaying with a larger MCrAlX powder size. The TBCs were deposited on two superalloy compositions, Alloy X4 and Alloy 1483, the latter of which has higher Cr and lower Al content for improved hot corrosion resistance. Furnace cycle experiments were conducted in dry O_2 and air with 10% water vapor at 1100°C and at 1150°C, with cycle lengths of up to 100h.

* corresponding author

KEYWORDS: Coating, oxidation, TBC, alumina, bond coat

3:50pm **A2-2-6 A New Approach to Protect Thermal Barrier Coatings Against CMAS Corrosion using Sol-gel Process**, ***G. Pujol*** *(pujol@chimie.ups-tlse.fr), F. Ansart, J.P. Bonino*, CIRIMAT, France, *A. Malié, S. Hamadi*, Snecma, SAFRAN Group, France

Thermal Barrier Coatings (TBCs) are widely used to protect critical metallic parts in hot sections of gas turbine engines. TBCs are designed to improve the durability of alloy components and the engine efficiency by increasing operating temperature.

Currently, the ceramic layer which provides thermal insulation is industrially deposited by either Air Plasma Spraying (APS) or Electron Beam Vapor Deposition (EBPVD) resulting in lamellar or columnar microstructures, respectively.

In working conditions, TBCs are subject to various kinds of degradation (erosion, F.O.D, oxidation…) which deteriorate integrity and mechanical properties of the system. Moreover, with the aim to increase the turbine inlet temperature, a new type of damage has been highlighted: corrosion by molten Calcium-Magnesium-Alumino-Silicates, better known as CMAS. These particles come from siliceous debris (sand, dust, volcanic ashes…) ingested with the intake air, and form deposits on airfoil surfaces. At the operating temperature, the glassy deposit can melt and infiltrate the ceramic TBC. In fact, its wetting characteristics and its low viscosity allow CMAS to penetrate porosity of the ceramic top-coat. This is particularly true for EBPVD coatings where the vertically oriented microstructure eases the infiltration.

Here, we propose to use sol-gel route, to synthesize new coatings to protect TBC systems from CMAS damage. This soft chemical process has already shown a real potential to make high purity nanocrystalline materials with a controlled morphology. Associated with dip-coating or spray-coating technique, this process allows to produce either thin or thick ceramic coatings with a non-oriented microstructure[1] (in opposition to EBPVD or APS coatings). Our aim, in this study, is to use sol-gel process to realize a protective layer deposited on the conventional EBPVD TBC in order to provide CMAS resistant capability and therefore improve their lifetime. This outer layer could be sacrificial, tight or non-wetting. In this work, several routes have been investigated. Various materials known to be good candidates[2] against CMAS attack have been synthesized and their efficiency in correlation with their microstructure and chemical formulation have been studied.

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[2] S. Krämer, J. Yang, C.G. Levi, Infiltration-Inhibiting Reaction of Gadolinium Zirconate Thermal Barrier Coatings with CMAS Melts, Journal of the American Ceramic Society. 91 (2008) 576-583.

4:10pm **A2-2-7 Interaction of CMAS with MOCVD Coatings in the System Y_2O_3-Al_2O_3**, ***N.K. Eils*** *(Nadine.Eils@dlr.de)*, *P. Mechnich*, *W. Braue*, German Aerospace Center (DLR), Germany

Calcium-magnesium-alumina-silicate (CMAS) particles deposit on protective ceramic coatings in gas turbine engines. High gas temperatures lead to partial or even complete melting of CMAS deposits and subsequent damage of the coatings due to CMAS infiltration, phase formation and spallation. Therefore the development of new coating materials, showing a high resistance against CMAS degradation, is aspired.

The interaction of a model CMAS powder with MOCVD coatings in the binary system Y_2O_3-Al_2O_3 was investigated. Heat treatments at 1200 °C and 1250 °C were carried out on coatings with binary compositions of $Y_3Al_5O_{12}$, $YAlO_3$, $Y_4Al_2O_9$, as well as on pure Y_2O_3 and Al_2O_3 coatings, respectively. The reaction behavior of these coatings in contact to CMAS powder was compared to each other. The investigations were focused on phase relationships and CMAS infiltration behavior. X-ray diffraction was used for phase identification; imaging as well as elemental analyses were carried out by means of scanning electron microscopy (SEM) combined with energy-dispersive X-ray spectroscopy (EDS).

In the reaction zones of each sample, crystallization processes were observed. Formation of anorthite and Mg,Al-spinel were found in aluminum rich coatings, while Ca,Y-oxyapatite, melilite and a new Ca,Y-garnet phase were found in yttrium rich coatings. The pure Y_2O_3 coating forms a continuous layer of oxyapatite in contact with CMAS and shows the best resistance against CMAS infiltration. Concerning the yttrium aluminates the coating with the highest yttrium content ($Y_4Al_2O_9$) reveals less CMAS infiltration and degradation in comparison to the binary $Y_3Al_5O_{12}$ and $YAlO_3$ coatings.

4:30pm **A2-2-8 Examination of CMAS-induced TBC Failure in Typical Service Conditions**, ***V.K. Tolpygo*** *(vladimir.tolpygo@honeywell.com)*, Honeywell Aerospace, US

A new form of CMAS-induced degradation of thermal barrier coatings is described. The principal feature of this process is chemical reaction of some of CMAS constituents with the TGO that bonds TBC to metallic substrate. Such reaction may cause local delamination along TBC-TGO interface and eventually lead to TBC spallation. This mechanism has been observed to reduce TBC lives well below the limit set by oxidation kinetics at a given service temperature. The reaction between CMAS and TGO occurs simultaneously with other commonly accepted degradation mechanisms, such as liquid-phase infiltration and chemical reactions at the TBC top surface. Several examples of CMAS-TGO interaction during burner rig testing of 7YSZ TBC at 1150°C, as well as CMAS-induced TBC failure on engine airfoils are shown. Possible mechanisms of CMAS penetration through TBC and mitigation methods are discussed.

Hard Coatings and Vapor Deposition Technology
Room: Royal Palm 4-6 - Session B4-1

Properties and Characterization of Hard Coatings and Surfaces

Moderator: C. Mulligan, US Army ARDEC, Benet Laboratories, J. Lin, Colorado School of Mines, ACSEL, B. Zhao, Exxon Mobile, USA

2:10pm **B4-1-1 Low-temperature Plasma Surface Hardening of Austenitic and Martensitic Stainless Steels**, ***M. Lei*** *(mklei@dlut.edu.cn)*, Dalian University of Technology, China, *X.M. Zhu*, Dalian Jiaotong University, China **INVITED**

Plasma surface hardening of austenitic and martensitic stainless steels has been performed at low process temperatures below 450° C by plasma-based low-energy ion implantation. A high nitrogen face-centered-cubic (f.c.c.) phase (γ_N) on the plasma-based low-energy nitrogen ion implanted Fe-Cr-Ni austenitic stainless steel and a high nitrogen hexagonal-close-packed (h.c.p.) phase (ε-$Fe_{2+x}N$) on the nitrogen-modified Fe-Cr martensitic stainless steel have a combined wear and corrosion resistance, respectively. The microstructure of the γ_N phase was constructed of the novel CrN_x and FeN_x bonds with a nitrogen concentration up to about 35 at.%. The metastable ε-$Fe_{2+x}N$ phase was observed as a high supersaturated nitrogen concentration up to about 40 at.%. The hardening surface layers on the austenitic and martensitic stainless steels possessed high microhardness for the γ_N phase with $HV_{0.10\ N}$ 20.0 GPa and for the ε-$Fe_{2+x}N$ phase layer with $HV_{0.25\ N}$ 15.7 GPa. The improved wear and corrosion behaviors of the γ_N phase and the ε-$Fe_{2+x}N$ phase were respectively investigated by tribological test on a ball-on-disc tribo meter and by electrochemical test using a standard three electrodes system in 3.5 % NaCl solution. The wear and corrosion resistance mechanism of the γ_N phase and the ε-$Fe_{2+x}N$ phase was explored based on dependence of the composition and microstructure on the wear and corrosion properties. The industrial application using the low-temperature plasma surface hardening has been carried out by the plasma-based low energy nitrogen ion implanted AISI 316L austenitic and AISI 420 martensitic stainless steels.

2:50pm **B4-1-3 Microstructural Origins of Stress Gradients in Nanocrystalline Thin Films: the Dominant Role of Grain Evolution Against Texture**, ***R. Daniel*** *(Rostislav.Daniel@unileoben.ac.at)*, *J. Keckes*, *C. Mitterer*, Montanuniversität Leoben, Austria

The gradual development of microstructure is inherently characteristic for nanocrystalline thin films. It is controlled by competitive growth of adjacent grains and is responsible for the development of depth gradients of stresses if the structure develops from fine at the film/substrate interface to coarse in the film bulk [1]. Film growth is, however, typically also accompanied by the evolution of texture as the preferential orientation of grains may change in the course of film development as a consequence of competitive atomistic processes on the surface of the growing film. This phenomenon has been reported for almost every transition metal nitride thin film material [2, 3]. As soon as the change of the grain size during growth of nanocrystalline films is accompanied with a change of texture, it is not possible to isolate the effect of the individual phenomena on the development of residual stresses. The knowledge of the origin of stress gradients in thin films is, however, crucial in controlling the stress state of these materials. Thus, we discuss in this paper the exclusive effect of the grain size on the development of stress gradients in thin nanocrystalline films irrespective of the film texture. As examples, the stress gradients in TiN films having exclusively either (111) or (100) texture were studied. The effect of the varying film texture on the development of stress gradients is further discussed for TiN films exhibiting a crossover of texture from (100) to (111) with increasing thickness. As an evidence of the depth gradients of stresses in strongly textured film materials, stress measurements of the cross-section of a TiN(100) film by spatially resolved synchrotron nanodiffraction experiments is given. It will be shown that the development of stress gradients in nanocrystalline films is predominantly given by the variation of the grain size, whereas the contribution of the texture changes has only a minor effect.

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3:10pm **B4-1-4 Effect of Tetramethylsilane Gas on the Fabrication of CrZrSiN Coatings by Cathodic Arc Deposition System**, ***T.C. Tseng***, *J.-W. Lee (jefflee@mail.mcut.edu.tw)*, Ming Chi University of Technology, Taiwan, Republic of China, *S.H. Huang*, National Chiao Tung University, Taiwan, Republic of China

The CrZrSiN coatings were deposited on Si wafer and tungsten carbide substrates by cathodic arc deposition system using CrZr target and tetramethylsilane gas. The tetramethylsilane gas flow rate was adjusted to fabricate the CrZrSiN coatings with different silicon contents. The crystalline structure of coatings was measured by a glancing angle X-ray diffractometer. Microstructures of thin films were examined by a scanning electron microscopy (SEM) and transmission electron microscopy (TEM) , respectively. The hardness, adhesion and tribological properties of thin films were measured by nanoindentation, scratch tester and ball-on-disk wear tests. It was found that the micro structure and mechanical properties were strongly influenced by the tetramethylsilane gas flow rate and Si content of the CrZrSiN thin films. The optimal silicon content for the Cr ZrSiN coating was proposed in this study.

3:30pm **B4-1-5 Toughness Measurement of Nanocomposite Coatings by a Micro Double Cantilever Beam Method**, ***S. Liu*** *(sl559@cam.ac.uk)*, University of Cambridge, UK, *X.Z. Ding*, *X.T. Zeng*, Singapore Institute of Manufacturing Technology, Singapore, *W. Clegg*, University of Cambridge, UK

Toughness is one of the most important mechanical properties of protective thin films, especially those under erosive environments. In this paper, a

method is presented for measuring the fracture toughness of hard coatings. Pre-cracked micro double cantilever beams of the coatings are fabricated using focused ion beam, which are subsequently compressed by nanoindentation with a flat diamond punch. The compression exerts a bending moment on the cantilever beams causing the pre- cracks to grow. Thus, the fracture toughness of the coating can be determined as a function of the compression load at the point of crack elongation. Crack growth has been studied experimentally and compared with FE simulations to evaluate effects such as friction between indenter tip and coating surface. This method has been demonstrated using materials of known toughness and found to be useful for materials with a large yield stress to toughness ratio. Finally, this technique was applied to determine the fracture toughness of different PVD hard coatings, which will also be compared and discussed here.

3:50pm **B4-1-6 Microstructure and Characterization of TaN Protective Coatings**, ***K.Y. Liu***, *F.B. Wu (fbwu@nuu.edu.tw)*, National United University, Taiwan, Republic of China

Tantalum-nitride, TaN, coatings were fabricated by magnetron sputtering technique. The microstructure of the TaN coatings was controlled by $N_2/Ar+N_2$ gas flow ratio. TaN coatings showed a columnar structure at a 0.1 $N_2/Ar+N_2$ gas flow ratio. With the increase of the $N_2/Ar+N_2$ gas flow ratio to 0.25, the microstructure of TaN coatings transformed to be nanocrystalline/amorphous . An amorphous structure was found under further increase of the flow ratio. The increase in reactive nitrogen content would suppress the crystallization of TaN coatings during sputtering. TaN multilayer coatings were fabricated by modulation of crystalline and amorphous TaN layers with $N_2/Ar+N_2$ gas flow ratio control. TaN single and multilayer coatings were characterized through thermal annealing, nano-indention and corrosion tests. With the introduction of amorphous/crystalline interface, the multilayer coatings exhibited superior mechanical properties and chemical stability than single layer TaN coatings.

4:10pm **B4-1-7 Structure and Residual Stress Analysis of Titanium Nitride Coatings Produced by DC Magnetron Sputtering**, ***G. Martinez***, *C. Ramana (rvchintalapalle@utep.edu)*, University of Texas at El Paso, US

Titanium nitride exhibits unique physical, chemical, optical and mechanical properties and find application in a wide variety of scientific and technological applications.[1-3] Due to their excellent physical and mechanical properties, TiN films have been in use as protective and wear and corrosion resistant coatings for industrial machinery tools. TiN coatings exhibit beautiful lustrous color and are useful for decorative applications while protecting the components from wear and corrosion. TiN films are also attractive for applications in micro- and nano-electronics. These electronic applications typically take the form of metallization materials or diffusion barriers. The optical properties of films, such as selective spectral range optical transmission and reflection, make these materials interesting for application in solar cells, optical filters, and potentially plasmonics. The present work was performed to understand the effect of film thickness in the nano-scale regime (5-100 nm) on the properties and phenomena of TiN coatings with a special attention towards microstructure and residual stress evolution. TiN samples were grown using DC sputtering method onto Si and MgO substrates. Samples were analyzed employing X-ray reflectivity (XRR), Grazing incidence X-ray diffraction (GIXRD), scanning electron microscopy (SEM) and ψ measurements. Increasing film thickness is found to induce the (111) texture development of TiN coatings. Residual stress calculated using a modified ψ non-destructive technique in Si and MgO substrates giving residual stress of 0.43 MPa and 2.229 MPa, respectively, both in compression. SEM data indicate that increased deposition time improves grain formation and size of the TiN coatings. Rutherford backscattering was used to accurately calculate the film thickness showing thickness in the range of 13.31nm to 119.87nm as well as the compositional percentage of titanium, nitrogen and oxygen in the films. The results are presented and discussed.

4:30pm **B4-1-8 Surface Directed Spinodal Decomposition at TiAlN / TiN Interfaces**, *A. Knutsson, I. Schramm, K. Grönhagen*, Linköping University, IFM, Nanostructured Materials, Sweden, *F. Mucklich*, Saarland University, Functional Materials, Germany, ***M. Odén*** *(magod@ifm.liu.se)*, Linköping University, IFM, Nanostructured Materials, Sweden

Cubic (c)- $Ti_{1-x}Al_xN$ coatings are unstable and isostructurally decompose to c-TiN and c-AlN at elevated temperature for compositions inside the spinodal. Both theoretical and e xperimental studies of this alloy have revealed the detailed characteristics of this decomposition. However, a the details of the early stage spinodal decomposition behavior and the resulting microstructure of $Ti_{1-x}Al_xN$ /TiN multilayers remains unclear . Such study is of interest since the kinetics of the spinodal decomposition is seen to differ compared to monolithic TiAlN. The characteristic of an interface-controlled decomposition is the formation of a layered microstructure parallel to the interface, i.e. surface directed spinodal decomposition (SDSD). If present in TiAlN/TiN layers it could explain the improved high temperature properties observed in these multilayers. Hence, in this study we investigate if SDSD is present in arc evaporated c-$Ti_{0.33}Al_{0.67}N$/TiN and c-$Ti_{0.50}Al_{0.50}N$/TiN coatings and discuss the prerequisites for such decomposition.

We have used DSC, XRD, STEM/TEM-EDX, and 3D atom probe tomography (APT) in combination with 2D phase field simulations to understand the decomposed morphology and the decomposition kinetics. The annealing procedure was chosen such that the spinodal decomposition was at an early stage, i.e. annealing at 700-900 °C with no isothermal period. DSC revealed that the isostructural spinodal decomposition, to c-AlN and c-TiN, in the multilayers has the same onset temperature regardless of composition. The onset is located ~100 °C lower compared to the monolithic coatings. Z-contrast STEM imaging confirms this by showing a decomposed structure of the multilayers at a temperature where it is not present in the monoliths. The APT shows an evolving AlN-rich layer followed by enrichment in TiN at the interfaces in the decomposed state. The phase field simulations also predict such SDSD. The simulations further show that the decrease of the total energy transpires over a longer time period in the multilayers compared to monoliths due to the SDSD. This is in line with the thermograms showing a broader spinodal decomposition peaks from the multilayers. We also note that the microstructure resulting from SDSD in TiAlN is highly dependent on the growth induced elemental fluctuations. The decomposition behavior of the coatings is discussed in terms of internal interfaces, elemental fluctuations, coherency stresses, and alloy composition. Understanding and controlling the evolving microstructure and the onset of the spinodal decomposition by interface architecturing, may facilitate optimization of the cutting performance of TiAlN coatings.

Hard Coatings and Vapor Deposition Technology
Room: Royal Palm 1-3 - Session B6-2

Coating Design and Architectures
Moderator: R. Daniel, Montanuniversität Leoben, M. Stüber, Karlsruhe Institute of Technology

2:10pm **B6-2-1 Design of Novel Protective Coatings for High Temperature Applications**, ***M. Schütze*** *(schuetze@dechema.de)*, DECHEMA-Forschungsinstitut, Germany **INVITED**

There is an increasing demand in high temperature technology for more cost-effective coatings and such that can provide protection under increasingly aggressive high temperature conditions. Powder-pack and slurry coatings have been widely used over the last 2 or 3 decades but still offer a significant potential with regards to these aspects. Recent research at DFI delivered a quantitative model based on thermodynamic and kinetic approaches to quantitatively design the powder pack process with regards to the optimum process parameters. Furthermore, ongoing research is directed towards the target-oriented development of a novel type of slurry coating including multi-element diffusion coatings and non-conventional coatings for extreme environments. The paper will discuss the manufacturing routes and parameters of all these types of coatings and will dwell to a limited extent also on their performance under high temperature conditions.

2:50pm **B6-2-3 Design of Diffusion Coatings Developed via Pack Cementation**, ***A. Naji*** *(naji@dechema.de)*, *M. Galetz, M. Schütze*, DECHEMA-Forschungsinstitut, Germany

Aluminization of steels using Pack Cementaion entails the risk of crack formation within the coating. This is due to a detrimental combination of the brittleness of the aluminium rich intermetallic phases that form, the coating thickness and the mismatch of the coefficients of thermal expansion (CTE) between the substrate and the coating. By means of a new coating design the desired coating properties can be achieved by predicting the required coating manufacturing parameters such as the process temperature, process time and powder composition. Thus, coatings consisting of intermetallic phases (iron and nickel aluminides), which are less brittle and have a CTE which is closer to that of the substrate can be designed with a controlled coating thickness that guarantees the well known good oxidation behaviour of aluminides. Furthermore, a modification using co-deposition of aluminium and another element such as silicon is considered in this coating design.

3:10pm **B6-2-4 Inhomogeneous Structural and Mechanical Properties of Thin Films and Coatings Revealed at the Micro- and Nano-Scale**, ***J. Keckes*** *(jozef.keckes@mu-leoben.at), R. Daniel,* Montanuniversität Leoben, Austria, *A. Riedl, M. Stefenelli,* Materials Center Leoben Forschung GmbH, Austria, *C. Mitterer,* Montanuniversität Leoben, Austria **INVITED**

Nanocrystalline and nanostructured thin films with grain size below 100nm exhibit typically inhomogeneous depth gradients of microstructure, strain and physical properties varying at the nano-scale. Currently, however, it is not trivial to reveal how these gradients relate to the macroscopic film behaviour. One of the main reasons is the lack of reliable experimental techniques which can provide thickness-dependent data with sub-micron resolution.

In this contribution, our recent results from position-resolved synchrotron X-ray diffraction (XRD) studies of microstructure and strain in nanocrystalline films will be presented. The experiments are based on position-resolved XRD performed using monochromatic beams with diameters down to 100 nm. On the examples of CrN, TiN and TiAlN coatings, it will be demonstrated that the newly developed approaches can be used to analyse lateral- and thickness-dependent gradients of strain, crystallographic texture, phases and grain size with sub-micron resolution.

Additionally, results from mechanical tests obtained from bending experiments on micro-cantilevers and indentation will be used to illustrate variability and anisotropy of mechanical properties in nanocrystalline coatings.

Finally, it will be demonstrated that the scanning X-ray diffraction studies and local mechanical characterization can be used as an effective tool to reveal structure-property relationship in inhomogeneous thin films and coatings at sub-micron scale.

3:50pm **B6-2-6 The Effects of Bilayer Periods on the Mechanical Properties of Cr-B-N/Ti-B-N Multilayered Thin Films.**, ***W.T.. Tsai***, *J.-W. Lee (jefflee@mail.mcut.edu.tw),* Ming Chi University of Technology, Taiwan, Republic of China

In this study, the Cr–B–N/Ti-B-N multilayered thin films was deposited using CrB2 and TiB2 targets by a pulsed DC reactive magnetron sputtering system at 250 °C and −150 V substrate bias. The bilayer periods of the Cr-B-N/Ti-B-N multilayer coatings were controlled in the range of 3 to 30 nm. The structures and bilayer periods (L) of multilayer coatings were characterized by an X-ray diffractometer (XRD). The microstructures of thin films were examined by field-emission scanning electron microscopy (FE-SEM). The bilayer periods of the multilayer coatings was evidenced by transmission electron microscopy(TEM). The surface roughness of thin films was explored by atomic force microscopy (AFM). The nanoindentation, scratch tests, Daimler–Benz Rockwell-C (HRC-DB) adhesion tests, pin-on-disk wear tests were used to evaluate the hardness, adhesion, indentation toughness and tribological properties of thin films, respectively. It was observed that the hardness and tribological properties were strongly influenced by the bilayer period of the Cr-B-N/Ti-B-N multilayer coatings. An optimal combination of mechanical and tribological properties behavior was found for a coating with a critical bilayer period of 5 nm.

4:10pm **B6-2-7 Ion Energy Distributions in Cathodic Arc Plasma of AlCr Composite Cathodes in Inert and Reactive Atmosphere**, ***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 past, the energy distributions of ions in vacuum arcs have been studied in great detail under various conditions, including their dependence on arc current level, strength of a magnetic field (if present), pressure and kind of background gases, and the distance from the plasma-producing cathode spots. Most of the work was done using pure elementary cathodes since the presence of two or more elements in the cathodes would most likely further complicate the situation when studying the physics of cathodic vacuum arcs. However, in many practical applications ternary or quaternary thin films are used. For their synthesis it is common to employ composite cathodes consisting of the elements of interest.

In the field of hard and wear-resistant coatings, thin 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 the present study, a mass-to-charge analyser was used to investigate the charge state resolved ion energy distribution functions of Al and Cr as well as the surrounding gases Ar, N_2 and O_2. The number of Al^{++} ions increased by changing the background gas following the sequence from Ar, N_2 to O_2 leading to a higher mean charge state of Al. In contrast, the Cr charge states were reduced. Cr^{+++} ions were only found in Ar atmosphere while the number of Cr^{++} ions strongly reduced in O_2 as compared to Ar and N_2 atmosphere. In terms of cathode composition, both Al ions, Al^{+} and Al^{++}, showed an increase in energy as the Al content in the cathodes was increased. The highest energies of up to 120 eV were recorded in O_2 atmosphere. The Cr ions showed a similar but less pronounced energy dependence on the cathode composition as the Al ions. The observed ion energy distributions were interpreted in the established framework of plasma generation at cathode spots and ion-gas interactions.

Fundamentals and Technology of Multifunctional Thin Films: Towards Optoelectronic Device Applications
Room: Sunset - Session C3-1

Optical Characterization Of Thin Films, Surfaces and Devices

Moderator: J. Krueger, BAM Berlin, Germany, T. Hofmann, University of Nebraska–Lincoln

2:10pm **C3-1-1 In Situ Observation of Sub-monolayer Films and Surface Reconstructions by Polarization Optical Spectroscopy**, ***C. Cobet*** *(christoph.cobet@jku.at),* Johannes Kepler University, Austria **INVITED**

Spectroscopic ellipsometry is a well known and established tool for various types of thin film analysis. It is used to determine for example the dielectric properties in the visible spectral range and film thicknesses directly (reference free) since many years. However, polarization optical methods in general can provide information far beyond these “conventional applications”. The very high accuracy in detecting polarization changes qualifies it for ultra thin film, sub-monolayer and even atomic surface reconstruction sensitivity. On the other hand the optical approach in general permits an application in different environments namely in ultra high vacuum (UHV), gases and in liquid environments. The combination of both capabilities gives us a very powerful tool to explore electronic properties as well as microscopic structure information of surfaces in application relevant surroundings. Together with well known complementary surface science methods like scanning tunnelling microscopy, low energy electron diffraction or photo electron spectroscopy and with the help of *ab-initio* model-calculations it was thus possible to elucidate the surface structures/reconstruction down to the atomic level of several semiconductors and metals under UHV conditions. Our achievements will be exemplarily demonstrated for various arsenides, copper and small organic molecules on Si. In case of these highly symmetric cubic substrates the results are mainly obtained by reflectance anisotropy spectroscopy (RAS/RDS) - a special ellipsometer/polarimeter configuration which yields a surface selective response. In case of the hexagonal III-Nitrides, which are typically grown by metal organic vapour phase epitaxy, surface terminations and reconstructions could be identified by ellipsometry even in gas-phase. Most recently polarization optical methods and scanning tunnelling microscopy were also successively applied to study metal surfaces in electrolytes. This promising approach will be demonstrated by current measurements on copper.

2:50pm **C3-1-3 The Surface Morphology and Optical Properties of Refining Glass Inorganic Nano-molecules**, ***M. Drajewicz*** *(drajewic@prz.edu.pl),* Rzeszow University of Technology, Poland, *M. Pytel,* Rzeszów University of Technology, Poland

New refining technology of soda – calcium – silicon glassy surfaces with inorganic compounds nano-molecules has been presented in the present study. In order to determine modification of the glass surface there were carried out SEM observation and EDAX analysis. The glass samples were subjected to the UV-VIS, photo-elasticity and ellipsometry examination. From obtained results it follows, that refining glass surface by nanopowder inorganic compounds provide to form very thin surface layer. This type of modification improves physical and chemical glass properties.

3:10pm **C3-1-4 Optical Constants of Uranium Trioxide Thin Films, 1.25 to 6 eV**, ***W. Bell***, *D. Allred (allred@physics.byu.edu),* Brigham Young University, US

The optical constants of uranium oxides are important for many applications including monitoring nuclear proliferation and domestic security. Uranium forms many different oxides in many phases, making the study of surfaces and thin films challenging. We used reactive DC magnetron sputtering to prepare uranium oxide thin films on silicon wafer over three thickness ranges, namely about 44nm, 114nm, and 413nm. The partial pressure of oxygen (in argon) was chosen to be high, 40 to 70%, to prepare totally oxidized, that is, UO_3 films. (A planetary system was used to improve sample thickness uniformity.) The x-ray diffraction pattern of the thickest film showed evidence of the presence of UO_3. We characterized the films’ thickness and optical constants via multiangle spectroscopic

ellipsometry (Woollam M-2000). We were able to obtain good fits for all samples. The constants of all three films had similar shapes, showing the typical dispersive behavior of a moderate band gap metal oxide. The n of the material started at about 1.95 in the IR (1.25 eV), rose to 2.2 at 3.1 eV – the direct band of all films studied – and fell thereafter. The imaginary index, k, was much lower in the IR and over most of the visible, began rising slowly at about 2.5 eV and steeply at 3.0 eV reaching a maximum of 0.55 at about 5.5 eV. The 114 nm and 413 nm films were found to have higher apparent optical constants than those of the 44nm film suggesting it was rough or contained voids. Varying the void fraction of the 44nm film as a function of depth within the film allowed its ellipsometric data to be fit reasonably well by constants obtained the 114nm sample. Subsequent AFM showed the 44nm sample to be considerably rougher than the other two (16nm rms roughness versus 7nm for the 413 nm film.

3:30pm **C3-1-5 Infrared Ellipsometry for Characterization of Thin Films**, ***KH. Hinrichs*** *(hinrichs@isas.de)*, Leibniz-Institut für Analytische Wissenschaften - ISAS - e.V., Germany **INVITED**

Ellipsometry is a sensitive and non-contact method for characterization of thin films. Depending on the spectral range from far infrared (FIR) to ultraviolet (UV), ellipsometry can probe conducting, structural, molecular and electronic properties, and thickness. [1,2] Ellipsometry in the mid infrared (MIR) spectral range is meanwhile established for structural analysis of thin films. Examples range from the studies of hydrogen monolayers, silicon oxides, metamaterials, metallic nanowires, metallic island films, polymer films, protein and other ultrathin organic films. [3-11] Recently, IR ellipsometry was introduced as versatile tool for in situ studies during growth or modification of smart surfaces and films in aqueous solutions, thereby used for identification, structural analysis and quantitative determination of optical properties. [8-10]

In the linear optics approach the material-related dielectric function can be described as a sum of the fundamental excitations. Interpretation of the optical response in this approach and the description of the layered sample in an optical model can reversely deliver information on the sample. Using optical models and best-fit simulations, the measured ellipsometric spectra can be interpreted with respect to structure and thickness. By exploring the anisotropic optical properties of vibrational bands, also molecular orientations [11] can be determined.

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4:10pm **C3-1-7 Thickness Optimization of OLED Encapsulation**, ***J.A. Zapien*** *(apjazs@cityu.edu.hk), C.H. To, C.S. Lee, F.L. Wong*, City University of Hong Kong, Hong Kong Special Administrative Region of China

Flexible multi-layer thin films are employed for protecting organic electronic devices against moisture permeation. Besides the inherent absorption associated with the encapsulating materials, internal reflections in the multi-layer configuration leads to interferences which further deteriorate the intensity and color balance of the transmitted light. In this study, the optical properties of a thin film barrier stack composed of alternative co-oxide (silicon dioxide (SiO2) and aluminum oxide (Al2O3)) layer and fluorocarbon (CFx) layer were determined from spectroscopic ellipsometry and transmission analysis. It was also found that the intermix layer on top of CFx and under co-oxide contained a new form of material which exhibited optical properties different from both of them. This new material was responsible for 10% of absorption layer. The result can be applied in thickness optimization in encapsulation design, thus provides a powerful tool to guide the development of enhanced light harvesting applications in OLED devices.

4:30pm **C3-1-8 Effect of Oxygen Gas Flow Rate on the Structure and Optical Properties of Sputter-deposited Gallium Oxide Thin Films**, ***E. Rubio***, *S. Samala, C. Ramana (rvchintalapalle@utep.edu)*, University of Texas at El Paso, US

Gallium oxide (Ga_2O_3), the stable oxide of gallium, finds attractive applications in luminescent phosphors, high temperature sensors, antireflection coatings, and solar cells. Ga_2O_3 has been recognized as a deep ultraviolet transparent conducting oxide (UV–TCO), which makes the material a potential candidate for transparent electrode applications in UV optoelectronics. While conventional transparent oxides are opaque in the UV region due to small band gap (~3 eV), Ga_2O_3 exhibits a wide band gap (~5 eV) and deep transparency to the UV region. In the present work, a detailed analysis of growth behavior, microstructure, and optical properties of β-Ga_2O_3 films grown by sputter deposition is perfromed. Ga_2O_3 thin films were deposited on Si(100) and quartz substrates by keeping the growth temperature constant at 500℃ and varying the flow rate of oxygen during deposition. The characteristic analysis of the samples was performed employing Rutherford Backscattering, X-ray diffraction and Ellipsometry. From the ellipsometry analysis of the samples it was found that the thickness for the samples varied in the range of 22.142-28.975 nm and the refractive index varied from 1.78 to 2.04. It was also found that the deposition rate decreases with increase in oxygen concentration and increases suddenly as the ratio of argon and oxygen reaches 5:5. As the amount of oxygen flow decreases the concentration of gallium in the films increases. The effect oxygen gas flow rate on the composition, crystal structure and optical properties is discussed.

4:50pm **C3-1-9 Optical Emission Spectroscopic Determination of Most Suitable Region for Micro-arc Oxidation on Metal Titanium**, ***H.J. Chu*** *(hjchu88@gmail.com), C.H. Chen, J.L. He*, Feng Chia University, Taiwan, Republic of China

Micro-arc oxidation (MAO) technique, with feature of the low-cost manufacturing, low environmental impact and feasibility for tailoring microstructure, is a relatively novel anodic technique for metal titanium in recent years. As has been revealed that microstructure and properties of the obtained MAO layer are strongly governed with two aspects, i.e. electrical power and electrolyte bath, it was however rarely been discovered to correlate with the discharge being created over the metal surface. Optical emission spectroscopy (OES) technique was thus employed in this study to reveal systematically how the optical-active species in the discharge rule the microstructure and properties of the obtained MAO layer that grown on metal titanium. During MAO process, pH value and power delivery mode were adjusted in a phosphate electrolyte bath, respectively and the discharge over the anodically charged titanium was monitored by an OES system.

Experimental results revealed that the anodic current is much higher in an alkaline bath than in an acidic one, indicating much abundance of the OH^- groups (and the associated sodium ions) participated into anode region. As a result, much higher intensity of the emission lines corresponding to the OH^- group and sodium was detected. Interestingly, rutile phase and $Na_2Ti(PO_4)_2$ phase were both detected in the obtained MAO layer, in addition to the anatase phase that formed when in an acidic bath. Moreover, only OH^- was detected at low discharge voltage and low anodic current (regardless of the pH value), apparently corresponding to an essential anodic current that was contributed by the TiO_2 formation through typical electron tunneling mechanism. Based on these OES findings, a contour map has been constructed to describe the most effective region to form the designated TiO_2 MAO layer.

Keywords: micro-arc oxidation (MAO), optical emission spectroscopy (OES), titanium,

5:10pm **C3-1-10 Deposition of Nanocrystalline SnSe Thin Films by Spin Coating Technique for their Application in Fabrication and Characterization of n-$MoSe_2$/Nc p-SnSe Heterojunction Diode**, ***K. Hingarajiya***, *G.K. Solanki, K. Patel (kdptflspu@yahoo.com), N. Gosai*, Sardar Patel University, India

Transition Metal Chalcogenides e.g. Tungsten diselenide, Molybdenum diselenide, tin selenide were found applications in optoelectronic devices like photoelectrochemical(PEC)Solar Cell, Schottky barrier and P-N junction diode etc. The present paper reports the preparation of Nanocrystalline semiconductor Tin Selenide (Nc p-SnSe) thin films for its electronic device applications. For this purpose, n-$MoSe_2$ crystals grown by Direct Vapour Transport (DVT) technique were used as a substrate and Nc p-SnSe thin films are deposited on to them by economical and simple "spin coating" technique in order to form n-$MoSe_2$/Nc p-SnSe hetrojunction devices. The effect of annealing and thereby particle size of deposited Nc p-SnSe thin films(with glass substrates) on optical band gap are studied by absorption spectroscopy in the wavelength range 200-2200 nm. The current voltage (I-V) measurements of the prepared devices are made in the temperature range 300K-420K under dark condition. The I-V characteristics of n-$MoSe_2$/Nc p-SnSe junction exhibits rectifying behavior that confirms the formation of diode. The diode parameters such as rectification ratio, reverse saturation current (I_0), ideality factor (η), barrier height (Φ_{b0}) and series resistance (R_s) are determined from I-V curves using thermionic emission diode equation. In addition to this Cheung's function and Norde method are also applied to estimate more realistic values of the device parameters. The conduction mechanisms are explained on the basis of the forward bias I-V characteristics using the power law.

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

Friction, Wear, and Lubrication; Effects & Modeling
Moderator: V. Fridrici, Ecole Centrale de lyon, O. Eryilmaz, Argonne National Laboratory, US, S.M. Aouadi, University of North Texas

2:10pm **E1-2-1 Tribology of Hard Carbon Coatings under Ultra- und Super-low Friction Conditions**, ***V. Weihnacht*** *(volker.weihnacht@iws.fraunhofer.de), S. Makowski, F. Schaller, A. Leson,* Fraunhofer IWS, Germany **INVITED**

Hydrogen-free tetrahedral amorp hous carbon (ta-C) films are known to display super-low friction behaviour under boundary lubrication conditions in combination with hydroxyl or carboxyl containing organic lubricants. There is a huge interest to use this effect for technical application in order to reduce friction loss e.g. on engine components or gears and using environmentally friendly lubricants at the same time. Although there are some tribological investigation and first approaches to explain the phenomenon there is still a lack of comprehensive data and understanding of superlubricity behaviour of ta-C. So far it is believed that some kind of a very thin tribochemically reacted friction layer which is formed on the ta-C surface is responsible for the extraordinary low friction. In this contribution a series of tribological investigations with a-C and ta-C coatings, deposited by laser-arc evaporation will be presented. The experiments concentrated on the dependence of lubricant type, sp3-content in the coating, and temperature on the friction and wear behaviour in oscillating sliding wear test. In further experiments, a piston ring on flat configuration with different configurations (coated/uncoated; coated/coated; uncoated/coated) was tested with different lubricants to find out also geometrical influences on tribological behaviour. After the tribological experiments, chemical investigations of mating surfaces in the tribocontact were performed to obtain information on tribofilms and transformation layers.The experimental findings help to get a deeper insight into the superlubricity behaviour of carbon coatings, especially the role of chemical and mechanical effects on friction and wear phenomena.

2:50pm **E1-2-3 Mechanical Properties and Tribological Behavior of a Silica and/or Alumina Coating Prepared by Sol- gel Route on Stainless Steel**, ***A. Marsal*** *(marsal@chimie.ups-tlse.fr), F. Ansart, V. TURQ, J.P. Bonino,* CIRIMAT, France, *JM. Sobrino, YM. Chen, J. Garcia,* Cetim, France

The significant development in the mechanical industry requires a constant evolution of skills, particularly in the area of functionalization and protection of metallic alloys surface. The wear of materials is one of the causes of loss of profitability. This study aims to develop solutions to extend the lifetime of stainless steel 316L or 304L whose raw materials are relatively expensive . The main objective in this study is to increase their durabilility by covering these stainless steels with a protecting thin ceramic film. Thanks to their high hardness values, ceramic coatings would present the best properties to fight against wear. Apart from the conventional deposition way such as PVD or CVD, the sol-gel method allows many choices of formulations avoiding a thermal treatment step at very high temperature.

In this work, we have achieved to optimize protective coatings of stainless steel against wear, using sol-gel method associated with dip-coating technique. We have chosen the silica and alumina compounds which are well known as good candidates to tackle this problem because of their intrinsic properties [1,2]. The combination of both oxides is a very promising way for that kind of application even if the literature is not very abundant on these topics. Several synthesis pathways have been investigated to reach this objective. We propose three new routes to achieve this type of coating. First a mixture of sols precursors of both oxides, second with the previous mixture with the incorporation of suspended particles of silica or alumina and the third one corresponding to a single sol precursor of silica or alumina loaded with oxide particles (silica and/or alumina).

This article investigates the various ratios alumina / silica. Processing parameters such as: i) the speed of withdrawal (that controls the coating thickness) and ii) the temperature of the thermal treatment after deposition, have been studied. Structural properties were evaluated by XRD, NMR and Raman. Tribological behavior of the coating was studied in order to select the suitable composition for the targeted application. The friction and the wear between a couple of materials were investigated using a pin on disk standardized test, ASTM G-99.

[1] W. Zhang, Characterization and tribological investigation of SiO2 and La2O3 sol–gel films, Applied Surface Science. 185 (2001) 34-43.

[2] T. Hübert, J. Schwarz, B. Oertel, Sol-gel alumina coatings on stainless steel for wear protection, Journal of Sol-Gel Science and Technology. 38 (2006) 179-184.

3:10pm **E1-2-4 Tribochemically Active Ti-C-S Nanocomposites - a New Concept for Self-lubricating Coatings**, ***J. Sundberg*** *(jill.sundberg@kemi.uu.se), H. Nyberg, E. Särhammar, K. Kádas,* Uppsala University, Sweden, *L. Wang,* Lanzhou Institute of Chemical Physics, China, *O. Eriksson, T. Nyberg, S. Jacobson, U. Jansson,* Uppsala University, Sweden

Surfaces that provide low friction as well as mechanical stability are desired in many technical applications. As these two requirements are usually fulfilled by changing material properties in opposite directions, a promising route is to design mechanically stable coatings that are tribochemically active, meaning that they have the ability to become modified by the tribological contact in a way that lowers the friction. A well-known example is nanocomposite coatings such as TiC/a-C, from which carbon can be graphitized to create a lubricating surface layer. Another class of materials is the transition metal dichalcogenides (TMDs), such as WS_2 and MoS_2. When subjected to the pressure and shear in a tribological contact, the TMD planes become horizontally aligned and thereby enable easy sliding. In the current work, the concept of tribochemically active coatings is applied in a new way by doping TiC/a-C coatings with sulfur, which can be released in the tribological contact to form low-friction compounds.

Coatings were deposited by magnetron sputtering from titanium and carbon targets, with incorporation of sulfur by reactive sputtering using H_2S gas. It was found that sulfur goes into the carbide phase, creating a doped TiC_xS_y phase in a matrix of amorphous carbon. The incorporation of sulfur leads to a lattice expansion of more than 10%. The possibility of release of sulfur was investigated by annealing, which lead to sulfur removal and lattice contraction.

First-principles calculations using supercells and the exact muffin-tin orbitals method were performed for TiC_xS_y, and the calculated lattice expansions were found to match the experimental ones. Furthermore, the density of states and charge density for TiC and TiC_xS_y were calculated, showing that the incorporation of sulfur leads to filling of antibonding states and that the sulfur atoms occupy larger volumes than carbon atoms.

Tribological testing against steel balls in an unlubricated pin-on-disk setup showed that increasing sulfur content lead to lower friction and longer lifetimes, an improvement that can be due to changes in microstructure as well as chemistry. However, one of the S-rich coatings was also tested against a W-coated steel ball, leading to a distinct friction reduction (to $\mu \approx 0.05$). Transmission electron microscopy in the wear track confirmed the local formation of horizontally aligned WS_2. It has thus been shown that nanocomposite coatings containing the newly discovered TiC_xS_y phase are tribochemically active, and offer new possibilities of designing self-lubricating material systems.

3:30pm **E1-2-5 Lubricious Silver Tantalate Films For Extreme Temperature Applications**, ***D. Stone***, *A. Harbin,* Southern Illinois University, US, *H. Mohseni, J.-E. Mogonye, T. Scharf,* University of North Texas, US, *C. Muratore,* Air Force Research Laboratory, Thermal Sciences and Materials Branch, US, *A. Voevodin,* Air Force Research Laboratory, Materials and Manufacturing Directorate, US, *A. Martini,* University of California Merced, US, *S.M. Aouadi (samir.aouadi@unt.edu),* Southern Illinois University, US

Silver tantalate was investigated as a potential lubricious material for moving assemblies in high temperature tribological applications. Three different approaches were explored for the creation of such materials on Inconel substrates: (1) powders produced using a solid state method which were burnished on the surface; (2) monolithic silver tantalate thin films deposited by magnetron sputtering; and, (3) an adaptive tantalum nitride/silver nanocomposite sputter-deposited coating that forms a lubricious silver tantalate oxide on its surface when operated at elevated temperatures. Dry sliding wear tests of the coatings against Si_3N_4 counterfaces revealed friction coefficients in the 0.06 - 0.15 range at T ~ 750 °C. Reduced friction coefficients were found on nanocomposite materials that contained primarily a $AgTaO_3$ phase with a small amount of segregated Ag phase, as suggested by structural characterization using X-Ray diffraction. Furthermore, cross-sectional transmission electron microscopy techniques determined that the reduced friction coefficient at T ~ 750 °C was primarily the result of the formation of a lubricious $AgTaO_3$ phase that reconstructs during the wear process into a mechanically mixed layer of $AgTaO_3$, Ta_2O_5, and Ag nanoparticles. The presence of nanoparticles of segregated Ag in the thin film further enhanced the performance of these materials by increasing their toughness.

3:50pm **E1-2-6 Lubricious Zinc Titanate Films for High Temperature Applications**, ***V. Ageh*** *(lanryb2@yahoo.com), H. Mohseni, T. Scharf*, University of North Texas, US

This presentation will discuss how defect structure in textured atomic layer deposited (ALD) transition metal oxides films determines friction and wear properties. Specifically this study focuses on the processing-structure-tribological property interrelationships of as-deposited and annealed ALD nanocrystalline zinc titanate ($Zn_xTi_yO_z$) films. Annealed films at 550°C exhibited improved friction (steady-state friction coefficient of ~0.12) and wear rate ($1x10^{-7}$ mm^3/Nm) compared to the as-deposited films. The $ZnTiO_3$ (104) texture, which is present at temperatures up to 550°C, resulted in improved friction and wear compared to other phases/structures, e.g., Zn_2TiO_4 cubic spinel structure, annealed at T>550°C. Nanoscale sliding-induced plastic deformation was possible when HRTEM observed $ZnTiO_3$ (104) stacking faults were sheared parallel to the sliding direction resulting in an intrafilm shear velocity accommodation mode. This subsurface aided in shear accommodation (prevented brittle fracture). Since there is predominately (104) slip (i.e., no interacting slips systems), this further translates to low friction and wear. Thus, it is feasible to generate high temperature lubricious oxides through microstructural control at the nanometer level.

4:10pm **E1-2-7 Study of the Friction Coefficient and Wear of Boride Coating Film on Stainless Steel AISI 410 at Different Temperatures**, ***E. García***, *M. Figueroa (mafguadarrama@hotmail.com), G Ramírez-Castro, I. Campos-Silva*, Instituto Politécnico Nacional, Mexico, *S. Muhl*, Universidad Nacional Autónoma de México - Instituto de Investigaciones en Materiales, Mexico, *A. Cavaleiro*, University of Coimbra, Portugal, *T. Polcar*, Czech Technical University in Prague, Czech Republic

In tribological one of the main environment parameters that affect the behavior of the surfaces is the temperature since this can cause surfaces to undergo changes in their mechanical and structural properties. At relative high temperatures, the oxidation layer can affect the tribological characteristics because this is the contact between two surfaces. The oxide layer can reduce or increase the wear rate and the friction coefficient because of a reduction in the contact or the generation of debris. Boriding is a technique used to increase the hardness and the wear resistance of the surface, particularly at high temperatures.

This work presents the results of a study of the tribological performance of a borided layer on the stainless steel AISI 410 at different temperatures under sliding motion wear testing. The borided layer was generated by the package boriding method at 950 °C for 1 hour. X-ray diffraction showed the presence of crystalline CrB, FeB and Fe_2B phases. The thickness of the boride layer was 11.9 ± 0.86 μm and the hardness was 24 GPa with a roughness of 120 nm. The sliding tests were performed on a pin on disk tester using an alumina ball counter-body (Al_2O_3), with an applied load of 1N. The friction coefficient was seen to increase by approximately by 29% with increasing the temperature from Room temperature to 450 °C, with the wear rate showing a similar behavior.

4:30pm **E1-2-8 Plasma Diffusion Treatments to improve the Tribological Performance of Ti-4Al-4Mo-2Sn**, *G. Cassar (glenn.cassar@um.edu.mt), B. Attard*, University of Malta, Malta, *A. Mattews*, ***A. Leyland***, University of Sheffield, UK

Ti-4Al-4Mo-2Sn is a high strength, forgeable alpha-beta alloy with good high temperature mechanical properties. This alloy has many potential applications in the aerospace industry, which is currently dominated by the widespread use of Ti-6Al-4V. It is increasingly understood that surface engineering treatments need to be designed for the specific substrate material to be treated (this being particularly important for Ti-alloys) and in this respect no study has yet been carried out for the improvement of the tribological properties of Ti-4Al-4Mo-2Sn by surface engineering means. Triode-plasma oxygen and/or nitrogen diffusion treatments have recently been shown to be extremely effective in reducing surface damage and increasing the wear life of several Ti alloys subjected to dry sliding, abrasion and impact wear.

This work focuses on the development of cost-effective enhanced-plasma processing techniques, which will permit the use of Ti-4Al-4Mo-2Sn in tribological applications – even under relatively high loading. The use of low pressure intensified plasmas (at various temperatures in the range of 600-800 ^oC) is shown to allow the diffusion of (for example) nitrogen, to generate deep hardened layers. The process parameters for the surface modification technique are selected such as to minimize degradation of mechanical properties and corrosion resistance in the Ti- alloy. The treated specimens were tested and characterized using a variety of techniques, including X-ray diffraction, electrochemical corrosion testing, optical and scanning electron microscopy, nanoindentation, and nanoscratch testing. Furthermore, the effects on the bulk substrate material were also studied by uniaxial tensile and fatigue testing. The results obtained indicate that the proposed technique is capable of significantly improving the tribological characteristics of the chosen Ti alloy without detriment to the substrate microstructure and mechanical properties. The treated surfaces demonstrate improved corrosion behaviour when compared to untreated control samples.

4:50pm **E1-2-9 Tribological Behavior of Pvd Coated Cemented Carbide Against Superduplex Stainless Steel**, *J.M. Paiva Jr. (josemariopaiva@hotmail.com)*, Faculdade de Tecnologia SENAI Joinville, Brazil, ***R. Torres***, *F.L. AMORIM, P.C. Soares Jr.*, Pontificia Universidade Católica do Paraná, Brazil

In this work three commercial coatings were tested in a pin on disc setup against UNS S32750super duplex stainless steel. In the first part of this project, adhesion and nano indentation measurements were performed in PVD coated cemented carbide substrates. The pin on disc tests were conducted in a CSM tribometer. The tribological pair consisted of PVD coated cemented carbide and super duplex stainless steel. The adopted load and speed, in the pin on disc tests, were 20N and 20 cm/s, respectively. The pin on disc test was conducted with and without lubrication. The results show that the friction coefficient and wear rate is linked to the coating chemical composition. Moreover, the silicon based coating show the lowest interaction with the stainless steel ball resulting in a low wear rate.

5:10pm **E1-2-10 Influence of the Normal Force and Abrasive Slurry Concentration on the Coefficient of Friction of Thin Films in Micro-abrasive Wear Tests**, ***B. Guerreiro***, *R.C. Cozza (rcamara@fei.edu.br)*, Centro Universitário da FEI – Fundação Educacional Inaciana "Padre Sabóia de Medeiros", Brazil

The purpose of this work is to study the influence of the normal force (*N*) and abrasive slurry concentration (*C*) on the coefficient of friction of thin films in micro-abrasive wear tests by rotative ball. Initially, a micro-abrasive wear testing by free rotative ball equipment was designed and constructed, able to measure the coefficient of friction on the tribo-system "thin-film – abrasive slurry – ball". After, experiments were conducted with thin films of TiN, TiC, CrN, TiAlN, HfN, ZrN, TiZrN, TiN/TiAl (multi-layer), TiHfC and TiHfCN, balls of AISI 52100 steel and abrasive slurries prepared with green silicon carbide (SiC) particles + distilled water. All tests were conducted without interruption, and the abrasive slurry was continuously agitated and fed between the ball and specimen. The tangential (*T*) and normal forces were monitored throughout the tests and the coefficient of friction (μ) was calculated by the equation $\mu = T/N$. The results obtained have shown that:

i) The hardness of the thin films presented influence on the coefficient of friction: high hardness was related with low coefficient of friction;

ii) The coefficient of friction behavior and magnitude were independent of the normal force: for the same thin film and different values of normal force, the coefficient of friction remained, approximately, unchanged;

iii) The concentrations of abrasive slurries affected the magnitude of the coefficient of friction: high abrasive slurry concentration was related with low coefficient of friction.

New Horizons in Coatings and Thin Films
Room: Sunrise - Session F1-1

Nanomaterials, Nanofabrication, and Diagnostics
Moderator: Y. Yamada-Takamura, Japan Advanced Institute of Science and Technology, Y. Gonzalvo, Hiden Analytical Ltd.

2:10pm **F1-1-1 The influence of Reaction Temperature and Volume of Oleic Acid to Synthesize SnS Nano Crystals by using Thermal Decomposition Method**, ***B. Liang***, National Cheng Kung University, Taiwan, Republic of China, *S.C. Wang*, Southern Taiwan University of Science and Technology, Taiwan, *Y.M. Shen, J.L. Huang (jlh888@mail.ncku.edu.tw)*, National Cheng Kung University, Taiwan, Republic of China

We report synthesis of SnS nano crystals and their size variation with the reaction temperature, and volume of the oleic acid (OA) solvent. These nano crystals were synthesized by using a tin precursor, Sn(OA)x prepared by tin oxide (SnO) with different moles of oleic acid, and mixture of sulfur and oleylamine (OLA) were injected into the solution at different temperatures under argon atmosphere. The SnS nano crystals show orthorhombic crystal structure, and the average particle size is increased from 20 nm to 50 nm and lastly to 200 nm with the increase in temperature from 150 °C to 180 °C and to 210 °C. Careful observations indicate a gradual change in the shape of these nano crystals from spherical to sheet

like structure with the increase of oleic acid volume (2 – 5 mmol). The tin sulfide (SnS) films will then grew by spin-coating method and subsequently the film will be applied as an absorber for solar cells in future work. The as-prepared SnS samples and films will be characterized using XRD, SEM and TEM to investigate the structure, phase composition, surface morphology and microstructure. The optical properties of SnS films will be studied by using UV-visible spectroscopy.

2:30pm **F1-1-2 Nanoparticles Deposition by Temporally Shaped Femtosecond Pulsed Laser: In Situ Plasma and Nanoparticles Diagnostic**, ***F. Bourquard*** *(florent.bourquard@univ-st-etienne.fr), J.P. Colombier, A.S. Loir, C. Donnet, R. Stoian, F. Garrelie,* Laboratoire Hubert Curien, UMR 5516, Université de Lyon, Université Jean Monnet, France

This study proposes the simultaneous *in situ* study of both components of the femtosecond laser ablation plume: vaporized plasma and nanoparticles. Metallic materials irradiation by a femtosecond laser is investigated by time-resolved optical spectroscopy. The atomic species quantities and kinetics are studied via one dimensional space and time-resolved emission spectroscopy. Nanoparticles size distribution is studied via optical extinction spectroscopy, thanks to comparison of experimental data with simulated radius-dependant optical extinction cross section, calculated thanks to Mie theory. Those results are then compared with *ex situ* SEM measurement of nanoparticles distribution produced by PLD.

Influence of temporal tailoring of the pulses shape has been explored by stretching femtosecond pulses into picosecond pulses, and splitting the pulses into double pulses with various delays. This permits to extend the duration of interaction by two different ways, separating the influence of duration versus pulse shape.

The results allow exploring the various mechanisms of material ejection close to characteristic time constants of the materials (electron-phonon coupling, thermal dilatation…). This gives insight on the opportunity to favour nanoparticles generation over plasma formation processes, and ultimately on the possibility to control nanoparticles size distributions via temporally shaping femtosecond laser pulses.

2:50pm **F1-1-3 Nanoparticle Synthesis via Laser-induced Plasma in Liquid Environment**, ***T. Ito*** *(tsuyohito@ppl.eng.osaka-u.ac.jp),* Osaka University, Japan **INVITED**

The tremendous interest in various nanostructures is stimulated by the multifunctional characteristics of such materials and the possibility to tune their properties controlling the size, morphology, chemical and phase composition, and surface states. Laser ablation in liquid (LAL) has attracted a lot of attention as one of synthetic techniques to prepare new attractive nanomaterials, with the ability to control both product chemistry and morphology in many systems. Recently, a number of novel nanostructures prepared via this approach have been reported, with diverse chemistries and morphologies. Here, we expand the technique, which was normally limited to the ambient pressure (1 atm), to higher (up to subcritical or even supercritical) pressures, in order to study the effect of pressure and prepare novel nanomaterials with unique properties.

The ablated target and liquid medium used in this study were Zn plates and deionized water, respectively. A nanosecond Nd:YAG laser with the wavelength of 532 nm was applied to irradiate Zn targets placed in a high-pressure cell with the inner volume of approximately 20 ml. The repetition pulse rate was 10 Hz, and the laser power was approximately 30 mJ/pulse. No heating, except for locally induced by laser pulses in pressurized water, was applied, while the pressure was varied from 0.1 MPa (1 atm) to ~30 MPa.

X-ray diffraction (XRD) measurements indicated that the resulted nanoparticles were ZnO. Their average size was approximately 10-20 nm depending on medium pressure, which was confirmed by both transmission electron microscopy observations and XRD measurements. The nanoparticles prepared at higher pressures demonstrated smaller sizes and more homogeneous size distribution. Photoluminescence spectroscopy was performed by using a 266-nm pulsed laser as the excitation source. All collected spectra exhibited a relatively sharp emission peak in the UV range and a broad emission band at ~570 nm. With the increase of medium pressure, the position of the former was shifting to narrower wavelengths (higher energies), while the relative intensity of the latter (at ~570 nm) was gradually increasing. Interestingly, a discontinuity in the visible emission enhancement of the product was observed near ~22 MPa, which is believed to be associated with the critical pressure of water (22.1 MPa).

More details on the Zn ablation, as well as the use of other targets/media, will be presented at the conference.

3:30pm **F1-1-5 Bonding of Metallic Nanoparticles**, ***M. Chandross*** *(mechandross@gmail.com), T. Boyle, B. Clark, P. Lu,* Sandia National Laboratories, US

In order to create novel nanosolders that bond at lower processing temperatures, it is important to understand the fundamentals of bonding between metallic nanoprticles. Next generation solders can potentially avoid issues with processing, reliability and manufacturing that plague conventional solders. We present the results of large scale molecular dynamics simulations aimed at revealing the mechanisms responsible for reactions at nanoscale metallic interfaces. Specifically, we study the bonding of Ag/Ag and Ag/Cu nanoparticles of varying radii at a range of temperatures. The specifics of the bonding process and the stable final states, both above and below the bulk eutectic temperature, will be compared to high resolution experiments conducted with an aberation correct STEM.

3:50pm **F1-1-6 The Preparation of FeS_2 Pyrite Nanocrystal Inks for Photovoltaic Thin Film**, ***S.C. Hsiao****, K.W. Wu, S.H. Huang, S.H. Chiu, L.H. Chou (lhchou@mx.nthu.edu.tw),* National Tsing Hua University, Taiwan, Republic of China

Semiconductor nanocrystals (NCs) are promising building blocks for next generation photovoltaic devices. FeS_2 (pyrite) NCs have been considered as a superior semiconducting material for solar energy conversion and photoelectrochemical applications since it possesses an appropriate band gap of ~1 eV and a very high absorption coefficient ($\alpha = 5x10^5$ cm^{-1}). These characteristics coupled with the low cost, environmental compatibility, and abundant elements in the crust make pyrite to be a potential candidate for solar cell absorption layer materials in the form of ultrathin films (< 100 nm). NCs coating technique, which requires a well-dispersed NC ink, is simple and low-cost compared with the traditional vacuum processes for depositing pyrite thin films. However, as the surface energy of NCs is significantly higher than that of larger particles, NCs will tend to agglomerate and disable the formation of continuous, smooth ultrathin films.

In this report, well-dispersed, stable pyrite NC inks were successfully produced by beads-milling technique and smooth pyrite thin films less than 50 nm were produced by coating the dispersed pyrite NC inks on various substrates. Such a work has not been reported up to date and will be interesting to the field.

Initially, 50 μm zirconia beads and a surfactant in a solvent were utilized for grinding and dispersing the pyrite NC clusters comprising pyrite NCs with sizes of 10 to 20 nm. The dynamic light scattering (DLS) was used to measure particle size distributions over time during the milling process. The NCs' size, shape, and dispersive condition after beads milling were observed by transmission electron microscopy (TEM). X-ray diffractometer (XRD) was employed both before and after beads milling process to check any structure and crystallinity changes of pyrite NCs.

Pyrite thin films less than 50 nm were then spin-coated using the well-dispersed NCs inks. In order to obtain high quality pyrite thin films, post annealing treatment at 400 °C were conducted. The grazing incidence XRD (GIXRD) patterns were applied to show the intensity and FWHM of pyrite peaks. The Hall measurements revealed the semiconducting character of the thin films. The photoelectron emission and Tauc plot will be utilized to determine the band diagram of pyrite thin films.

4:10pm **F1-1-7 Morphological and Optical Properties of AlN Nano-islands Prepared by Plasma Enhanced Chemical Vapor Deposition**, *Z. Bouchkour,* Université de Limoges - CNRS, France, *E. Thune,* ENSCI-CNRS, France, *C. Jaoul (jaoul@ensil.unilim.fr), J.C. Orlianges,* Université de Limoges - CNRS, France, *R. Guinebretière,* ENSCI-CNRS, France, *P. Tristant,* ***C. Dublanche-Tixier****,* Université de Limoges - CNRS, France

With a band gap of 6.1 eV [1], AlN appears to be an ideal material for the development of deep ultraviolet, vacuum UV, and extreme detectors [2] The 6.1 eV band gap permits the visible background to be intrinsically suppressed and the detectors to operate at room temperature. Results of a LED based on aluminium nitride with an emission wavelength of 210 nm (which is the shortest ever reported) have been recently published [3]. The estimated efficiency of this AlN LED is still lower than for commercial LED but it could be greatly improved by the introduction of carrier confinement structure such as quantum dots. With quantum dots, restrictions due to material properties are shifted or lifted [4] and thus AlN nanostructures could be used successfully in the applications previously mentioned.

In this work, ultrathin AlN films were grown by plasma enhanced chemical vapor deposition (PECVD). The precursors used were nitrogen (N_2) as plasma source and nitride precursor and trimethylaluminium (TMA) as aluminium precursor diluted in Ar. A particular attention has been paid to control the deposition time using a shutter above the substrate holder. The surface morphology of the films has been observed by AFM (Atomic force

microscopy) in tapping mode under ambient atmosphere at room temperature, in order to characterize the size and surface density of nano-islands on the surface. To verify the crystalline development and preferential orientations relative to the substrate, X-ray diffraction measurements are performed. Spectroscopic ellipsometry (SE) measurements were used to determine the optical properties of the samples and to extract the optical band-gap energy (Eg).

The presence of the shutter greatly improved both cristallinity and chemical composition of the films. Deposition at different time allowed proposing a growth mechanism with a favorable time range to obtain isolated nano-islands. The evolution of Eg versus the deposition time showed that the quantum confinement theory was followed.

[1] J. Li, K.B. Nam, M.L. Nakarmi, J.Y. Lin, H.X. Jiang P. Carrier, S.-H. Wei, Appl. Phys. Lett. 83, 5163 (2003)

[2] J. Lia, Z.Y. Fan, R. Dahal, M.L Nakarmi, J.Y. Lin, H.X. Jiangb, App. Phys. Letters 89, 213510 (2006)

[3] Y. Taniyasu, M. Kasu, T. Makimoto, Nature 441 (7091), 325 (2006)

[4] J. Stangl, V. Holy, G. Bauer, Rev. Mod. Phys. 76, 725 (2004)

4:30pm **F1-1-8 Effect of Indium Concentration on Luminescence and Electrical Property of Indium Doped ZnO Nanowires**, ***S.Y. Lim***, National Cheng Kung University, Taiwan, Republic of China, *R.C. Wang*, National University of Kaohsiung, Taiwan, *C.P. Liu*, *S. Brahma*, *J.L. Huang (jlh888@mail.ncku.edu.tw)*, National Cheng Kung University, Taiwan, Republic of China

Indium-doped ZnO nanostructures are regarded as promising candidates for transparent conductors, gas sensors, and photodetectors due to their good physical properties. In this work, we report the structure, microstructure, luminescence and electrical property of ZnO nanowires doped with indium (In) and, effect of In concentration on these properties. Indium doped ZnO nanowires have been grown on Si substrate by Chemical Vapor Deposition (CVD) method, at relatively low temperature (550 °C). A thin ZnO layer with (0002) preferred orientation was deposited on the Si substrate as seed layer by sputtering, which facilitates the growth of well-aligned ZnO nanowires. The average diameter and length of these nanowires varies from 50-180 nm and 10-15 μm, respectively. These nanowires are single crystals having (0001) growth direction. Series of experiments were carried out to estimate the possible solubility of In in ZnO. The maximum solubility of In in ZnO, that has been achieved by this growth process is 3.4 at. %. Photoluminescence (PL) study shows both UV emission and visible luminescence. Careful observation indicates a red shift in the UV emission in the PL pattern and the intensity of the green emission is increased with increasing indium content. Effect of indium concentration on the electrical properties of these nano-wires has also been investigated.

4:50pm **F1-1-9 Carbon Monoxide-induced Reduction and Healing of Graphene Oxide**, *B. Narayanan*, *S.L. Weeks*, Colorado School of Mines, US, *B. Macco*, Eindhoven University of Technology, Netherlands, *J.-W. Weber*, Eindhoven University of Technology, Netherlands, *M.C.M. van de Sanden*, Dutch Institute for Fundamental Energy Research, Netherlands, *S. Agarwal*, ***C. Ciobanu*** *(cciobanu@mines.edu)*, Colorado School of Mines, US

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, we 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.

5:10pm **F1-1-10 Studies on the Optoelectronic Characteristics of the V_2O_5-PtO_2 Core-shell Nanowires**, ***K.Y. Pan***, National Tsing Hua University, Taiwan, Republic of China, *K.C. Chen*, Chinese Culture University, Taiwan, Republic of China, *H.C. Shih (hcshih@mx.nthu.edu.tw)*, National Tsing Hua University, Taiwan, Republic of China

V2O5-PtO2 core-shell nanowires have been successfully synthesized through a two-step process. Firstly, high-quality V2O5 nanowires were fabricated by thermal evaporation. Secondly, PtO2 layers were deposited on V2O5 nanowires by atomic layer deposition (ALD). SEM photos show abundant and intensive V2O5 and V2O5-PtO2 core-shell nanowires on the silicon substrates. From HRTEM images of V2O5 core-shell nanowires, it is clear that the depositions of PtO2 particles are quite compact on V2O5 nanowires. The diameter of V2O5 nanowires is 196nm, and the diameters are 215 nm and 247nm at different cycles: 50 cycles and 100 cycles, respectively. By XRD, EDS and XPS results, the core-shell nanowires are composed of V2O5 and PtO2. According to the field emission examination at working function (5.3 eV), the field enhancements(β) of V2O5 nanowires, V2O5-PtO2 core-shell nanowires with 50 cycles and 100 cycles are 573, 1089 and 1487. To further investigate the optoelectronic properties of V2O5-PtO2 core-shell nanowires, the tests of Raman spectra and I-V curve were handled as well.

Applications, Manufacturing, and Equipment
Room: California - Session G3-1

Atmospheric and Hybrid Plasma Technologies
Moderator: H. Barankova, Uppsala University, D. Pappas, EP Technologies, LLC

2:10pm **G3-1-1 High Performance Thin Films for Aerospace Applications**, ***A. Ranade*** *(alpana.n.ranade@boeing.com)*, *M.A. Matos*, The Boeing Company, US

The usefulness of polymer-based materials and coatings in aircraft components is two-fold. First, weight reductions are highly desirable to decrease fuel consumption and second, polymer-based materials are usually less expensive and more convenient to manufacture than alternative transparent materials such as glass. However, when used in applications with strict optical requirements, these polymeric surfaces can be susceptible to erosion which results in increased haze and decreased clarity. For example, when staple 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. Still, improvements to the processes involved can decrease the required long drying times and can offer long term solutions in which the resistance to erosion is maintained overtime. Advanced thin film coatings based on Plasma Deposition Technologies can improve the durability of many components on aircrafts. These technologies can be exploited to generate materials with high performance, which are also environmentally friendly and produced with waste free processes. We are currently focusing our efforts in the development and study of thin films that improve resistance to material erosion when deposited on polymeric substrates for applications in the aerospace industry and defense.

2:30pm **G3-1-2 The Effect of Processing Parameters and Substrate Composition on the Corrosion Resistance of Plasma Electrolytic Oxidation (PEO) Coated Magnesium Alloys**, ***R. Hussein***, *D. Northwood*, *X. Nie (xnie@uwindsor.ca)*, University of Windsor, Canada

Magnesium alloys are considered one of the more promising materials for future use in many engineering applications. However, due to their high chemical and electrochemical reactivity, magnesium alloys have poor corrosion resistance in aqueous environments. Improving their corrosion resistance by coating can greatly extend their application. One promising coating method is plasma electrolytic oxidation (PEO). The nature of the coating formed, and the ultimate corrosion performance, depends on the both the processing parameters (electrolyte, current density, current mode, processing time) and specific Mg-alloy substrate. In the present study, PEO coatings were produced on three different Mg-alloys (AJ62, AM60B and AZ91D) using different processing parameters. Optical Emission Spectroscopy (OES) was used to characterize the plasma species and other parameters and scanning electron microscopy and XRD were used to characterize the coatings. The corrosion resistance was evaluated using potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) tests in an aqueous 3.5% NaCl solution. Relationships are drawn between PEO processing parameters and substrate composition and the corrosion performance.

2:50pm **G3-1-3 PVD-Quality Coatings at Atmospheric Pressure**, ***D.N. Ruzic*** *(druzic@illinois.edu)*, *Y.L. Wu*, *Z. Ouyang*, *P. Raman*, *T.S. Cho*, University of Illinois at Urbana-Champaign, US **INVITED**

PVD-Quality coatings made with a laser-assisted plasma-coating technique at atmospheric pressure (LAPCAP) for depositing thin yttria-stabilized-zirconia (YSZ) films has been developed at Illinois. This technique allows columnar-structured YSZ films with a thickness of 1~5 μm to be prepared on a Ni-based superalloy substrate at atmospheric pressure. The

atmospheric pressure plasma is generated in a microwave-induced plasma torch system with a gas temperature T_g of more than 2,000 °C. A pulsed laser ablates a YSZ sample that is inside the plasma-torch plume. The ablation energy desnisty is adjusted to produce atomic flux as opposed to clusters. In this manner, deposition is atom-by-atom just as in PVD systems. Optical emission spectroscopy (OES) technique has been used to spatially analyze some critical characteristics of plasma, such as electron density ($n_e > 10^{15}$ cm^{-3}), electron temperature ($T_e \sim 1$ eV), and plasma gas temperature ($T_g \sim$ 800-1200 °C). The thermally grown oxide (TGO) layer is found to affect the film morphology significantly, and characteristics of TGO grown by pre-heating the substrate to 800-1200 °C are investigated. TGO in the form of α-Al_2O_3 with a thickness of ~ 1 µm is found to provide a means to deposit high quality, adhesive thin YSZ films on substrates with columnar microstructure, same as seen in films by high-vacuum electron-beam PVD method. The morphology and characteristics of the films have been compared at various deposition temperatures (100-1200 ºC) and laser energy density (1-10 J/cm^2). Aluminum Oxide of different phases were also made with plasma coating at atmospheric pressure without laser assistance using solid Aluminum cylinders and a Helium/nitrogen gas mixture, with a thickness of 1-2 µm obtained on a stainless steel substrate. The morphology of both films were analyzed using microanalysis techniques such as scanning electron microscope (SEM), focused ion beam (FIB), X-ray photoelectron spectroscopy (XPS), and X-ray diffraction (XRD). The ability to make PVD-quality thin film coatings without the need for a vacuum system opens up a host of new applications which will be dicussed.

3:30pm **G3-1-5 Atmospheric Plasma Treatment Inside Hollow Substrates**, ***H. Baránková****, L. Bardos (Ladislav.Bardos@Angstrom.uu.se)*, Uppsala University, Sweden

Atmospheric plasma treatment of surfaces brings about a number of application options including inner treatment of hollow substrates and tubes. This work describes first results of both the atmospheric plasma surface treatment and the PECVD of carbonaceous films in narrow holes and tubes with the inner diameter of about 10 mm. The experiments were carried out by the Hybrid Hollow Electrode Activated Discharge (H-HEAD) atmospheric plasma source. The air plasma column inside the steel pipe increased the surface energy within seconds which provides a better adhesion of subsequent lacquers or coatings. The PECVD was tested by carbon precursors represented be alcohol vapor or a simple LPG (Liquefied Petroleum Gas). The plasma treatment was examined by the contact angle measurements. The carbonaceous coatings were studied by SEM and Raman spectroscopy. Options and arrangements for treatments of longer and broader tubes are briefly discussed.

3:50pm **G3-1-6 ICP Dual Frequency Discharges: A Potential Tool for Large Area Plasma Processing**, ***A. Mishra*** *(anurdi@gmail.com), T.H. Kim, K.N. Kim, G.Y. Yeom,* Sungkyunkwan University, South Korea

The plasma processing is being extensively used in microelectronic industry for manufacturing various electronic devices. Presently, the semiconductor industry is looking forward to move for fabrication of electronic devices at a few tens of nano-meter level. However, the device fabrication cost increases as the size of electronic device reduces. Therefore, large area wafer size is necessary to be adopted in order to improve productivity and optimize the fabrication cost of such microelectronic devices. According to a technology trend forecast, the wafer size will be 450 mm in diameter within a few years.

The most significant challenge for fabrication on a large area wafer size is to precisely control the distribution of plasma species over the substrate. Various ideas, such as segmented and gridded antennas, capacitively coupled plasmas (CCP) and very high frequency capacitively coupled plasmas (VHF-CCPs) have been proposed and implemented to achieve large area plasma sources with enhanced discharge uniformity over the substrate. Due to ability of being operated at low pressure, high plasma density, easier plasma uniformity control and the separation of discharge production and ion acceleration mechanism of the ICP sources turned the research direction towards developing and investigating the ICP sources for large area microelectronic device fabrication. However, scaling up conventional ICP sources pose some problems such as increased antenna impedance that, in turn, increase RF voltage drop across the antenna and therefore, decrease average power transfer efficiency to the discharge and produces azimuthal non-uniformity due to the standing wave effect. To overcome this issue, a novel approach of dual frequency dual antenna inductively coupled plasma (DFDA-ICP) source has been adopted. The experiments that demonstrate center to edge plasma density control, modulation of plasma parameters, electron energy distribution (EED) and Ion Energy distribution (IED) will be described in this presentation.

4:10pm **G3-1-7 Effects of Low Energy Plasma Immersion Ion Implantation of Nitrogen on Titanium**, ***R. Rao*** *(rammohanrao.k@gmail.com),* GITAM Institute of Technology, GITAM University, India

Plasma immersion ion implantation (PIII) of nitrogen on titanium at variable energies has been performed. The samples after metallographic polishing and ultrasonic cleaning were placed in the evacuated chamber of the implanter. The post implanted samples were subjected to X-ray diffraction and Scanning Electron Microscopic studies for the phase analysis and surface topography. After implantation a layer of titanium nitride with crystallographic orientations (111) and (200) had been formed.

Potentiodynamic polarization tests of the post implanted samples in Hank's solution were performed. Formation of nitrides in post implanted solution showed a higher resistance to corrosion at lower implantation energy.

Coatings for Use at High Temperature
Room: San Diego - Session A2-3

Thermal and Environmental Barrier Coatings
Moderator: R. Trice, Purdue University, D. Litton, Pratt & Whitney, V. Maurel, Mines-ParisTech, France

8:00am **A2-3-1 Environmental Barrier Coatings for Turbine Engines: Current Status and Future Directions**, ***D. Zhu*** *(Dongming.Zhu@nasa.gov)*, NASA Glenn Research Center, US **INVITED**
Ceramic environmental barrier coatings (EBC) and SiC/SiC ceramic matrix composites (CMCs) will play a crucial role in future turbine engine systems because of their ability to significantly increase engine operating temperatures, reduce engine weight and cooling requirements. Advanced EBC systems for low emission CMC combustors and turbine airfoils are currently being developed under the NASA Fundamental Aeronautics and Intergraded System Research Programs to meet engine emission and performance goals. This paper emphasizes the NASA's EBC system development paths for SiC/SiC ceramic matrix composites, focusing on the evolution of advanced EBC systems and material stability challenges that have been overcome in the last decade. Advanced EBC-CMC component testing and demonstrations under the NASA development programs will be discussed, and degradation modes and temperature capabilities of the state-of-the-art environmental barrier coating systems on SiC/SiC CMCs will be reviewed. The next generation turbine EBC systems still needs to be validated when using new compositions such as multicomponent hafnia, rare earth - transition metal alloyed silicates and high stability EBC bond coat systems. The EBC system development aiming at prime-reliant, enabling turbine engine CMC turbine airfoil temperature capability and long-term durability will largely benefit from the advances in the coating vapor processing techniques and sophisticated simulated engine high pressure and high velocity combustion environmental durability testing, combined with creep and fatigue loading conditions.

8:40am **A2-3-3 Y_2SiO_5 Coatings Fabricated by RF Magnetron Sputtering**, ***P. Mechnich*** *(Peter.Mechnich@dlr.de)*, German Aerospace Center (DLR), Germany
Owing to its high stability, Yttrium monosilicate (Y_2SiO_5) is considered a very promising candidate material for protective coatings of ceramics and ceramic matrix composites. In particular, protection against high-temperature oxidation and recession in water-vapor rich environments is required. In the preset work, Y_2SiO_5 coatings were deposited on CVD-SiC pre-coated C/SiC, and Al_2O_3-based ceramic substrates by RF-magnetron sputtering, respectively. Despite a polycrystalline Y_2SiO_5 target was employed, XRD-analysis reveals that Y_2SiO_5 coatings are non-crystalline in the as deposited state. Microstructural analysis shows a dense, glaze-like coating morphology, exhibiting a good conformity. As deposited, glassy Y_2SiO_5 is stoichiometrically homogenous, and virtually free of cracks and macropores. Annealing performed at 1200°C induces crystallization of the low-temperature polymorph X1-Y_2SiO_5. Moreover, formation of closed macroporosity is observed, which is due to the coalescence of former nanopores. Annealing of the CVD-SiC coated substrates in reducing and oxidizing atmospheres produces multiple, serious effects. Crack formation is explained by the glaze-like properties along with thermal expansion mismatch. In reducing atmosphere a significant decomposition of Y_2SiO_5 to Y_2O_3 is observed at the coating surface. On the other hand, in oxidizing atmosphere the SiC substrate forms SiO_2 which reacts with Y_2SiO_5 to highly porous $Y_2Si_2O_7$ at the coating/substrate interface. In case of oxide substrates, no undesired interface reactions occur below the eutectic temperature, therefore sputtered Y_2SiO_5 coatings may be suitable protective overlays for hot flowing water-vapor rich atmospheres.

9:00am **A2-3-4 Optimum Design of High Temperature Thermal Radiation Energy Reflection Coatings for SiC/SiC Components**, ***Y. Kagawa*** *(kagawa@rcast.u-tokyo.ac.jp)*, National Institute for Materials Science, Japan **INVITED**
Thermal radiation energy reflection coatings using all oxide ceramic materials have been designed. All oxide ceramics, such as Al_2O_3, ZrO_2 etc., base multi-scale laminate structure is modified to obtain maximum efficiency of reflectance of thermal radiation energy from high temperature radiation source. Systematic analysis has been done for optimization of the reflectance using interaction behavior between electromagnetic wave and the multilayer laminate structure. Effects of individual layer shape/dimension and interface morphology between oxide ceramics on the reflectance are also incorporated in the analysis. Thermal radiation energy transfer model, which includes high temperature heat source T_s and coating temperature T_c, (T_s>T_c) is used for optimization of the microstructure. Discussions are made for future application of the coatings for SiC/SiC components; especially contribution for simple cooling system and reduction of cooling energy loss.

9:40am **A2-3-6 Tridimensional Analysis of Interfacial Defects Consequences on Delamination of Thermal Barrier Coatings**, ***R. Soulignac*** *(romain.soulignac@ensmp.fr)*, Mines-ParisTech, France
Thermal barrier coatings (TBC) used for aerospace turbine blades endure severe thermal and mechanical loadings. Modeling their lifetime is a major challenge for aeronautical industry. The considered material is the Ni-base superalloy AM1 coated with (Ni, Pt) Al and Y_2O_3 yttria-stabilized ZrO_2 zirconia. A previous lifetime model [1] was established using mechanical compression tests on thermally damaged specimens: the maximum strain before spallation was defined as a failure criterion, which evolves with damage.

This study aims to model the delamination propagation of the ceramic layer. Mechanical compression tests were conducted in order to measure the delamination area during the propagation. The delaminated area was measured using image analysis and evaluated as a function of the applied mechanical loading. The delamination rate was derived from this measurement performed for different ageing at high temperature. Infrared thermography is used as non-destructive tests (NDT) for damaged areas estimation. An image correlation software also allows us to obtain local strains during the test.

A macroscopic cohesive zone model (CZM) was finally identified to model the propagation of the delamination. Based on original 3D measurements [2], interfacial roughness and measured porosity are meshed. A finite element analysis (FEA) including CZM and microstructure details was performed to assess the criticality of the interfacial defects.

REFERENCES

[1] C. Courcier and V. Maurel and L. Rémy and S. Quilici and I. Rouzou and A. Phelippeau, *Interfacial damage based life model for EB-PVD thermal barrier coating*, Surface and Coatings Technology 205 (2011) 3763-3773.

[2] V. Maurel and R. Soulignac and L. Helfen and F. N'Guyen and T.F. Morgeneyer and A. Köster and L. Rémy, *3d damage evolution measurement in tbc using synchrotron laminography*. Oxidation of Metals, Accepted for publication, 2012.

10:00am **A2-3-7 Adsorption of Various REs Atoms on NiAl and Al2O3 Surface: An Implication for Grain Boundary Diffusion in Thermal Barrier Coatings**, ***T. Zhang***, *H.B. Guo (guo.hongbo@buaa.edu.cn)*, Beihang University, China
We use first-principles density functional theory to investigate adsorption of five reactive elements (REs), including Hf, Zr, Y, Dy and La atoms, on the β-NiAl(110) surface and α-Al2O3(0001) surface. We find that Hf, Zr, Y, Dy and La atoms all preferentially adsorb on Ni-Ni bridge sites on β-NiAl(110) surface while on α-Al2O3(0001) surface, the energetically favorable sites for all five REs are threefold-hollow sites. On the β-NiAl(110) surface, a binding order of Y, Dy < La < Hf, Zr was obtained while on the α-Al2O3(0001) surface, the binding order of Dy, Y < La < Zr < Hf was achieved. As known, in first-principles theory, a grain boundary can be viewed as composed of two surfaces, thus the surface adsorption of REs can partially reflect their properties in grain boundaries. Thereby, the adsorption energies in the present studies may provide some implications about the inhibition ability of REs on the diffusion of Al and O atoms in grain boundaries of β-NiAl based bond coat alloy and alumina layer in thermal barrier coatings.

10:20am **A2-3-8 Microstructure and Thermal Oxidation Behavior of Yttria-Stabilized Hafnia Coatings**, ***E. Rubio***, *M. Noor-A-Alam, S. Stafford, C. Ramana (rvchintalapalle@utep.edu)*, University of Texas at El Paso, US
High-temperature coatings are critical technologies for future power-generation systems and industries. Thermal barrier coatings (TBCs), which are usually the ceramic materials applied as thin coatings, protect engine components and allow further increase in engine temperatures for higher efficiency. Thus, the durability and reliability of the coating systems have to be more robust in compared to current natural gas based engines. A near and mid-term target is to develop TBC architecture with a 1300 °C surface temperature tolerance. Understanding the structural evolution thermal behavior of the TBC-bond coat interface, specifically the thermally grown oxide (TGO), is fundamentally important. In the present work, the attention

is directed towards y ttria-stabilized hafnia (YSH) coatings on alumina (α-Al_2O_3) to simulate the TBC-TGO interface and understand the phase evolution, microstructure and thermal oxidation of the coatings. YSH coatings were grown on α-Al_2O_3 substrates by sputter deposition by varying coating thickness in a wide range of ~30-1000 nm. The effect of coating thickness variation on the structure, morphology and the residual stress was investigated using X-ray diffraction (XRD) and high resolution scanning electron microscopy (SEM) . Thermal oxidation behavior of the coatings is evaluated using the isothermal oxidation measurements under static conditions. X-ray diffraction analyses revealed the existence of monoclinic hafnia phase for relatively thin coatings indicating that the interfacial phenomena are dominant in phase stabilization. The evolution towards pure stabilized cubic phase of hafnia with the increment of coating thickness is observed. The SEM results show the morphology of the sample with different thicknesses, and the average grain size increase in the range ~15-500 nm. Residual stress was calculated employing XRD techniques by changing the magnitudes of ψ-angle .Relation between residual stress and structural change is also studied. The results obtained on the thermal oxidation behavior indicate that the YSH coatings show initial mass gain in the first 6 hours and sustained structure for extended hours of thermal treatment.

10:40am **A2-3-9 Tribocorrosion Mechanisms in Laser Deposited Titanium-based Smart Tribological Composite Smart Coating**, ***P. Olubambi*** *(polubambi@gmail.com), M.L. Lepule, B. Obadele,* Tshwane University of Technology, South Africa, *J.O. Borode*, Federal University of Technology, Nigeria

Although titanium based alloys and composites have been widely utilized as smart materials for varying engineering applications, their relatively poor tribological properties have limit their effective applications as smart tribological composite coatings in the emerging surface engineering technology. In this study, the tribocorrosion mechanisms of titanium-based smart composite coatings deposited using laser materials deposition on austenitic stainless steel is investigated. Titanium and nickel powders were blended with zirconium in a turbular mixer, and the blended feedstock powders were laser deposited onto 316 austenitic stainless steel at varying laser processing parameters. Tribocorrosion behaviour of the composite coatings in sulphuric acid under varying loads was studied under sliding wear-corrosion set up using a CETR UMT-2 tribometer. Results revealed that the TiNi and TiNi-ZrO2 in a pseudoplastic state exhibited lower coefficient of friction as compared with 316. Wear resistance of TiNi alloy was mainly dependent on the recoverable strain limit, and also, on the effects of the reinforcing zirconium particles. Nevertheless, the coatings displayed a comparatively lower corrosion sesistance than the based stainless steel.

Hard Coatings and Vapor Deposition Technology
Room: California - Session B3-1

Deposition Technologies for Diamond Like Coatings
Moderator: K Böbel, Bosch GmbH, C. Engdahl, Crystallume

8:00am **B3-1-1 Physical Vapor Partial Filtering for Chemical Composition Control in Hybrid PECVD / EB-PVD Process**, ***C. Jaoul*** *(jaoul@ensil.unilim.fr),* Université de Limoges - CNRS, France, *F. Meunier,* Sulzer Sorevi, France, *P. Tristant, J.P. Lavoute, C. Dublanche-Tixier*, Université de Limoges - CNRS, France

Electron-beam physical vapor deposition (EB-PVD) is a widely used process to obtain metallic or ceramic coatings for many applications including space, turbine, optical and biomedical industry. The principle is the evaporation of a solid ingot by a focused electron beam at low pressure. If a discharge is created between substrate holder and chamber wall, a part of vapor is ionized and coating microstructure can be modified. When ionic deposition is associated with reactive gas such as N_2, O_2 there is reaction between metallic vapor and fragments produced in the plasma to form nitrides or oxides of the metal evaporated. The control of chemical composition or stoechiometry in the deposit can be achieved by changing reactive gas partial pressure.

Carbide films can be obtained with the introduction of gazeous hydrocarbon in the EB-PVD reactor. But one has to note that even without any evaporation a coating of amorphous hydrogenated carbon (a-C:H) is formed on the cathode by plasma enhanced chemical vapor deposition (PECVD). So, in association with evaporation, there is two sources of “vapor” (including ions, atoms, radicals,…) incoming at the cathode, leading to an hybrid PECVD / EB-PVD process. To our knowledge, this technique has never been reported in the literature to synthesize doped a-C:H thin films. For example, the introduction of small amount of Si can improve the tribological properties of the coating. It is thus proposed to demonstrate in this paper the feasibility of doping a-C:H by silicon with the evaporation of Si ingot in hydrocarbon plasma discharge.

Actually, the difficulty is to obtain a carbon rich film with small and controlled silicon content. To keep unchanged the a-C:H matrix, the control of the chemical composition cannot be realized by changing hydrocarbon partial pressure or the cathodic bias. To reduce the silicon evaporation rate, it would be natural to consider the decrease of electron-beam power or the modification of beam sweeping. But, when the ingot surface is not homogeneously melt, the evaporation rate is unstable and this leads to very poor reproducibility. The proposed solution is a partial mechanical filtering of evaporated vapor using baffles with different opened surfaces placed just above the Si ingot. Measurements of instantaneous deposition rate with quartz crystal microbalance are reported showing that vapor flux is in relation with the opened surface of the filter. Chemical composition analysis by ERDA-RBS and X-ray photoelectron spectroscopy (XPS) of a-C:H:Si films are also presented and discussed. Silicon content in the a-C:H film could be controlled (between 1 and 5 at.%) by changing filter.

8:20am **B3-1-2 A Multi Source PECVD Technology for Extremely Planar, Thick and Large-scale DLC Coatings**, ***S. Meier*** *(Sven.Meier@iwm.fraunhofer.de), S. Schnakenberg,* Fraunhofer Institute for Mechanics of Materials, IWM, Germany

Due to their outstanding properties DLC (diamond-like carbon) coatings are applicable in the prevention of friction and wear in tribological systems.

The properties of various DLC coating systems have been further improved in recent years. Many commercial applications would simply not be possible were it not for the effectiveness of these coatings. DLC coatings on the needles of fuel injection pumps used in combustion motors is only one example of many applications. Problematic however, is the ability to achieve extremely planar surfaces when coatings are thick and component geometries and sizes are large. A prime example of such an application requiring an extremely planar surface and specific coating thickness is sliding and counter rings for use in gas pipeline gas seals. In order to make acceleration and deceleration of these in contact sliding and counter rings as risk-free as possible, a coating thickness of 6 micrometers is desirable. Even with sealing rings often having a circumference greater than 500 mm, deviations from the desired coating thickness commonly only in the nanometer range in the circular and radial directions are allowed so as not to influence the sealing ring’s aerodynamics and thus, its ability to function correctly.

A pre-condition for the necessary deposition parameters is a new RF-PECVD device design, developed at IWM. Unlike commercial RF-PECVD devices, there is a flexible reactor design with a usable volume which can be easily extended. This novel technique operates completely clean (without deposits outside of the substrate electrode) and has the capability of being scaled up.

This RF-PECVD technology can also be equipped with a microwave ring resonator relatively easily. Through this method it is possible to produce crystalline diamond coatings and DLC coatings simply through use of just one chamber.

8:40am **B3-1-3 A Comparison on the Influence of Different Inert Gases for Reactive HiPIMS and DCMS CN_x Deposition Processes**, ***S. Schmidt*** *(sussc@ifm.liu.se),* Linköping University, IFM, Thin Film Physics Division, Sweden, *Zs. Czigány*, Hungarian Academy of Sciences, Research Centre for Natural Sciences, Hungary, *G. Greczynski, J. Jensen, L. Hultman*, Linköping University, IFM, Thin Film Physics Division, Sweden

Neon, argon, and krypton were used to explore the role of inert gases for the deposition process of carbon-nitride (CN_x) thin films in reactive high power pulsed magnetron sputtering (HiPIMS) and direct-current magnetron sputtering (DCMS) modes. The thin film synthesis and the plasma characterization took place in an industrial deposition chamber, where a pure graphite target was sputtered in Ne, Ar or Kr / N_2 atmosphere. The N_2-to-inert gas flow ratio was varied between 0 % and 100 % at a constant deposition pressure of 400 mPa. For both deposition modes, the applied average target power was similar. The carbon discharges were investigated using mass spectrometry measurements performed at the substrate position. Here, the ion flux was analyzed with regards to composition and ion energy. The ion energy distributions (IEDs) were measured for inert and reactive gas ions, C^+, and $C_xN_y^+$ (x, y < 2) ions. These results are related to the corresponding thin films with regards to their chemical bonding and microstructure obtained by X-ray photoelectron spectroscopy and transmission electron microscopy, respectively.

IED functions in HiPIMS mode exhibited generally a broader distribution, thus an increased mean energy, compared to DCMS. This was most pronounced for C^+ and reactive gas ions, whereas only minor differences were found for the inert gas ions. HiPIMS and DCMS processes involving

Ne and small contents of N_2 yielded the highest particle energies. This was mirrored in the microstructure of the thin films as an ordering towards fullerene-like was obtained when Ar and Kr were used as inert gas, whereas CN_x films deposited in Ne atmosphere were fully amorphous. HiPIMS processes yielded the most distinct fullerene-like structure compared to films synthesized by DCMS due to pulse assisted chemical desorption processes. Moreover, the efficiency to dissociate and ionize N_2 increases with decreasing inert gas mass, which is reflected by increased N^+/N_2^+ ratios in the plasma and elevated N contents in thin films deposited in Ne containing atmosphere.

9:00am **B3-1-4 Deposition and Characterization of Advanced DLC Coatings Deposited by Low Frequency Plasma Enhanced Chemical Vapour Deposition (LF PECVD)**, *C. Chouquet*, DMX sas, France, *C. Ducros*, CEA/Liten/DTNM/LTS, France, *F. Schuster*, CEA Cross-Cutting Programme on Advanced Materials, France, *A. Billard*, LERMPS-IRTES, France, ***F. Sanchette*** *(frederic.sanchette@utt.fr)*, ICD-LASMIS, Nicci, UTT Antenne de Nogent, France

A very recent paper [1] describes precisely an analysis of the energy consumption due to friction in passenger cars and its consequences. As an example, one-third of the fuel energy is used to overcome friction in the engine. Introduction of low friction coating technology such as diamond-like carbon (DLC) coatings on engines parts has improved engines efficiency by reducing this energy consumption.

This work brings the main results obtained by using low frequency plasma enhanced chemical vapour deposition (LF PECVD) for depositing advanced DLC type coatings. Thus, amorphous hydrogenated carbon (a-C:H), Si-containing a-C:H (Si-C:H) and a-C:H/Si-C:H multilayered films have been deposited by low frequency plasma enhanced chemical vapour deposition (LF PECVD) from cyclohexane-hydrogen and tetramethylsilane-argon mixtures for the a-C:H and Si-C:H layers respectively.

Structural and mechanical properties of single layers have been first studied. Then, previous results have been exploited to develop a-C:H/Si-C:H multilayered coatings. Some results show the possibility to obtain thick multilayered coatings (~10µm), with period thickness down to 25 nm. Surface texturing was also investigated in order to improve the tribological properties of a DLC/steel lubricated sliding contact. A direct coating texturing process based on a laser lithography technique has been developed and used for patterning hydrogenated amorphous carbon (a-C:H) layers. The effects of cavity dimensions on friction and wear behaviors were highlighted. It has been shown that creation of small and shallow cavities on a DLC layer allowed a significant reduction of friction coefficient of a DLC/steel contact comparing to a system with a non-textured DLC film.

[1] Kenneth Holmberg, Peter Andersson, Ali Erdemir

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9:20am **B3-1-5 State-of-the-Art of DLC Coatings: Industrial Deposition Methods and Tribological Applications 60 Years after the Discovery of DLC**, ***J. Vetter*** *(joerg.vetter@sulzer.com)*, Sulzer Metaplas, Germany **INVITED**

DLC coatings of the a-C:H type were first described by Schmellenmeier in 1953. First patents for deposition methods for industrial applications were filed in the 70's, e.g. Weißmantel et.al. .Ta-C coatings deposited by the filtered arc were published by. Aksenov et. al. in the 70's. In the 80's, the a-C:H:Me coatings were developed by Dimigen et. al. . Another big step was the introduction of non metal doped a-C:H:X coatings, e.g. X: Si,O, named diamond like nanocomposites (DLN) beginning of the 90's by Dorfmann et. al., now applied as Dylyn®. Other X elements were introduced later on: N, F, B. DLC coatings are deposited by a variety of techniques. PVD techniques, PA-CVD techniques, or a hybrid process of PVD plus PA-CVD are among the most common methods for the DLC coating types. The PVD deposition technique for the adhesion promoting metallic interlayers and hard supporting under layers is magnetron sputtering however electron beam evaporation is also used (specifically for Cavidur®). Magnetron sputtering and arc evaporation (direct, filtered arc) of carbon targets are used to deposit hydrogen free DLC (a-C, ta-C) coatings. Special solutions for a-C:H coatings have been developed which combine carbon sputtering using argon as the sputtering gas and adding carbon containing gases. The PA-CVD techniques are based on glow discharges, mainly using either pulsed DC or RF. Typically, an additional activation source (e.g. electron injection) is utilized to stimulate the carbon gas decomposition and the ionization. Ion source processes, MW discharges and PLD are additional deposition methods. DLC coatings were commercialized initially in the two application areas: I) coating of hard discs in the nm-scale in the mid 80's. II) coating of automotive parts for racing in the early 90's (Cavidur®). The breakthrough for automotive applications was in the late 90's, when VW introduced the unit pump system. The ta-C coating was introduced to the automotive industry for tappets by Nissan in 2007. The demand to further reduce the CO_2 emission is the main driver for the application of the DLC coatings on automotive parts. Large scale automotive applications demand coating systems especially designed for mass production. Also in demand, are coating systems designed to coat large and heavy parts like gears of wind power transmissions. Today, the application of industrial DLC coatings is wide spread and covers tribological applications for combustion engines, transmission systems, medical applications, semiconductor equipment, plastic manufacturing, cutting tools, forming tool, various general engineering parts, decorative applications and more.

10:00am **B3-1-7 Modification of Femtosecond-Pulsed Laser Deposited Diamond-Like Carbon films by Temporal Pulse Shaping**, *F. Bourquard (florent.bourquard@univ-st-etienne.fr), T. Tite, A.S. Loir, C. Donnet*, Laboratoire Hubert Curien, UMR 5516, Université de Lyon, Université Jean Monnet, France, *H. Ftouni, O. Bourgeois*, Institut Néel, UPR 2940 CNRS, France, ***F. Garrelie***, Laboratoire Hubert Curien, UMR 5516, Université de Lyon, Université Jean Monnet, France

In the context of femtosecond PLD, this study is based on the modification of the temporal shape of energy deposition of laser ablation of a graphite target. This modification is accomplished by splitting laser pulses of 50 fs duration into double pulses with variable delays or stretching them into longer pulses, leading to interaction durations from hundred of femtosecond to tens of picoseconds.

The ablation plume is examined by means of temporally and spatially resolved optical spectroscopy, coupled with ablation rate measurements. This gives insight on the quantities and the kinetics of the species constituting the plume, which are modified by the temporal shaping. The influences of those ablation plume properties on the obtained Diamond-Like Carbon (DLC) films are explored. Raman spectroscopy and electrical conductivity measurements have been performed in order to characterize respectively the structure and sp^3 contents of the films.

This work provides better understanding on the importance of the temporal envelop of the pulses in regard to the characteristic durations (electron phonon coupling, heat conduction…) of the ablated material. It permits also to explore the influence of femtosecond generated ablation plumes properties on the deposited Diamond-like Carbon layers.

10:20am **B3-1-8 Thermal Stability of DLC-MoS_2 Thin Films in Different Environments**, ***H. Niakan*** *(hamid.niakan@usask.ca), C. Zhang, J. Szpunar, Q. Yang*, University of Saskatchewan, Canada

Diamond-like carbon (DLC) based coatings are ideal for low friction and wear resistant applications. Those may expose the coatings to high temperature environments or to localized elevated temperature induced by. Therefore, the thermal stability of DLC based films is a key property for their long-term performance. In this investigation, DLC-MoS_2 composite thin film was synthesized using biased target ion beam deposition (BTIBD) technique in which MoS_2 was produced by sputtering a MoS_2 target using Ar ion beams while DLC was deposited by an ion source with CH_4 gas as carbon source. A pure DLC film deposited under similar conditions without sputtering was used as reference sample. After the deposition, DLC and DLC-MoS_2 thin films were heat-treated in ambient air, N_2 and vacuum environments at different temperatures ranged from 100 to 600 º C for 2 h, respectively. The effect of annealing on the structure, mechanical and tribological properties of the resulting films were studied by means of Raman spectroscopy, scanning electron microscopy, X-ray diffraction, nanoindentation, and ball-on-disc testing. DLC-MoS_2 thin films showed a slower rate of graphitization and higher structure stability throughout the range of annealing temperatures, indicating a relatively higher thermal stability.

10:40am **B3-1-9 Advanced PECVD Process Control through the use of RF and Plasma Key Parameters for Transfer of Layer Properties**, ***T. Grotjahn*** *(tobias.grotjahn@iwm.fraunhofer.de), S. Schnakenberg*, Fraunhofer IWM, Germany, *R. Plötze*, P.H.F. Beratung, Germany, *R. Rothe*, Plasmetrex GmbH, Germany, *S. Meier*, Fraunhofer IWM, Germany

Plasma enhanced surface treatment and coating processes are widely used techniques for surface modification and coatings, among others for the deposition of diamond-like carbon coatings. For layer optimization and layer property transfer usually the "trial-and-error"-method is used. Not only is this method very time consuming but it is often rather complex to transfer a layer of established properties to another device. To improve the layer transferability it is necessary to develop a better understanding between the RF-network, the plasma state and the interaction between the plasma and the substrate surface.

To solve this problem the PEVCD chamber has been equipped with several additional self-constructed and calibrated RF-sensors at numerous positions in the matching network to measure voltage, current and phase angle. The plasma is monitored by non-invasive diagnostic methods. The behavior of the resonance frequency, the plasma resistivity and, indirectly, the collision rate are monitored in-situ by Nonlinear-Extended-Electron-Dynamics. The

plasma chemistry is analyzed by Optical Emission Spectroscopy. By the analysis of the emission band shape of diatomic molecules the gas temperature is determined. Based on the actinometrical approach, it is possible to calculate the electron temperature and the particle densities of emitting species.

To obtain a time-resolved overview of all of these parameters a monitoring system, which connects all of these parameters, was developed. Furthermore, we studied the behavior of the RF-parameters related to the plasma state and the resulting layer properties according to the load condition of the chamber at different generator powers and gas fluxes. The aim of the investigations was to define the influence of the RF-parameters and the plasma state on layer properties. Two main results were achieved in this work. Firstly, it is possible to transfer established layer properties directly to different substrate sizes and to another devices. This is possible by characterizing the process by means of some of these outlined parameters. Secondly, a new process control technique for exactly this procedure was developed.

11:00am **B3-1-10 High-rate Deposition of Dense Hydrogenated Amorphous Carbon Thin Films using High Power Impulse Magnetron Sputtering Based Process**, ***A. Aijaz*** *(asim@ifm.liu.se), K. Sarakinos, M. Raza, U. Helmersson*, Linköping University, IFM, Plasma and Coatings Physics, Sweden

High-rate deposition of hydrogenated amorphous carbon thin films (a-C:H) is commonly performed by using a hydrocarbon precursor in chemical vapor deposition (CVD) based processes. In order to obtain the ionized depositing fluxes, which are essential for the synthesis of dense a-C:H such as diamond-like a-C:H, the process is coupled with a plasma, as in radio frequency plasma enhanced CVD processes. However, the resulting films exhibit low density phases such as polymeric or graphite-like a-C:H. Increasing the plasma density in such an arrangement will further promote the ionization and dissociation of hydrocarbon species which will beneficially influence the control over the energy and flux of the depositing species. High plasma density based physical vapor deposition (PVD) processes such as high power impulse magnetron sputtering (HiPIMS), has shown to facilitate the synthesis of dense and sp^3 rich hydrogen-free a-C in Ar as well as in Ne ambient [1]. In this work we use HiPIMS based process to synthesize a-C:H thin films using C_2H_2 precursor in an Ar ambient. The process is based on the hybrid arrangement of HiPIMS and direct current magnetron sputtering (DCMS) where the film synthesis is performed at varied fractions of C_2H_2 and HiPIMS powers to investigate the influence of the gas phase composition and the ionization of the depositing species on the film properties. The deposition rate and mass density, determined by X-ray reflectometry (XRR), show that the films with a ten-fold increase in the deposition rate, as compared to the conventional HiPIMS process (pure HiPIMS in Ar ambient), and mass density reaching 2.32 g/cm^3 can be synthesized. The films exhibit low H content of 8% and a hardness of over 25 GPa, as measured by elastic recoil detection analysis (ERDA) and nanoindentation methods respectively. The results demonstrate that the HiPIMS based process provides an efficient means of tailoring the properties of a-C:H such as deposition rate, mass density, hardness as well as H content.

Hard Coatings and Vapor Deposition Technology
Room: Royal Palm 4-6 - Session B4-2

Properties and Characterization of Hard Coatings and Surfaces

Moderator: C. Mulligan, US Army ARDEC, Benet Laboratories, J. Lin, Colorado School of Mines, ACSEL, B. Zhao, Exxon Mobile, USA

8:00am **B4-2-1 Plasma Immersion Ion Deposition of Diamond-like Carbon Coatings on Inner Surface of Long Pipes for Industry Applications**, ***K. Coulter*** *(ken.coulter@swri.org), R.H. Wei*, Southwest Research Institute **INVITED**

In this presentation we discuss the latest research conducted at Southwest Research Institute® (SwRI®) in depositing diamond-like carbon (DLC) and other functionalized coatings on the inner surface of long pipes/tubes using plasma immersion ion deposition (PIID). Deposition of hydrogenated DLC of a few micrometers on the external surface of three-dimensional parts has been conducted for many years, and the PIID technology, a plasma-enhanced chemical vapor deposition (PECVD) process, has found some limited success for industrial applications. However, it is challenging to deposit these coatings on the inner surface of long pipes/tubes due to the difficulty of plasma generation at high aspect ratios. SwRI has developed technologies and demonstrated that tubes/pipes up to 25m long (100 mm in dia.) and as small as 16mm in dia. (by 3m long) can be coated with DLC. In addition to the "standard" DLC coatings for increased abrasion/erosion resistance, corrosion resistance and low friction, other surface functional coatings have been developed to obtain other physical properties including hydrophobicity, anti-scaling, and anti-icing. In this presentation, we will discuss the method for generating plasma inside the pipes, the characteristics of the plasma, and the microstructural, mechanical, and physical properties of various deposited films. The practical application examples will also be presented.

8:40am **B4-2-3 Microstructural Investigation of Erosion Resistant TiN-TiAlN Laminated Coatings Deposited by Arc Ion Plating**, ***T. Takahashi*** *(takahashi@kcs-europe.de), R. Cremer, P. Jaschinski*, KCS Europe GmbH, Germany

Erosion is one of the serious problems in gas turbine engines in aircrafts. The erosive damage of the turbine blades results in the reduction of the fuel efficiency, service life as well as reliability of the components, and hence required to be minimized in operation. One of the effective technological solutions is the deposition of erosion resistant coatings on the components.

In this work, approximately 20 μm thick TiN-TiAlN erosion resistant coatings were deposited on turbine blades using industrial arc ion plating (AIP), and their surface morphology, microstructure, and mechanical properties were investigated. The film microstructure consists of the laminated TiN and TiAlN with varied architectures. The X-ray diffraction confirmed the mixture of cubic TiN and TiAlN phases with the lattice parameters of 0.424 nm and 0.415 nm, respectively. The film hardness was measured to be 2600 HV by nanoindentatation.

The formation of the so-called macro-particles, and the possible incorporation thereof into the film is known to be an intrinsic problem of cathodic arc deposition processes. The detailed microstructural investigations with combination of a focused ion-beam technique enabled to capture the incorporation of the macro-particles into the growing TiN-TiAlN coatings. The growth of the TiN-TiAlN laminated structure was found to be locally disturbed by the macro-particles incorporated depending on their sizes. The possible effect of the incorporated macro-particles on the coating failure behavior will also be discussed.

9:00am **B4-2-4 Shake-up Features in Titanium Nitride Bilayer Systems used to Model Ultra-hard TiN/ Si_3N_4 Nanocomposites**, ***D. Jaeger*** *(dominik.jaeger@empa.ch), J. Patscheider*, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland

Nanocomposite coatings composed of two phases with atomically sharp phase boundaries show interesting mechanical properties. These properties often originate from their typically high interface to volume ratio.

The topic of this talk addresses interfacial properties of two-dimensional bilayer systems, which are used as model systems to describe the interfaces occurring in nanocomposite coatings. The presented systems are TiN interfaces in contact with silicon (Si), silicon nitride (Si_3N_4) and aluminum nitride (AlN). The primary tool used to analyze the interfaces of bilayer systems is X-ray Photoelectron Spectroscopy (XPS) with emphasis put on the shake-up feature of the Ti 2p photoelectron line. Shake-ups in TiN are observed as an additional peak on the lower binding energy side of the energy lines of the Ti 2p orbitals.

Angle-resolved XPS (AR-XPS) and X-ray Photoelectron Diffraction (XPD) results were used to interpret the crystalline structure of the different TiN/AlN and TiN/Si_3N_4 bilayer systems. The revealed interface properties show a correlation between the shake-up intensity and the interface morphology, oxygen content, interfacial charging and the shake-up energy. The results indicate that AlN grows crystalline on single-crystalline TiN, while Si_3N_4 only shows a crystalline growth behavior in the first 0.6 nm. The crystalline growth of Si_3N_4 in the initial stages is hindered in cases, where a bias voltage is applied to the substrate during Si_3N_4 deposition.

It is shown that the increase in the shake-up intensity is correlated to intrinsic and extrinsic interface charging. The obtained results, in combination with theoretical structure models from literature, show that in one to two monolayer thick interlayers a build-up of intrinsic interface charging is unlikely.

9:20am **B4-2-5 Diamond Coatings' Adhesion and Residual Stresses Assessment by Inclined Impact Tests**, *K.D. Bouzakis (bouzakis@eng.auth.gr)*, *G. Skordaris*, Aristoteles University of Thessaloniki, Greece, *S. Makrimallakis*, Fraunhofer Project Center for Coatings in Manufacturing (PCCM), Germany, *E. Bouzakis*, Fraunhofer Project Center for Coatings in Manufacturing (PCCM), Greece, *S. Kombogiannis*, Aristoteles University of Thessaloniki, Greece, ***O. Lemmer***, CemeCon AG, Germany

The inclined impact test was employed for assessing diamond coatings (DC) adhesion. This test has been established as a very efficient method for characterizing quantitatively the film adhesion, since the oblique loading direction induces shear stresses into the film and its interface to the substrate. Inclined impact tests were conducted on diamond coated specimens at various loads and cycles. The related imprints were evaluated by confocal measurements and EDX micro-analyses. According to the attained results, after a certain number of impacts dependent on the applied load, damages in the film interface occur resulting in coating-substrate detachment. In this way, coating residual stresses are released leading to a film swelling (bulge formation). In the bulge, the film residual stresses are eliminated. Furthermore, the bulges are destroyed after a restricted number of repetitive impacts. The development of swellings on diamond coatings due to film detachments during the inclined impact test can be effectively described by appropriate FEM simulations.

9:40am **B4-2-6 Study Of Structural and Mechanical Properties Of CrAlYN/CrY Multilayer Thin Film Deposited On M2 Steel**, ***M.T. Tahmasebian Myandoab*** *(tahma@atauni.edu.tr)*, *I. Efeoglu*, *V. Ezirmik*, *Y. Totik*, *E. Demirci*, Atatürk University, Turkey, *O. Baran*, Erzincan University, Turkey

New generation of Ti-free coatings like as CrN, CrAlN, CrAlCN and CrAlYN coatings have combination of high temperature abrasion and oxidation resistance with low thermal conductivity. So these kinds of coatings have applications in industries like as automotive and airspace for protection of special alloys and in high speed dry machining tool coatings. But for using these coatings to their full potential beside metallurgic methods, coatings' structural engineering is essential. Besides coatings with multilayer nanoscale structures compared to simple ones have more hardness and better oxidation resistance. In this study, two CrY, one Cr and one Al targets used to deposit CrAlYN/CrY thin film on M2 steel in nine runs with different configurations by unbalanced closed field magnetron sputtering system (CFUMBS). The variables were targets voltages and pulse parameters were applied to the substrate and reactive gas flow rate was constant. Coatings' composition, morphology and structure were analyzed by a variety of techniques including SEM, and XRD.

10:00am **B4-2-7 Growth of ZrO_2 by Heat Treating ZrN Thin Film in Vacuum**, ***J.H. Huang*** *(jhhuang@ess.nthu.edu.tw)*, *J.-W. Hsieh*, *G.P. Yu*, National Tsing Hua University, Taiwan, Republic of China

ZrO_2 is an excellent corrosion protective coating for metal substrates especially in salt water. In our previous study [1], a wettability problem was encountered when depositing ZrO_2(N) thin films on stainless steel substrate. Instead of directly depositing ZrO_2, the oxide coating can be produced by oxidizing ZrN thin film which has no wetting issue on stainless steel. The purpose of this study was to produce ZrO_2 by heat treating ZrN thin films on stainless steel substrate and investigate the oxidation mechanism of ZrN films in vacuum. ZrN thin films were deposited on Si and 304 stainless steel substrates using hollow cathode discharge ion-plating (HCD-IP), and were annealed in vacuum (5×10^{-6} Torr) at temperatures ranging from 700 to 1000°C and over durations ranging from 1 to 4 hr. The result showed that ZrO_2 was grown on top of ZrN that remained as the major phase (~ 60%) in the films even annealing at 1000°C for 4 hr in vacuum. This was attributed to the fact that the surface oxide was protective in vacuum, and therefore the diffusion of oxygen was hindered and remained an intact surface. Retained ZrN could be observed on the surface layer in stainless steel-based specimens even annealed at 800°C for 4 hr. After 500-hr salt spray test, the ratios of corrosion area for all the oxidized ZrN films were less than 0.2%, indicating an excellent corrosion resistance. Thus, by heat treating ZrN thin film in vacuum, ZrO_2 can be grown from ZrN without peeling and crack formation, which may provide good corrosion protection. Moreover, the stress in ZrN thin films could be relieved without significant change in properties as the specimens were annealed at 1000°C for 1 hr in vacuum.

[1] Jia-Hong Huang, Tzu-Chun Lin, Ge-Ping Yu, Surf. Coat. Technol. 206(2011)107.

10:20am **B4-2-8 Structural and Elastic Properties of Ternary Metal Nitride $Zr_{1-x}Ta_xN$ Alloys Thin Films: Relationship with the Working Gas Pressure**, ***P. Djemia*** *(djemia@univ-paris13.fr)*, LSPM-CNRS, Université Paris 13, Sorbonne Paris-Cité, France, *L. Belliard*, UPMC-Institut des NanoSciences de Paris, France, *G. Abadias*, Institut P' - Universite de Poitiers, France

We investigated the structural 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 working pressure was varied in the 0.19-1.0 Pa range by increasing the Ar flow from 12 to 68 sccm, while maintening the N_2 partial pressure before the onset of the compound target mode. The structural properties of the ternary $Zr_{1-x}Ta_xN$ compounds were characterized by X-ray Diffraction (XRD) and X-ray reflectivity (XRR), whereas the picosecond ultrasonics and Brillouin light scattering techniques were employed to measure their acoustic and elastic properties as function of the chemical composition and the working gas pressure. The thermal stability of these $Zr_{1-x}Ta_xN$ films is also studied, based on their structural and mechanical response upon vacuum annealing at 850°C for 3h.

10:40am **B4-2-9 High Temperature Tribological Properties of CrAlTiN Coating**, ***T. Polcar*** *(polcar@fel.cvut.cz)*, University of Southampton, UK, *A. Cavaleiro*, University of Coimbra, Portugal

In this study, we analyzed the high temperature tribological behavior of CrAlTiN coatings deposited on WC substrates by low cathodic arc technique. The coatings chemical composition, Al 31 at.%, Cr 16 at.%, Ti 7 at.% and N 46 at.%, and the bonding state were evaluated by X-ray photoelectron spectroscopy. The mechanical properties of the coatings were studied by scratch-test and nanohardness depth sensing indentation (hardness approx. 38 GPa). The morphology of the coatings surface, ball scars, wear tracks and wear debris as well as the oxidized samples was examined by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX). The structure and oxidation resistance were analyzed using high temperature X-ray diffraction (XRD) and thermal gravimetric analysis (TGA), respectively, up to 1300 °C. Wear testing was carried out using a high temperature tribometer (pin-on-disc) with alumina balls as counterparts. The evaluation of the friction coefficient with the number of cycles (sliding distance) was assessed at different temperatures and the wear rates of the coatings and balls were determined; the maximum testing temperature was 800 °C. The coating showed an excellent thermal stability and wear resistance. The friction reached a maximum at 500 °C and then decreased, whereas the wear rate was negligible up to 600 °C and increased significantly at higher temperatures.

To analyze the worn surfaces, several surface analytical techniques were applied: Raman spectroscopy was used to analyze the wear debris and wear track surface, chemical profile of the top surface part of the wear track was obtained by X-ray photoelectron spectroscopy (XPS), and the wear track cross-sections prepared by focused ion beam (FIB) were directly observed by transmission electron microscopy (TEM). Two findings emerge from our study: i) the surface of the wear track is not oxidized even after the sliding test at 800 °C, and ii) the coating nanolayered structure produced by sample rotation acts as an effective barrier to crack propagation at the nanoscale.

11:00am **B4-2-10 On Hardness and its Benefit to the Characterization and Optimization of Coatings**, ***M. Fuchs*** *(marcus.fuchs@s2003.tu-chemnitz.de)*, Chemnitz University of Technology, Germany, *N. Schwarzer*, Saxonian Institute of Surface Mechancis, Germany

Among other material properties like elastic modulus *E*, hardness *H* is widely used in literature to mechanically characterize thin films or coatings with respect to their resistance to plastic deformation. However, hardness is not a generic material parameter as it can be biased by surface structures (e.g. surface roughness) or other material properties (e.g. intrinsic stresses). For instance, it will be shown how simple surface roughness can lead to false apparent **ultra-hardness** results. Therefore, this work will show that its benefit for the mechanical characterization of coated or treated surfaces is limited. In addition, hardness is not a physical parameter and, thus, cannot be used for both engineering and optimization of coatings by means of model-driven simulations. Possible alternatives like yield strength will be highlighted instead and their advantages over hardness will be explained.

11:20am **B4-2-11 Microstructure, Properties and Microtribological Performance of Magnetron-sputtered V-C Coatings**, *M. Stüber (michael.stueber@kit.edu)*, Karlsruhe Institute of Technology, Germany, ***P. Stoyanov***, Karlsruhe Institute of Technology, and Fraunhofer-Institute for Mechanics of Materials IWM, Germany, *E. Nold*, Fraunhofer-Institute for Mechanics of Materials IWM, Germany, *M. Dienwiebel*, Karlsruhe Institute of Technology, and Fraunhofer-Institute for Mechanics of Materials IWM, Germany, *S. Ulrich*, Karlsruhe Institute of Technology, Germany

Transition metal carbides exhibit superior mechanical and tribological properties at a wide range of environmental conditions and contact pressures. More recently, vanadium carbide coatings have been considered for a number of industrial applications (e.g. automotive components, cutting tools, ball bearings) due to their high corrosion resistance and mechanical stability at elevated temperatures. While some studies have provided significant new insights on deposition methods of vanadium carbides, the friction and wear mechanisms of these coatings have received little attention. The goal of this study is to provide an excessive understanding of the mechanical and microtribological properties of various vanadium carbide-based (VC_{1+x}) coatings. More generally, we are studying the influence of V:C ratio over a wide range contact pressures. The coatings are prepared using non-reactive d.c. magnetron sputtering with a segmented VC/graphite target (i.e. target diameter of 75 mm, 500 W target power, substrate temperature < 150°C, and Ar gas pressure of 0.6 Pa). The resulting V:C ratios vary between 1:1 and 1:3. The microstructures of the as deposited coatings are characterized using X-ray diffraction and cross-sectional focused ion beam imaging, while elemental analysis is performed by means of X-ray photoelectron spectroscopy, electron probe microanalysis, and micro-Raman spectroscopy. Mechanical properties measurements show that the hardness, H, of the coatings decreases with increasing the carbon concentration (i.e. H ranges between 1500 and 3100 HV for the low and high vanadium concentration respectively), which correlates well with the adhesion results obtained from scratch tests. However, reciprocating microtribological tests, performed with varying normal loads between 120 mN and 1 N, reveal higher friction values and increased wear with the high vanadium content coatings. This sliding behavior is attributed to differences in the third body formation and velocity accommodation modes, which are analyzed *ex situ* by means of micro-Raman spectroscopy and atomic force microscopy.

Keywords: vanadium carbide, non-reactive d.c. magnetron sputtering, microtribology, third bodies, velocity accommodation modes

11:40am **B4-2-12 Adherent Amorphous Hydrogenated Carbon Coatings on Steel Surfaces Deposited by Enhanced Asymmetrical Bipolar Pulsed-DC PECVD Method and Hexane as Precursor**, *G. Capote (gcapoter@unal.edu.co)*, *J. Olaya*, National University of Colombia, Colombia, *G. Faria*, *G. Martins*, *E. Corat*, ***V. Trava-Airoldi***, Institute for Space Research, Brazil

Amorphous hydrogenated carbon (a-C:H) coatings have attracted significant attention recently due to their low friction, high degree of hardness, high elastic modulus, chemical inertness, biocompatibility, and high wear resistance. These films are mostly obtained by plasma decomposition of a hydrocarbon-rich atmosphere. It is usually accepted that surface chemisorption of carbon carrying neutral radicals is the main channel for the film growth. In a-C:H films deposited by hexane decomposition, the structure is composed of sp^2 hybridized clusters interconnected by sp^3 hybridized carbon atoms. The major disadvantage of hard a-C:H film 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 a-C:H films on steel substrates, a thin amorphous silicon interlayer was deposited as an interface. This interlayer was obtained at low temperature by using low energy ion implantation. Amorphous silicon interlayer and a-C:H films were grown by employing an asymmetrical bipolar pulsed-DC PECVD system, using silane and hexane atmospheres, respectively. The a-C:H 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 a-C:H 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 and electrochemical impedance spectroscopy on a 3% solution of NaCl. The results showed that the use of the amorphous silicon interlayer, deposited by low energy ion implantation, improved the a-C:H film deposition onto steel substrates, producing good adhesion, low compressive stress, and a high degree of hardness. The composition, the microstructure, the mechanical and tribological properties of the films were strongly dependent on the self-bias voltages. The tests confirmed the importance of the intensity of ion bombardment during film growth on the mechanical and tribological properties of the films.

Hard Coatings and Vapor Deposition Technology
Room: Royal Palm 1-3 - Session B7-1

Computational Design and Experimental Development of Functional Thin Films

Moderator: B. Alling, Thin Film Physics Division, IFM, Linköping University, D. Holec, Montanuniversität Leoben, Austria

8:00am **B7-1-1 Nanoengineered Oxide and Nitride Thin Films with Unique Functionalities**, ***H. Wang*** *(wangh@ece.tamu.edu)*, *J. Lee*, *A. Chen*, *M. Myers*, *C. Tsai*, *Q. Su*, *Y. Zhu*, *L. Chen*, *L. Jiao*, *J. Jian*, *W. Zhang*, *F. Khatkatty*, *C. Jacob*, Texas A&M University, US, *Q. Jia*, Los Alamos National Laboratory, US, *J. Driscoll*, University of Cambridge, UK, *J. Gan*, *J. Cole*, Idaho National Lab, US **INVITED**

The talk focuses on various nanostructured functional oxide and nitride thin films for high temperature superconductors (HTS), solid oxide fuel cells, transparent conducting oxides, nitride radiation tolerant materials and others. Wires that carry electrical current without resistance are fabricated by coating metal substrates with the HTS $YBa_2Cu_3O_{7-\delta}$ (YBCO). Using ***nanolayer*** architecture and ***nano-particle*** doping approaches, YBCO coated conductors with dramatically enhanced transport properties can be achieved. Another way of nanoengineering is to process self-assembled vertical-aligned nanocomposite (VAN). We have successfully demonstrated several VAN systems. These VAN systems show interesting lattice epitaxial relationship along the vertical grain boundaries, which enables highly strained films with thickness higher than 100nm. Using vertically aligned nanopore structure, highly efficient thin film cathodes with superior ionic conductivity can be made in thin film solid oxide fuel cells. Enhanced low field magnetotransport properties have been observed in various VAN systems. Nitride coatings with single layer or nanolayers have been demonstrated as superior diffusion barrier and corrosion resistant coatings for fuel claddings in advanced nuclear reactors. Detailed microstructural characteristics of these nanostructured ceramic thin films will be discussed and correlated with their unique functionalities. Conventional TEM studies are coupled with in situ TEM and high resolution STEM analysis.

8:40am **B7-1-3 Modeling Amorphous Materials from First Principles**, ***E. Holmstrom*** *(erik.holmstrom@gmail.com)*, *R. Lizarraga*, Instituto de Fisica, Universidad Austral de Chile, Valdivia, Chile **INVITED**

We present a stochastic quenching (SQ) approach to obtain theoretical amorphous structures. The quenching is performed by using an *ab initio* code following a path that minimizes the forces between the atoms until they are close to zero. For a large enough cell, the resulting amorphous structure shows the same

pair-correlation distribution as obtained by a standard molecular dynamics (MD) simulation. However, the calculations are considerably speeded up compared to an *ab intio* MD simulation. Once an amorphous structure that describes the system at hand is obtained, state-of-the-art DFT methods can be applied to calculate, for instance, theoretical XPS and NMR spectra. Results will be presented for monatomic amorphous metals, bulk metallic glasses, amorphous oxides, hard coating materials as well as amorphous graphene.

9:20am **B7-1-5 Advanced Modelling of Amorphous Ceramics**, ***J. Houska*** *(jhouska@kfy.zcu.cz)*, University of West Bohemia - NTIS, Czech Republic

In this paper we discuss algorithms for ab-initio modelling of structures, electronic structures and properties of amorphous ceramics. All materials simulated were also prepared experimentally. We focus on the possibilities and limitations of the modelling, and on the comparison of representative examples of calculated and experimental results.

First, we describe the simulation algorithm which allows one to predict atomic structure of amorphous materials. We show examples of bonding structure analysis in C:H (simple case where the key quantity is "only" the CC bond order), SiBCN (complex case due to different bonding preferences of individual elements, and the necessity to distinguish between bonding valence electrons and electronic lonepairs) and Zr(Si)BCN (even more complex due to a mixture of covalent and metallic bonding). [1-3]

Second, we go through special cases, such as (i) presence of implanted Ar ions in sputtered materials (which can e.g. affect their homogeneity due to segregation of Si around Ar in SiBCN), (ii) formation of isolated gas

molecules (N_2 or H_2; which cannot diffuse out due to the periodic boundaries) during the simulation or (iii) intentional presence of isolated molecules in a material. [4]

Third, we summarize quantities which control (or can be used to predict) selected functional properties of amorphous materials. In the case of electrical conductivity this includes not only the band gap but also weights of electronic states on individual elements and bonds (particularly around the Fermi level) and electronic mobility (which depends on localization of electronic states). In the case of thermal stability this includes not only the static amorphous network characteristics (bond types, coordination numbers) but also temperature-dependent dynamic quantities (formation rate of N_2 molecules, rate of bond-breaking processes). [5]

[1] Surf. Coat. Technol. 203, 3770 (2009); [2] J. Vac. Sci. Technol. A 25, 1411 (2007); [3] J. Phys.: Condens. Matter 23, 025502 (2011); [4] J. Phys.: Condens. Matter 18, 2337 (2006); [5] Acta Materialia 59, 2341 (2011)

9:40am **B7-1-6 Dynamics of Ti, N, and TiN_x (x = 1 - 3) Admolecule Transport on TiN(001) Islands and Surfaces**, ***D. Edström***, *D. Sangiovanni, V. Chirita (vio@ifm.liu.se), L. Hultman,* Linköping University, IFM, Thin Film Physics Division, Sweden, *I. Petrov, J. Greene,* University of Illinois at Urbana-Champaign, US

We use the Modified Embedded Atom Method (MEAM) to perform realistic large scale classical Molecular Dynamics (MD) of the typical processes occurring in the initial nucleation of TiN thin film growth. The simulations are carried out at 1000 K, a reasonable growth temperature, and follow the dynamics of Ti, N, and TiN_x (x = 1 - 3) admolecules, on TiN(001) islands. We perform statistically independent MD runs of 2 and 5 ns, for total simulation times of several microseconds, which allow the quantification of average residence times on islands and a detailed analysis of the corresponding descent mechanisms on the (001) terrace. Results show significant differences, in terms of diffusion on islands and descent mechanisms, for each adspecies. We find that Ti adatoms descend from islands exclusively via push-out exchange with island edge atoms and reside on islands for significantly shorter times than N adatoms. This effect is primarily due to the much lower diffusion rates on islands of N adatoms, which ultimately descend onto the terrace either via direct hopping or push-out exchange with island edge and corner atoms. The dynamics of TiN_x (x = 1 - 3) admolecules are considerably more complicated, due to the additional rotational degrees of freedom engaged in the transport of these adspecies. Thus, TiN dimers exhibit the most complex descent mechanisms, which involve combinations of push-out exchange with edge atoms and direct hops over island edges. Surprisingly, we find TiN_2 trimers to have the shortest residence times on islands and to descend onto the terrace only via direct hops over island edges. TiN_3 tetramers, however, are essentially stationary on the TiN(001) islands, and no descent events are recorded in this case. These results demonstrate that tetramers lead directly to island-on-island growth on TiN(001) and have a critical effect on TiN thin film growth modes.

10:00am **B7-1-7 *Ab Initio* Study of the Effect of Al Addition on Surface Kinetics of Ti, Hf and Zr Nitrides**, ***C. Tholander*** *(chtho@ifm.liu.se), B. Alling, F. Tasnadi,* Linköping University, Sweden, *I. Petrov, J. Greene,* University of Illinois at Urbana-Champaign, US, *L. Hultman,* Linköping University, Sweden

Understanding of the diffusion properties in nitrides helps us to find ways to improve the growth of materials, e.g. thin films. Using different surfactants during growth could, for example, increase or decrease adatom mobility by modifying the diffusion barriers , with consequences for the growth modes.

In our work we have investigated the changes in surface kinetics due to Al substitution in low indexed surfaces of TiN, HfN and ZrN using first principles calculations. The adatom diffusion paths for Ti, Al, Hf, Zr and N have been investigated using both magnetic and non-magnetic nudged elastic band DFT calculations. We also present adatom energy surfaces for selected adatoms on TiN, HfN and ZrN.

The substitution of Ti for Al has been shown to have significant effects on the diffusion paths. For example on TiN(001) the Ti adatoms bind harder to the hollow site positions around the Al substitution, decreasing their mobility. In other cases Al substitution decreases the diffusion barriers and increase the mobility of the adatoms.

10:20am **B7-1-8 First-principles Study of Electronic, Elastic and Thermodynamic Properties of CrN**, ***L. Zhou*** *(liangcai.zhou@tuwien.ac.at),* Vienna University of Technology and Montanuniversität Leoben, Austria, *D. Holec,* Montanuniversität Leoben, Austria, *P.H. Mayrhofer,* Vienna University of Technology, Austria

We used Density Functional Theory with generalized gradient and local density approximations together with selectively applied on-site Coulomb interaction to study electronic, vibrational, thermodynamic and elastic properties of CrN in various configurations, including antiferromagnetic (AFM), nonmagnetic (NM), ferromagnetic (FM) and paramagnetic (PM) states. The analysis of the electronic structures reveals that nitrogen under-stoichiometry induced by nitrogen vacancies, interstitials or anti-sites in CrN contributes to the metallic behavior. The phonon density of states (PDOS) shows that orthorhombic and cubic AFM, cubic FM and cubic PM CrN are vibrationally stable phases at zero pressure, while cubic NM CrN exhibits non-zero PDOS for imagine frequencies for zero as well as under high pressure. The thermodynamic data obtained from the quasi-harmonic approach are used to discuss the transition from AFM orthorhombic to PM cubic phase. Finally, heat capacity, linear thermal expansion coefficient, bulk modulus, and elastic constants are calculated as functions of temperature and critically compared with the available experimental data.

10:40am **B7-1-9 Importance of Finite Temperature Effects in *AB INITIO* Simulations of Materials for Hard Coating Applications**, ***I. Abrikosov*** *(igor.abrikosov@ifm.liu.se), P. Steneteg, O. Hellman, L. Hultberg, F. Tasnadi, N. Shulumba, O. Vekilova, B. Alling,* Linköping University, Sweden **INVITED**

Ab initio electronic structure theory is known as a useful tool for prediction of materials properties, for their understanding, as well as for determination of parameters employed in higher-level modeling. However, majority of simulations still deal with calculations in the framework of density functional theory (DFT) with local or semi-local functionals carried out at zero temperature. In this talk we underline the importance of explicit treatment of finite temperature effects in *ab initio* simulations of materials for hard coating applications and present new methodological solutions, which go beyond traditional approach and allow us to calculate materials properties at elevated temperature. In particular, we study elastic properties of TiN within a wide temperature interval [1]. Single crystal elastic constants C_{11}, C_{12} and C_{44} are calculated. In all cases strong dependence on the temperature is predicted, with C_{11} decreasing by more than 30% at 1800 K as compared to its value obtained in conventional static calculations at T=0K. We observe that the material becomes substantially more isotropic at high temperatures. Next, we suggest first-principles method for the calculation of thermodynamic properties of magnetic materials in their high-temperature paramagnetic phase [2]. It is based on *ab initio* molecular dynamics (AIMD) and simultaneous redistributions of the disordered but finite local magnetic moments. We apply this disordered local moments molecular dynamics method to simulate equation of state of CrN [2,3] and thermodynamic properties of $Cr_{1-x}Al_xN$ alloy. Our results unambiguously demonstrate importance of taking into account finite temperature effects in theoretical calculations of thermodynamic and elastic properties of materials. [1] P. Steneteg, O. Hellman, O. Yu. Vekilova, N. Shulumba, F. Tasnadi, and I. A. Abrikosov, in preparation. [2] P. Steneteg, B. Alling, I. A. Abrikosov, Phys. Rev. B **85**, 144404 (2012). [3] B. Alling, T. Marten, and I. A. Abrikosov, Nature Materials **9**, (2010) 283; B. Alling, T. Marten, and I. A. Abrikosov, Phys. Rev. B **82**, (2010) 184430.

Fundamentals and Technology of Multifunctional Thin Films: Towards Optoelectronic Device Applications
Room: Sunset - Session C4-1

Thin Film Growth and Characterization for Optoelectronic Devices
Moderator: K. Yu, Lawrence Berkeley National Laboratory, US, A. Ranade, The Boeing Company

8:00am **C4-1-1 Fabrication and Characterizations of CIGS Films Using One-step Electrochemical Co-deposition Methods**, ***Y.M. Yeh*** *(ymyeh@mail.wfu.edu.tw),* WuFeng University, Taiwan, *H. Chen,* National Chi-Nan University, Taiwan, Republic of China, *S.M. Liu,* WuFeng University, Taiwan, *S.T. Huang, Y.J. Chen,* National Chi-Nan University, Taiwan, Republic of China

Due to the advantages of low cost, fast and large-area production, electrodeposition has become one of the mainstream fabrication methods of the CIGS solar cells. In this study, CIGS film was formed using one-step electrochemical deposition at various deposition potential voltages in solution with diverse pH values. M ultiple material analyses such as X-ray diffraction (XRD) analysis, scanning electron microscope (SEM) images, energy diffraction spectrometer (EDX), X-ray photoelectron spectroscopy (XPS) and secondary ion mass spectroscopy (SIMS) were used to examine the electro-deposition parameters. The results reveal that the Ga could not be deposited on the substrate in stirred conditions. In unstirred conditions, quaternary CuInGaSe compound could be formed with various Cu/In/Ga/Se ratios grown in various deposition parameters. The experimental results

indicate that the pH value of the solution and electric potential play important roles on determining the composition of the CIGS film. UV spectrometer was performed to measure the bandgap of the CIGS thin film. The electrodeposited CIGS film shows promises for future solar cell applications.

8:20am **C4-1-2 Preparation of CdMnS Thin Film: Applications in Photoelectrochemical Cell**, ***J.S. Dargad*** *(jsdargad@rediffmail.com)*, Dayanand Science College, Latur, Swami Ramanand Teerth Marathwada University, Nanded, Maharashtra, India

A new class of dilute magnetic semiconductor (DMS, CdMnS) thin film based photoelectrochemical cell is presented. DMS thin films are synthesized on both glass and stainless steel substrates using a chemical growth process. The preparation parameters (such as growth temperature, time, reaction pH, precursor concentrations, etc) were optimized to yield characteristically oriented films. The layer thickness was found to be decreased with an increase in Mn^{2+} concentration. The composition of the as-grown samples was determined by an EDS technique. The electrochemical cells were then formed out of these series of films as the active photoelectrodes, an electrolyte and a counter electrode. The cells were then characterized through their dark and photosensing properties. The other cell parameters were determined from these studies and the cell performance has been evaluated with a special reference to Mn^{2+} concentration in CdS. A significant enhancement in performance has been observed for a cell with electrode composition of x = 0.01.

8:40am **C4-1-3 Fabrication and Characterization of High-efficiency CdTe-based Thin-Film Solar Cells**, *Y. Yan (yanfa.yan@utoledo.edu)*, ***N. Paudel***, The University of Toledo, US **INVITED**

CdTe-based thin-film solar cells with conversion efficiencies better that 15% have been fabricated on commercial Pilkington SnO_2:F-coated soda-lime glass without anti-reflection coating. The CdS window layers were grown by either magnetron sputtering or chemical bath deposition. The CdTe absorber layers were synthesized by close-spaced sublimation method. Cu/Au layers were used as the back contacts. We have achieved cells with open circuit voltage higher than 0.840 V and fill factor better that 75%. The structure of the cells and the quality of the CdTe thin films have been characterized by electron microscopy, X-ray diffraction, and optical spectroscopy. The correlation between the cell performance and material quality will be discussed in the presentation.

9:20am **C4-1-5 The Optimization of Indium Codoping Concentration in 100-nm-thick GZO Films for Low Resistivity and High Humidity Resistance Properties**, ***H. Song*** *(song.huaping@kochi-tech.ac.jp)*, *H. Makino*, *N. Yamamoto*, Kochi University of Technology, Japan, *S. Kishimoto*, Kochi National College of Technology, Japan, *T. Yamamoto*, Kochi University of Technology, Japan

Ga-doped ZnO (GZO) films are promising transparent conductive oxide (TCO) films for use in electrodes of flat display panels and window layers of thin film solar cells. Control of the humidity resistant properties of GZO films is a crucial research topic for practical wide applications, including optoelectronic devices with substrates based on flexible polymer materials having highly water-absorption coefficients in near future. For 200-nm-thick GZO films deposited on glass substrates, we have optimized oxygen gas flow rates (OFRs) introduced in the chamber during the deposition, and achieved humidity resistant GZO films; The relative change in electrical resistivity ρ after 500 hours humidity test (temperature of 60 °C and relative humidity of 95%) could be controlled to be less than 10%. Nevertheless, for wide applications, an issue about how to obtain durable thinner GZO films is still open. For as-deposited 100-nm-thick GZO films with a ρ of 3.71 μΩm, the relative change in resistivity $\Delta\rho$ after the test was 32.6%. Very recently, we proposed a novel technology to co-doped indium (In) species together with the control of OFR to improve the humidity resistant properties of 100-nm-thick GZO films. As a result, for the 100-nm-thick GZO:In film with the ρ of 4.09 μΩm before the test, we have found a reduced $\Delta\rho$ of 12.3% after the humidity test. In this study, we optimized both the contents of In codoped and the magnitude of OFRs to achieve humidity resistant GZO films. GZO films with different contents of In codoped were grown on glass substrates at 200 °C by ion plating with dc arc-discharge under various OFRs ranging from 0 to 25 sccm. The In contents in the deposition source (the sintered ZnO tablets with a Ga_2O_3 content of 3 wt.%) were 0.25, 0.5 and 0.75 wt.%.Analysis of X-ray diffraction measurements results shows that for 0.25 wt.% In-codoped GZO films, an increase in OFRs gives rise to the deterioration of the alignment between *c*-axis orientation of columnar in polycrystalline GZO films. On the other hand, for 0.50 and 0.75 wt.% In-codoped GZO films, further increase in OFR of more than 15 sccm improves the alignment above accompanied with an increase in ρ. Analysis of data obtained by Hall effect measurements shows that an increase in In contents enhances the humidity resistant properties for GZO films at any given OFR. We optimized both In contents and OFRs not only to enhance the reduction of $\Delta\rho$ but also minimize ρ. As a result, we have ensured the durability of 100-nm-thick GZO:In films to humidity : $\Delta\rho$=6.5% for GZO:In transparent films with low ρ of 4.54 μΩm after the humidity test.

9:40am **C4-1-6 Effects of Native Defects on the Electrical and Optical Properties of Cadmium Oxide**, ***K. Yu*** *(kmyu@lbl.gov)*, Lawrence Berkeley National Laboratory, US, *L. Reichertz*, RoseStreet Laboratories, US, *S. Grankowska*, Warsaw University, Poland, *D. Detert*, *O. Dubon*, University of California, Berkeley; Lawrence Berkeley National Laboratory, USA, *A. Anders*, *W. Walukiewicz*, Lawrence Berkeley National Laboratory, US

We have recently demonstrated that intentional doping of CdO results in an ideal uncompensated material with extremely low resistivity ($\rho<10^{-4}\Omega$-cm) and an excellent transmission window in the range from 400 nm to >1500 nm, making this material an ideal transparent conductor for photovoltaics with low band gap absorbers [1]. These exceptional electrical and optical properties were obtained typically in polycrystalline CdO synthesized by a variety of methods including pulsed laser deposition (PLD), filtered cathodic arc deposition and RF sputtering. Here, we present a systematic study of the electrical and optical properties of CdO thin films grown by RF sputtering. In particular we studied the effects of defects in undoped and In-doped CdO samples under different deposition and annealing conditions. We found that at low growth temperatures (<200°C), a fast growth rate tends to trap both oxygen vacancies and compensating defects in the film resulting in materials with high electron concentration of $>2x10^{20}/cm^3$ and relatively low mobility (~30-50 cm^2/V-s). Reducing the growth rate to ~2-3 nm/min results in high quality material with electron concentration of $\sim1x10^{20}/cm^3$ and mobility >100 cm^2/Vs. In order to identify the dominating defects in the films, we have also carried out thermal annealing in N_2 or O_2 ambient. Annealing in O_2 ambient consistently reduces electron concentration and increases mobility, suggesting that the dominating defects in sputtered CdO films are oxygen vacancies. Sputtering with an Ar/O_2 (80%/20%) plasma results in high resistivity CdO films ($\rho>10^{-2}\Omega$-cm) with low electron concentration of $10^{18}/cm^3$, most likely due to the increased incorporation of excess O resulting in anon-stoichiometric material. However such material is not stable and an increase in the electron concentration is observed at brief annealing as short as 1 second at 300°C, suggesting outdiffusion of O and increase of the O vacancy concentration. This conclusion is further supported by more pronounced annealing effects observed in thinner samples. Intentional doping with In donors leads to an increase of both the electron concentration and the mobility. With proper doping CdO films with electron concentration of more than 10^{21} cm^{-3} and electron mobility higher than 100 cm^2/Vs can be achieved, indicating greatly reduced ionized impurity scattering effects in in this material. We will also discuss the effect of defects and intentional doping on optical properties of as grown and annealed CdO films.

[1] K.M Yu, et al., J. Appl. Phys. **111** 123505 (2012).

10:00am **C4-1-7 Study of the Instability of Amorphous InGaZnO Thin Film Transistor under the DC and AC Drain-bias Stress**, ***L.W. Lin*** *(ltslees@gmail.com)*, *T.C. Chang*, *S.Y. Huang*, *M.C. Yang*, National Sun Yat-Sen University, Taiwan, Republic of China, *K.H. Yang*, University of Toronto, Canada, *M.H. Wu*, *M.C. Chen*, *K. Mai*, *Y.J. Chiu*, National Sun Yat-Sen University, Taiwan, Republic of China, *B.L. Yeh*, Advanced Display Technology Research Center, AU Optronics, Taiwan

This study investigates degradation behavior of AC drain-bias stress under illumination for InGaZnO thin film transistors. In the previous study, we reported the gate-to-drain capacitance-voltage curve exhibited degradation of the hump phenomenon during the DC drain-bias stress. However, it observes different degradation behavior after the AC drain-bias stress, which the hump phenomenon disappeared but the Vth shift was observed. Significantly, the degradation behavior during the AC drain-bias stress is related with the duty-ratio and frequency of the AC pulse waveform. The experiment results indicate the pulse-width (PW) time during the drain bias makes the holes trapping at interface defect between insulator/active layer, and on the other hand during the puls-base (PB) time the hole trapping induces surface band banding make electron inject into the interface defect, resulting in the electron and hole recombine within the interface defect. Moreover, we calculate the charge trapping density and physics-position of charge trapping by using the capacitance-voltage curves. Finally, this work also employs different intensity of illumination during the stresses and the simulation system to further clarify the mechanism of degradation behavior.

10:20am **C4-1-8 Microwave-assisted Hydrothermal Synthesized Nitrogen-doped TiO_2 Photocatalysts for Enhanced Visible Light Response**, ***W.C. Huang***, *J.M. Ting (jting@mail.ncku.edu.tw)*, National Cheng Kung University, Taiwan

This work reports the synthesis and characterization of N-doped TiO_2 mesoporous beads prepared by a two-cycle rapid microwave-assisted hydrothermal method using three different types of nitrogen dopants: diaminohezane, triethylamine, urea. In the first cycle, TiO_2 mesoporous beads with controlled structures were synthesized at 200°C. The obtained beads were then subjected to a second cycle of microwave-assistaed hydrothermal process for dpoing with one of the aforementioned dopants. The sue of a secon cycle is to maintain the integrity of the beads, which otherwise would be easily destroyed if the synthesis and doping processes are carried out at the same time. The crystalline structure of the N-doped TiO_2 was examinedusing X-ray diffraction. The surface state and structure were investigated using X-ray photoelectron spectroscopy and scanning electron microscopy, respectively. The absorption of N-doped TiO_2 in the range of visible light was confirmed using UV-Vis spectroscopy. The self-assembled N-doped TiO2 redshift in adsorption edge up to 500nm. The obatined TiO_2 was also dissloved in methyl blue solution to function photocatalyst and the catalytic activity was determined. The photocatalytic activity of all N-doped TiO2 can be found the N-doped TiO2 used dianimohexane as the nitrogen dopant decompose the organic pollution more complete and rapid than others .

10:40am **C4-1-9 Effect of Thermal Annealing on Nickel Oxide Doped AZO Transparent Conducting Thin Films Prepared by DC Magnetron Sputtering System**, ***Y.D. Jo*** *(003easter@hanmail.net)*, Pusan National University, Republic of Korea

The NiO doped AZO (NiO:AZO) thin films with different NiO weight percent range between 0 and 5.0 wt. % were synthesized by DC magnetron sputtering method using composite targets in argon atmosphere at room temperature, and then forming gas annealing process was carried out at 400°C for 1hour. The electrical, structural and optical properties were detailedly and extensively studied. The electrical resistivity of as-deposited NiO:AZO films was found to increase with increasing of NiO concentration due to the effect of decreasing of electrical mobility was more considerable than enhancing of carrier concentration. After N_2/H_2 annealing process, the electrical resistivity was remarkably reduced to $7.67\times 10^{-4}\,\Omega$cm which is the best value of this study at 3.0 wt. % NiO doping concentration, due to enhancing electrical mobility and carrier concentration. The improvement of electrical mobility was due to enhancement of crystallinity and increasing carrier concentration caused from generation of Ni metal sub-nano particles in NiO:AZO films after forming gas annealing. Meanwhile, the average optical transmittance was over 80% for all films except forming gas annealed 5.0 wt. % NiO:AZO films. Band gap widening (3.64 eV at 5.0 wt. %) was observed in annealed NiO:AZO films owing to the Burstein-Moss shift.

11:00am **C4-1-10 Characteristics of Plasma Generated by ICP-CVD with Various H2/SiH4 Ratios and the Resultant Properties of nc-Si-H Thin Films**, ***J.H. Hsieh*** *(jhhsieh@mail.mcut.edu.tw)*, *Y.L. Lai*, Ming Chi University of Technology, Taiwan, Republic of China, *C. Li*, National Central University, Taiwan, Republic of China, *J. Setsuhara*, Osaka University, Japan

Nc-SiH thin films were deposited with an ICP-CVD system attached with four internal antennas, under the variation of H_2/SiH_4 ratios (R). During deposition, the generated plasma was characterized using a Langumir probe and an optical emission spectrometer (OES). The films' properties were characterized using Raman spectrometry and FTIR. The results were correlated with those obtained from probe and OES studies. It was found that the crystallinity of nc-Si:H film was significantly affected by plasma density which was increased with the increase of R, but only to a certain extent. Both the plasma density and Xc reached the maximum at R=10, then leveled off. According to OES results, the ratio of IHa*/ISiH* also showed the same trend. Also, it was found that the crystallinity could be proportionally related to the increase of I*(SiH2+SiH3)/I(SiH+SiH2+SiH3) in FTIR spectra.

11:20am **C4-1-11 Optoelectronic Characterization of *p*-type NiO_x and *n*-type TiO_2 Thin Films Deposited by Laser Ablation**, ***A. Hirata*** *(hiragustavo@gmail.com)*, CNyN-UNAM, US

Nickel oxide (NiO) has been used in photoelectrochromic devices due to its *p*-type intrinsic behavior. Titanium oxide (TiO_2) is an n-type semiconductor with excellent photocatalytic properties. In this work, Ni and Ti films were deposited by the PLD technique at room temperature and oxidized at 550ºC in air for 2 hours to form NiO and TiO_2, respectively. The third harmonic (λ= 355 nm) of a YAG:Nd pulsed laser operated at an energy fluence of 3 J/cm^2 and 10 Hz repetition rate was used for the laser ablation experiments. Microstructural development and chemical composition of the films were analyzed by SEM, XRD, AES/XPS and XRD techniques. Hall Effect and Van der Pauw measurements confirmed p- and n-type behavior of NiO and TiO_2 films, respectively. Heterojunctions have been fabricated by deposition of **p**-type NiO on **n**-type TiO_2 on ITO coated glass substrates. The relationship between electrical and photocatalytic properties of NiO and TiO2 thin films will be discussed.

Support from DGAPA-UNAM (Grant No. IN114010) and CONACYT (Grant No. 100555) and technical assistance by E. Aparicio, D. Dominguez and I. Gradilla are acknowledged.

Tribology & Mechanical Behavior of Coatings and Engineered Surfaces
Room: Golden West - Session E2-3

Mechanical Properties and Adhesion
Moderator: R. Chromik, McGill University, D. Bahr, Washington State University, M.T. Lin, National Chung Hsing University, Taiwan

8:00am **E2-3-1 Deformation and Fracture of Wear-Resistant Laser Oxide Coatings on Metallic Substrates**, ***S. Lawrence*** *(samantha.lawrence@wsu.edu)*, Washington State University, US, *D. Adams*, Sandia National Laboratories, US, *H. Zbib*, *D. Bahr*, Washington State University, US, *N. Moody*, Sandia National Laboratories, US

Thermal exposure of oxidizing metals with concentrated laser irradiation in ambient atmosphere produces metastable dielectric layers with characteristic colors. While most work has focused on continuous wave (CW) laser exposure of metallic substrates, relatively few groups have studied pulsed laser colorization and no studies have addressed mechanical behavior. Oxides on titanium and stainless steel substrates are particularly interesting; the properties of the film and substrate combination control wear and fracture of the oxide with a strong contribution from plastic deformation in the substrate. Films were found to be comprised of multiple crystalline phases with misfit strains leading to through-thickness cracking. Traditional quasistatic and dynamic nanoindentation with multiple tip radii and nanoscratch testing probed mechanical properties, fracture, and wear behavior. Oxides have elastic moduli lower than the metallic substrates, but hardnesses that are much higher, on the order of 10-16GPa. Applying an energy and fracture mechanics analysis, fracture properties and residual stress can be determined from pre-cracked films. Finally, NanoECR results indicated that defect structure and electromechanical response vary with processing conditions. Combining microscopy, diffraction, and indentation techniques provides a unique approach for defining wear behavior of laser-fabricated oxide films in harsh conditions. This work was supported by DTRA Basic Research Award # IACRO 11-4471I, NSF Grant NSF/DMR-0946337, and by Sandia National Laboratories, a Lockheed Martin Company for the USDOE NNSA under contract DE-AC04-94AL85000.

8:20am **E2-3-2 Influence of Film Thickness on Fragmentation and Contact Damage of Diamond-Like Carbon (DLC) Coated Titanium Substrates**, ***D. Bernoulli***, *A. Wyss*, *K. Häfliger*, ETH Zurich, Laboratory for Nanometallurgy, Switzerland, *K. Thorwarth*, *R. Hauert*, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland, *G. Thorwarth*, DePuy Synthes Companies, Switzerland, *R. Spolenak (ralph.spolenak@mat.ethz.ch)*, ETH Zurich, Laboratory for Nanometallurgy, Switzerland

Diamond-like carbon (DLC) coatings are characterized by its high hardness and the outstanding tribological behavior. They are hence used as sliding partners in friction pairs in many industrial applications. However, wear and loose particles trapped between the friction pairs can lead to the apparition of locally applied high pressure on the DLC coating. This effect results in contact damage of the coating and, depending on the penetration depth, influences the substrate. In the case of a soft and compliant substrate, the contact damage leads to cracking and imprinting of the hard and brittle DLC coating into the soft and compliant substrate. Mechanical loading can occur during service life or processing and may lead to the formation of cracks and delaminated areas. The failure mode upon contact damage and mechanical loading of DLC coated titanium substrates has been investigated in this work. DLC coatings with a thickness varying from 50 nm up to 4 μm have been deposited.

The contact damage could be diminished by taking a stiffer substrate. However, this approach is often not suitable since the substrate material is given by the industrial application. In the case of a soft and compliant substrate (e.g. titanium), a suitable interlayer combination which is deposited between substrate and DLC coating can show similar properties as a stiff substrate. The stress field distribution upon indentation has been

determined by finite element modeling (FEM) and the contact damage has been simulated by microindentation and then analyzed by scanning electron microcopy (SEM), load-displacement curves and focused ion beam (FIB) cuts. It has been observed that the cracking morphology and the stress field distribution in the substrate/interlayer/DLC system strongly depends on the thickness of the DLC coating and interlayer as well as on the interlayer material.

The mechanical loading was simulated by uniaxial loading and the damage pattern was recorded in situ by optical, scanning electron (SEM) and atomic force microscopy (AFM). The cracking analysis shows that a 50 nm DLC coating exhibits localized areas with a high crack density whereas thicker coatings show regular crack patterns with equidistant cracks. In addition, strain at onset of fragmentation decreases with increasing film thickness and a widening of existing cracks upon further straining has been observed.

8:40am **E2-3-3 Influence of Application Technology on the Erosion Resistance of DLC-Coatings**, *U. Depner-Miller (depner@mpa-ifw.tu-darmstadt.de)*, ***H. Scheerer***, *J. Ellermeier*, *M. Oechsner*, Technische Universitat Darmstadt, Germany, *K. Bobzin*, *N. Bagcivan*, *T. Brögelmann*, *R. Weiß*, RWTH Aachen University, Germany, *K. Durst*, *C. Schmid*, Friedrich-Alexander-University Erlangen-Nuernberg, Germany

Various components need protection against superimposed corrosion and wear (abrasion, erosion) loading, e.g. in off-shore applications. The goal of the research has been to develop PVD multilayer coating by systematically altering the layer architecture in order to protect components against corrosive environments and erosive loadings. A Diamond-Like-Carbon (DLC) toplayer of the multilayer coating system is responsible for the erosion resistance and a multilayer architecture below ensures a good corrosion protection.

Our investigation is focused on the influence of the application technology (PVD or PECVD) and the resulting coating properties of the DLC toplayer. The investigated PECVD-toplayer was produced by a mixture of ethyne and hydrogen gas, whereas the PVD-toplayers were deposited from a graphit-target and different mixtures of ethyne and argon gas. The applicated DLC-toplayers are characterized by hardness values between 11 and 18 GPa (nanoindentation) and similar adhesion properties (scratch test). Residual stresses of the DLC-toplayers were determined by means of focused ion beam milling and tracking of the resulting relaxation strains by digital image correlation. Values of up to 2 GPa in compression have been determined. Under the erosion load (combination of abrasive and fatigue loading) the abrasive degradation of the investigated coatings has been found to depend mainly on coating hardness. As expected, the hardest DLC-toplayer (PECVD) shows least abrasive degradation. However, when tested under cyclic loading, the coating exhibiting the highest hardness values (PECVD) show the most severe fatigue damage of all DLC-coatings investigated..

9:00am **E2-3-4 Elevated Temperature Nanoindentation of Multilayered Coatings**, *G. Mohanty (Gaurav.Mohanty@empa.ch)*, *J. Wheeler*, *R. Raghavan*, EMPA Swiss Federal Laboratories for Materials Science and Technology, Switzerland, *B. Bellaton*, *P. Kempe*, CSM Instruments SA, Switzerland, ***J. Michler***, EMPA Swiss Federal Laboratories for Materials Science and Technology, Switzerland

One of the primary motivations for development of instrumented indentation was to measure the mechanical properties of thin films. Characterization of thin film properties as a function of temperature is important for both engineering design and scientific considerations. The major challenge in elevated temperature testing of thin films is to obtain clean load-displacement data for shallow indentation depths that correspond directly to the deformation behavior and to avoid artifacts of testing like thermal drift and noise. Thermal drift arises due to thermal expansion/contraction of the indenter load column and gets convoluted with the deformation data being recorded by the instrument. The compliance of the sample mounting can change as a function of temperature making the extraction of accurate modulus values difficult for thin coatings.

Keeping these challenges in view, we have developed a novel high temperature nanoindentation system that can perform accurate nanoscale measurements up to 400 degrees C in vacuum at pressures as low as 10e-6 mBar to prevent oxidation. This system utilizes an active surface referencing technique that measures the differential displacement between the indenter tip during indentation, and a reference sitting on the sample surface. The most important aspect of this active referencing system is the elimination of frame compliance making it suitable for accurate property extraction of thin films as a function of temperature. The challenges associated with elevated temperature nanoindentation testing and recent progress made by us in its application to thin film measurements will be presented. Relevant design modifications and operational refinements that have resulted in minimizing drift rates to less than 7nm/min at 400 degrees C will be discussed. Noise level in measurements was found to be negligible with increase in testing temperature. Case studies on multilayered films will be presented to illustrate the best practices and experimental considerations in nanomechanical testing of thin films at elevated temperatures.

Multilayered thin films exhibit superior mechanical properties compared to their single layered constituents. Metal / metal and metal / ceramic multilayers of Al/W and Al/TiN deposited by magnetron sputtering on silicon substrates were chosen as they form model systems to study the size dependence of mechanical properties of the systems as a function of temperature. W and TiN were used to prevent interlayer diffusion during the deposition and elevated temperature testing of these systems.

9:20am **E2-3-5 Energy Loss and Internal Frictions Study of Nanocrystalline Metal Thin Films**, ***M.T. Lin*** *(mingtlin@nchu.edu.tw)*, *C-J. Tong*, *Y-T. Wang*, National Chung Hsing University, Taiwan, Republic of China

A novel designed capacitance measurement system has been used to measure energy loss mechanical behaviors of the ultra thin metal films. In order to measure the metal film samples in the very small scale, a paddle like test specimen has been designed. It is used to carry out metal film on top. Al and Cu thin films are widely used in the electronic interconnections or MEMS structures. Previously, there were many studies on mechanical properties of them, but they usually focus on the quasistatic properties or dynamic properties in larger scale. The goal of this study is to experimentally investigate the dynamic properties of Al and Cu thin films at room temperature under high vacuum conditions. We measured energy loss through decay of oscillation amplitude of a vibrating structure following resonant excitation. We closely examine those film thicknesses and grain sizes with respect to the dynamic properties of films. The measurement results include gas damping effect on sample decay, resonance frequencies change of various thicknesses paddle samples, stiffness and mass influence on resonance frequencies, and the thickness dependence of internal friction in Cu and Al films. In these results, we found that the environmental pressure has significant effect on the sample decay rate and the pressure changes linearly versus the sample decay rate. Resonance frequencies of paddle samples have been obtained and the values were compared with fundamental theory calculation and Finite Element Method simulation. We also determine the internal friction of the thin and ultra thin metal films. The internal frictions of the thin and ultra thin metal films do not depend strongly on the film thickness but presently different trends in Cu and Al films.

9:40am **E2-3-6 Effect of the Anisotropic Growth on the Fracture Toughness Measurements Obtained in the Fe_2B Layer**, ***E. Hernandez-Sanchez***, *G. Rodriguez-Castro*, Instituto Politecnico Nacional, Mexico, *M. Romero-Romo*, UAM-A, Mexico, *I. Arzate-Vazquez*, *I. Campos-Silva (icampos@ipn.mx)*, Instituto Politecnico Nacional, Mexico

In borided low-carbon steels, the morphology displayed by the Fe_2B layer is saw-toothed, and the layer-substrate interface has a columnarity extent. The layer morphology can be explained because the diffusion process is of strongly anisotropic nature. So, the mechanical properties are affected by the anisotropy along the boride layer.

One important mechanical parameter in design is the fracture toughness value. In recent years, several attempts to determine the fracture toughness of different borided steels have been carried out using the Vickers microindentation test.

The purpose of this work is to estimate fracture toughness along the Fe_2B layer using the Berkovich nanoindentation technique. First, the boriding of AISI 1018 steel was developed by the powder-pack method at a temperature of 1273 K with an exposure time of 8 h. The boride layer thickness was estimated in 210 microns. Berkovich nanoindentations tests were performed on the “pure zone” of the Fe_2B layer at distances of 25, 50 and 75 microns from the surface of the borided steel, where the indentation loads were varied between 10 to 500 mN at each distance. The behavior of the hardness as a function of the indentation load showed the presence of the indentation size effect (ISE) at the different distances from the surface, in which the apparent hardness values of the Fe_2B layer were estimated by the model of geometrically necessary dislocations. In addition, the measurements of the cracks emanated from the corners of the indentation marks were evaluated for the different applied loads.

Finally, the mechanisms of various crack patterns and existing models used to estimate the fracture toughness such as stress-analysis-based model and energy-based models were discussed as a function of the anisotropic nature of the boride layer.

10:00am **E2-3-7 Characterising Micromechanical Deformation of Commercially Pure Zirconium**, ***T.B. Britton*** *(b.britton@imperial.ac.uk)*, University of Oxford and Imperial College London, UK, *J. Gong, D. Lloyd, A. Wilkinson, S. Roberts*, University of Oxford, UK **INVITED**

Extraction of fundamental materials properties, such as the critical resolved shear stress (CRSS) required to move dislocations and anisotropic single crystal elastic constants requires isolation and testing of individual microstructural units. We have performed these tests on single samples within polycrystal samples using nanoindentation [1], micro-pillar compression and micro-cantilever testing [2]. The study was performed on 99.98% pure zirconium.

Nanoindentation was performed to extract indentation hardness and modulus as a function of crystal orientation (measured with EBSD). Evaluation of the local flow fields around two of these indents was performed using HR-EBSD and reveals evidence of a complex stress state, indicating the inherent difficulty in interpreting nanoindentation results to quantitatively assess key mechanical properties (similar to a prior study in Ti [2]).

To simplify the testing geometry and therefore the applied stress state, we have fabricated small scale mechanical test specimens using FIB (similar to previous work in titanium [3]) and observed both differences in the activation of each slip system as well as a mechanical size effect.

Micro-pillars offer a simple geometry for uniaxial testing but in practice understanding the strain state is difficult. In our experiments mechanical instabilities and difficulties in making a 'perfect' test specimen at the small scale result in non-uniform deformation states and difficulties interpreting the onset of plastic strain. This makes rational extraction of key parameters not trivial.

Micro-cantilevers with an equilateral cross section provide a slightly more complex strain state (i.e. bending) but their stable deformation process is well suited to continuum based modeling approaches to extract mechanical properties. Each cantilever was milled to contain a volume of material at a particular orientation with respect to the beam design in order to apply the maximum shear stress to an individual slip system (i.e. single slip) and they were carefully measurement and then tested with a nanoindenter. The load-displacement response was recorded and compared to the deformation of a similar 3D finite element crystal plasticity model [4]. The CRSS in the model until the experiment and simulation load-displacement curves matched well.

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10:40am **E2-3-9 Super-hard or Super-tough? - Nanomechanics for Improving the Toughness and Durability of Hard Nanocomposite Films**, ***B Beake*** *(ben@micromaterials.co.uk)*, Micro Materials Ltd., UK, *V. Vishynakov*, Manchester Metropolitan University, UK, *A.J. Harris*, Micro Materials Ltd, UK, *J.S. Colligon*, Manchester Metropolitan University, UK, *J. Smith, M. Davies*, Micro Materials Ltd, UK

The link between the deposition conditions, microstructure, mechanical properties and tribological performance of hard nanocomposite films is currently an area of intense research. Understanding the link between mechanical properties and tribological performance will be key to their successful applications. Rather than be super-hard, it may be desirable that they are super-tough.

TiFeN, TiN and TiFeMoN nanocomposite films with a wide range of mechanical properties have been deposited on Si using a dual ion beam system to investigate the correlation between mechanical properties and performance. Mechanical properties were determined by nanoindentation, tribological behaviour assessed by nano-scratch testing and their dynamic toughness by nano-impact testing.

Failure behaviour of the films was strongly correlated with the ratio of hardness to modulus (H/E) in the film. In the nano-scratch test nanocomposite thin films of TiFeN with very high H/E ratios failed dramatically at low critical load, with failure leading to large-area delamination. Films with slightly lower H/E were found to possess a more optimum combination of hardness and toughness for applications where they could be exposed to high shearing forces and do not show the same failure behaviour. In the nano-impact test films with high resistance to plastic deformation (H^3/E^2) showed improved performance at low impact forces but not at higher forces.

Their suitability for high temperature applications has been investigated using a recently developed modification to a commercial nanoindentation instrument (NanoTest) enabling nano-scale friction measurement at 750C.

11:00am **E2-3-10 Fatigue Property Improvements of Ti Alloys by Metallic Glass and TiN Thin Films**, ***C.M. Lee***, Department of Materials Science and Engineering and Graduate Institute of Applied Science and Technology, National Taiwan University of Science and Technology, Taipei 10607, Taiwan, Taiwan, Republic of China, *J.P. Chu (jpchu@mail.ntust.edu.tw)*, National Taiwan University of Science and Technology, Taiwan, Republic of China, *J.-W. Lee*, Ming Chi University of Technology, Taiwan, Taiwan, Republic of China

Thin film metallic glasses (TFMGs) with unique physical and mechanical properties have attracted interest in the past decade. With the aim of taking their advantages to their applications, a 200-nm-thick TFMG ($Zr_{50}Cu_{27}Al_{16}Ni_7$) film with a 10nm titanium adhesion layer and a hard coating TiN film were coated on a substrate. Effects of these two types of films on the four-point bending fatigue property improvements of Ti alloys were investigated. The fatigue life improved ~17 times and ~4.5 times by TFMGs and TiN coatings, respectively, all under a stress of 675MPa. It is demonstrated that both TFMG and TiN films with high strength retarded the cracks propagated during fatigue cycles, resulting in increased fatigue life. The especially significant improvement from TFMGs was largely attributable to improved ductility and flexibility and to increased adhesion strength from the titanium adhesion layer.

11:20am **E2-3-11 Microstructure and Properties Characterization of WC-Co HVOF Coatings Obtained From Standard, Superfine and Modified by Nanocarbides Feedstock Powders**, *G. Moskal (grzegorz.moskal@polsl.pl), K. Szymański,* ***H. Myalska***, Silesian University of Technology, Poland

Microstructural and basic mechanical properties characterization of WC - based coatings obtained by standard HVOF method was showed in this article. Three different feedstock powders of WC-Co 83-17 type was used to deposition of coating o steel substrate. First of them was the standard powder of Amperit 526.074 type, second one it was powder by Inframat from category of Infralloy™ S7400superfine powders. And the last it was the standard Amperit 526.074 modified by nanoparticles of carbides. The aim of investigation was related to comparison of microstructure and some mechanical properties of coatings depending of used types of powders and characterization of nanocarbides influence on basic mechanical properties of coatings. The range of investigations included short characterization of feedstock powders by SEM, EDS, XRD and EBSD method and their technological properties as well. In second step the characterization of deposited coatings were made, especially evaluation of theirs overall quality, porosity, micro-hardness distribution, adhesion of coatings to substrate alloys and theirs tendency to cracks. To characterization of coatings microstructure the same methods were used. Adhesion to substrate alloy and tendency to crack of coatings were characterized by bend test and Brinell hardness measurement on polished top surface of carbide coatings.

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New Horizons in Coatings and Thin Films
Room: Sunrise - Session F2-1

High Power Impulse Magnetron Sputtering

Moderator: D. Lundin, Université Paris-Sud 11, France, J. Sapieha, Ecole Polytechnique de Montreal

8:00am **F2-1-1 Applications of HIPIMS Metal Oxides**, ***V. Sittinger*** *(volker.sittinger@ist.fraunhofer.de), O. Lenck, S.K. Gurram, D. Niewerth, G. Bräuer*, Fraunhofer IST, Germany **INVITED**

The high degree of ionization of the sputtered material during the coating process is one of the main features of HIPIMS (High Power Impulse Magnetron Sputtering). The use of HIPIMS leads to better film quality for hard coatings based on metal nitrides and to more conformal coatings during via fillings with high aspect ratios used in microelectronics. Metal oxides are used in many applications like optical coating for filters or transparent conducting oxides (TCOs) with fields of application in photovoltaics, low emissivity coatings, heat mirrors or panel heaters as well as touch panels and displays. At Fraunhofer IST a TCO and optical films has been developed with HIPIMS technology which were applied on glass substrates and photovoltaic absorbers. We will see that HIPIMS is beneficial for metal oxide coatings therefore an overview on applications in industry and research will be given.

8:40am **F2-1-3 Optical Coatings Prepared by HiPIMS – Does this Technology Meet our Expectations?**, *M. Hala, R. Vernhes, O. Zabeida, J.E. Klemberg-Sapieha,* ***L. Martinu*** *(lmartinu@polymtl.ca),* Polytechnique Montreal, Canada

Film growth under intense ion bombardment leads to significant microstructural rearrangement and material's densification. In this context, compared to the more traditional PVD and PECVD techniques, there has been a lot of progress in generating very dense plasmas in pulsed discharges, especially in the case of High Power Impulse Magnetron Sputtering (HiPIMS). For more than a decade, the latter technique has been intensively studied for its unique capability to obtain thin films from a high flux of highly ionized materials. Now, after so many years of investigation, it is time to conclude if this approach meets our expectations. In the present work, we specifically evaluate its capabilities with respect to the fabrication of optical coatings.

In the first part of this work, we study the deposition of high (H) and low (L) refractive index metal oxides in reactive O_2/Ar gas mixtures under high power impulse conditions using a relatively large range of pulse frequencies, pulse durations and discharge voltage and current levels accessible by using different and complementary power supplies. We show that discharge operation in the transition mode between metallic and poisoned target surfaces can give rise to stable deposition conditions and complete hysteresis suppression. Examples include representative H and L optical films such as Nb_2O_5, Ta_2O_5, and SiO_2 exhibiting low absorption, attractive deposition rate, and systematically low internal stress.

In the second part, we demonstrate fabrication of multilayer optical interference filters using the HiPIMS process. Such filters are then compared with those obtained by more traditional sputtering techniques. Evaluation of the overall coating and process performance allows one to judge on the applicability of HiPIMS for meeting the challenging optical filter requirements.

9:00am **F2-1-4 Epitaxial (001) Oriented Mo/V Superlattice Grown on MgO(100) by HiPIMS**, *S. Shayestehaminzadeh, H.P. Gíslason,* ***S. Ólafsson*** *(sveinol@hi.is),* University of Iceland

Epitaxial (001)-oriented Mo/V superlattices have been grown by HiPIMS (High power impulse magnetron sputtering) on single-crystalline MgO(100) substrates at growth temperatures ranging from 30 to 700 °C. Superlattice periods of Mo/V 4/4 ML to 16/16 ML were studied. The as-deposited films were characterized by x-ray reflection and diffraction techniques.

Various types of bcc superlattices grown on MgO(100) substrates have been well studied during the last 20 years using magnetron sputtering methods. The best known superlattices are based on Fe/V and Mo/V repeat structures [1,2] but there are more structures such as Nb/Ta, Mo/Nb and Nb/W. Fe/V superlattices can be grown with good quality at temperature of around 200-300°C while for Mo/V a temperature of 700°C is needed to obtain similar quality [1,3]. The main difference in temperature is due to the lower mobility of the molybdenum atoms at the Mo surface during the growth. This study aims to investigate the effect of the HiPIMS process on reducing the growth temperature of Mo/V superlattices using the high energy ionized Mo, V species in the HiPIMS plasma. HiPIMS sputtering parameters such as voltage and pulse length have been optimized relative to the each growth temperature and the requirement of keeping the growth rate as close to conventional magnetron sputtering as possible.

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Structure and magnetic properties of Fe/V (110) superlattices

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9:20am **F2-1-5 High Power Impulse Magnetron Sputtering of Compound Targets**, ***A. Anders*** *(aanders@lbl.gov),* Lawrence Berkeley National Laboratory, US, *E. Oks,* High Current Electronics Institute, Russian Federation, *R. Franz, C. Clavero, R. Mendelsberg,* Lawrence Berkeley National Laboratory, US

Preferential sputtering from compound targets is well known: the elements of higher sputtering yields are removed from the target at a greater rate, leading to enrichment of the target surface region with the remaining elements of lower sputtering yields. In high power impulse magnetron sputtering, the situation is a bit more complicated since the sputtered atoms are ionized and participate in the sputtered process (self-sputtering). When using compound targets we therefore deal with multiple ion species that cause sputtering, each having different specific sputtering yields, and ionization and target-return probabilities. The situation will be illustrated with sputtering of lanthanum hexaboride, producing boron-rich plasma.

9:40am **F2-1-6 TiO_2 Coatings Deposited by Arc Free Deep Oscillation Magnetron Sputtering**, ***J. Lin***, Colorado School of Mines, ACSEL, US, *B. Wang,* Colorado School of Mines, US, *W. Sproul (bsproul@cox.net),* Reactive Sputtering, Inc., US, *Y. Ou,* Colorado School of Mines, US, *I. Dahan,* Nuclear Research Center, Beer-Sheva, Israel

In this study, nanocrystalline TiO_2 films were reactively sputtered onto glass and steel substrates in a balanced magnetron sputtering system using the new deep oscillation magnetron sputtering (DOMS) and conventional pulsed dc magnetron sputtering (PDCMS) techniques. No external substrate bias or heating were used for the depositions. For the DOMS TiO_2 depositions, different peak target discharge currents (powers) were used. The crystalline phase and microstructure of the TiO_2 coatings were characterized and compared. With DOMS, a virtually arc free high power pulsed magnetron sputtering process for TiO_2 has been observed. The TiO_2 films deposited by PDCMS exhibited only the anatase phase whereas the TiO_2 coatings deposited with DOMS showed different crystalline phases depending on the peak discharge current. For the TiO_2 coatings deposited with DOMS at a relatively low target peak current of about 50 A or less, only the anatase phase was observed. With an increase in the peak target current for the DOMS coatings, an increase in the amount of the rutile phase in the coatings was observed along with an increase in the density and a decrease in the grain size of the TiO_2 coatings. At high peak target currents of 200 A or greater, only the rutile phase was produced. The mechanical and optical properties of the anatase and rutile TiO_2 coatings will also be discussed.

10:00am **F2-1-7 Deposition Rate Enhancement in HiPIMS at Preserved Ionized Fraction of the Deposition Flux**, ***J. Capek*** *(jcapek@kfy.zcu.cz),* University of West Bohemia, Czech Republic, *M. Hala, O. Zabeida,* Ecole Polytechnique de Montreal, Canada, *J.E. Klemberg-Sapieha,* Ecole Polytechnique de Montréal, Canada, *L. Martinu,* École Polytechnique de Montréal, Canada

Deposition rate enhancement of Nb coatings prepared by HiPIMS through the control of the magnetic field (B) at constant average pulse target power density of 2.5 kW cm^{-2} was systematically investigated. In this work, the value of B of a 50 mm magnetron was controlled by applying paramagnetic spacers with different thicknesses in between the magnetron surface and the target. We found that a weaker B (a thicker spacer) led to an increase in the deposition rate, a_D, by a factor of ~4.5 (from 10.6 to 45.2 nm min^{-1}) compared to the configuration without any spacer (i.e., strong B). Moreover, the ionized fraction of the deposition flux onto the substrate was preserved despite of a large difference in discharge characteristics (magnetron voltage and discharge current) depending on B. However, the maximum a_D value was still about 33 % lower in comparison to the DC magnetron sputtering mode at an identical average power. We demonstrate that the a_D is governed by different processes depending on B: (i) attraction of target ions back to the target is the dominant effect leading to reduced a_D for strong fields B (i.e., high discharge current and low magnetron voltage), while (ii) nonlinear dependence of the sputtering yield on the ion energy, attraction of target ions back to the target, and the transport mechanism need to be taken into account in order to explain the a_D loss for weak B (i.e., low discharge current and high magnetron voltage). Finally, we offer a theoretical explanation of the observed results proving that this study is applicable to HiPIMS discharges in general.

10:20am **F2-1-8 Optimization of the Substrate Conditions by Monte Carlo Modeling of Sputtered Particle Transport**, ***D. Lundin*** *(daniel.lundin@liu.se), C. Vitelaru,* Université Paris-Sud 11, France, *N. Brenning,* Royal Institute of Technology, Sweden, *T. Minea,* Université Paris-Sud 11, France

It is well known that energetic bombardment of the substrate during thin film growth strongly affects elementary processes like adsorption, diffusion and chemical reactions, as well as microstructure and stoichiometry. In high power impulse magnetron sputtering (HiPIMS) the deposition flux consists of neutrals as well as a large fraction of ionized sputtered material, which opens up new and added means for the synthesis of tailor-made thin films. Although much experimental work has been carried out during the last decade to reveal the various physical mechanisms operating in HiPIMS, still many questions remain, in particular how to optimize this technique for different coating recipes. One route towards better understanding of HiPIMS is through computational modeling. It has the possibility to benchmark mechanisms separately, which can rarely be done experimentally, as well as unify complex discharge physics to better

describe the overall effects on the entire deposition process. In this talk we present a new 3D Monte Carlo (MC) code, which simulates the transport of sputtered material in a magnetron discharge. The simulated energy distributions of the sputtered particles parallel as well as perpendicular to the cathode surface at several points above the target surface, and for different operating pressures, have been recorded and benchmarked against experimental profiles obtained using laser-induced fluorescence. Focus in this work is on the substrate, where detailed information on the energy and angular distributions, as well as the composition of the incoming material flux is presented.

10:40am **F2-1-9 Temporal Characterization of Ion Dynamics in High Power Impulse Magnetron Plasma by Means of Plasma Monitor, Ridded Retarding Field Energy Analyzer and Modified Katsumata Probe**, ***M. Cada*** *(cada@fzu.cz), P. Adamek, J. Olejnicek, Z. Hubicka*, Institute of Physics of the ASCR, v.v.i., Czech Republic

The High Power Impulse Magnetron Sputtering System (HiPIMS) equipped with 2" in diameter target has been investigated by means of time-resolved mass- and energy-resolved analyser (plasma monitor) from Hiden Ltd., gridded retarding field energy analyser (RFEA) from Impedans Ltd. and so called modified Katsumata probe. All the methods allow to determine ion velocity distribution functions (IVDF) in forward direction to substrate as a function of retarding electric field. However, except plasma monitor latter methods are not able to resolve the mass of particles. The newly developed modified Katsumata probe uses a static magnetic field created by Sm-Co permanent magnets to intercept the most of plasma electron and pull them away back to the plasma bulk. Furthermore, the plasma monitor and the modified Katsumata probe are characterized in very small angular acceptance in comparison with the gridded RFEA. The high power impulse magnetron sputtering system was equipped with pure metallic targets (titanium or iron). As working gas a mixture of Ar and O_2 was used. The working gas pressure ranging between 0.5 Pa to 5 Pa. All the diagnostic instruments were placed at position of substrate. All the measurements were carried out under the same conditions as the thin oxide films TiO_2 and Fe_2O_3 were deposited. A comparative study of all the aforementioned methods has been carried out.

Results clearly demonstrate an influence of angular resolution on measured IVDF. Unlike gridded RFEA the modified Katsumata probe was able to distinguish different groups of ions coming on the substrate in different times of plasma pulse. The gridded RFEA has angular acceptance more than 70° and ions reaching its input orifice originate from different direction unlike the modified Katsumata probe which accepts ions only from cone of a small solid angle. The temporally resolved investigation with plasma monitor revealed that sputtered particles reach a substrate later on. All the plasma diagnostic methods revealed significantly enhanced energy tail in ion velocity distributions measured in HiPIMS in contrast to dc magnetron or mid-frequency pulsed-dc magnetron. An influence of working gas pressure on velocity distributions of argon, metallic and reactive gas ions specifically on presence of high-energy tail is discussed. The plasma monitor proved that under certain plasma conditions appearance of double ionized sputtered and working gas particles can be observed.

11:00am **F2-1-10 Mechanism of the Instabilities in HiPIMS Discharge and Correlation with Deposition Conditions**, ***A. Hecimovic*** *(ante.hecimovic@rub.de), T. de los Arcos, V. Schulz von der Gathen, J. Winter*, Institute for Experimental physics 2, Ruhr University Bochum, Germany

Recently an inhomogenity of the HiPIMS discharge has been reported (1,2). In our previous papers we demonstrated and explained the influence of the power and pressure on the instabilities. Furthermore we investigated transition form stochastic to periodic behaviour. In this contribution an explanation of the shape and mechanism of the instabilities is presented, based on the experimental observations. The experimental results of a 4 camera setup, photomultiplier tube data correlated with the biased flat probe are presented. The theory combines a particle approach together with a global approach in demonstrating that both violation of the β limit and modified Rayleigh–Taylor instability could be responsible for the shape of the instability. Further optical emission spectroscopy experiments provide an understanding on the correlation between instabilities and the deposition conditions.

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11:20am **F2-1-11 Influence of High Power Impulse Magnetron Sputtering (HIPIMS) Pulse Shape Regarding Voltage and Current Time Evolution on Plasma Characteristics, Deposition Rate and Ionization for Titanium Aluminum**, ***F. Papa*** *(fpapa@hauzer.nl),* Hauzer Techno Coating, BV, Netherlands, *H. Gerdes, R. Bandorf, F. Lenz, G. Braeuer,* Fraunhofer Institute für Schicht und Oberflächentechnik, Germany, *T. Krug*, Hauzer Techno Coating, BV, Netherlands

The characteristics of High Power Impulse Magnetron Sputtering (HIPIMS) are strongly dependent on the pulse shape, length and continuity. It has been found that the current characteristics of such discharges depend strongly on the voltage which is applied to the cathode as well as the time at which this voltage is applied. For short pulses (16 µs), a square wave voltage output gives rise to a triangular current waveform with a maximum cathode current corresponding to the maximum output voltage. If a triangular type voltage waveform is used, the timing of the current maximum will not correspond to that of the voltage maximum on the cathode. This leads to a significant change in the plasma characteristics as well as deposition rate. Longer pulses (500 µs) can also be created using a combination of shorter (16 µs) pulses or by a square wave voltage output. The current characteristics of these type discharges also vary significantly over time. Titanium Aluminum (50/50 atomic %) has been sputtered using several types of HIPIMS power supplies with pulse lengths from 16 µs to 500 µs. Pulses with square and triangular type waveforms as well as "packages" of these waveforms have been used to generate the various discharges. It has been found that for an approximate peak cathode current density of 0.5 A/cm^2, the average power (to the cathode) corrected deposition rate can vary from 50% to 80% of the DC rate depending on the nature of the pulses. Time resolved OES measurements of titanium, aluminum and argon neutrals and ions also show that the degree of ionization of the sputtered species strongly depends on the relationship of the voltage/current timing and current evolution in time. The ion to deposited particle ratio of arriving particles at the substrate is calculated using ion flux values from a Langmuir probe and deposition flux values from a Quartz Crystal Monitor (QCM). This gives a relative estimate of the efficiency of the various pulse types with regards to ionization at the substrate at a constant peak current density.

Hard Coatings and Vapor Deposition Technology
Room: Royal Palm 4-6 - Session B4-3

Properties and Characterization of Hard Coatings and Surfaces

Moderator: C. Mulligan, US Army ARDEC, Benet Laboratories, J. Lin, Colorado School of Mines, ACSEL, B. Zhao, Exxon Mobile, USA

2:10pm **B4-3-1 Novel Method for Deposition of Protective Coatings on Internal Surfaces**, ***T. Casserly*** *(tcasserly@sub-one.com), J. Bae, J. Wickersham,* Sub-One Technology, US, *B. Williams*, URS Flint, US **INVITED**

A novel hollow cathode plasma immersion ion processing method is utilized to deposit diamond like carbon (DLC) coatings on the internal and select external surfaces of metallic pipes and components. The hollow cathode effect (HCE) occurs when high energy electrons oscillate between opposing cathodes causing multiple ionization events. Plasmas taking advantage of the HCE typically have ion and electron densities hundreds of times higher than conventional plasma discharges. This phenomenon allows for very high deposition rates in excess of 3 microns per minute for optimized DLC coating applications as compared to typical chamber based deposition rates on the order of 1-2 microns per hour. DLC coatings have high density, high hardness, and strong adhesion while providing excellent wear resistance with low friction. DLC coatings are also chemically inert in most environments providing protection of the coated substrate from corrosive attack. By introducing different precursor gases, the vacuum-based plasma deposition process can produce coatings with properties tailored for specific applications. In summary, this high speed hollow cathode plasma deposition technology enables DLC based coatings to increase component life in applications where the internal surface of pipes and other parts are exposed to corrosive and abrasive environments.

2:50pm **B4-3-3 Prediction of DLC Friction Lifetime Based on a Local Archard Factor Density Approach**, ***F. Alkelae***, *S. Fouvry (siegfried.fouvry@ec-lyon.fr)*, LTDS - Ecole Centrale de Lyon, France

Diamond-like carbon coatings, displaying low and stable coefficient of friction, are potentially very interesting palliatives for fretting wear applications. The purpose of the research work is to investigate the coating endurance as a function of the fretting loadings conditions such as the contact pressure, sliding amplitude. Fretting wear tests have been performed applying a 12.7 mm radius 52100 steel ball against a 2µm DLC coating deposited on 52100 plane substrate. Normal forces between 5 and 57 N, inducing maximum Hertzian contact pressures from 430 to 1000 Mpa have been tested. Sliding amplitudes from ± to ±100 µm have been investigated. The coating endurance (Nc) is related to a friction coefficient criterion fixed at a 0.3 threshold value (Fig. 1). This analysis demonstrates that above a 650 Mpa contact pressure, the coating endurance is unstable and controlled by a coating delamination process. Below this threshold pressure, the coating endurance is monitored by a progressive abrasive wear process. This analysis shows that the coating endurance in the low pressure domain can be formalized using a single local Archard's wear parameter expressed as a function of the contact pressure (pmax), the sliding amplitude (dg) and the contact radius (a). By considering this analysis, a single master endurance curve along which all the studied test conditions are aligned has been identified (Fig. 2). In addition the endurance modeling, dedicated expertises of fretting scars combining SEM, EDX and micro raman investigations have been performed to elucidate the fretting wear damage scenario.

Fig. 1 : Definition of the coating endurance criterion related to a threshold friction condition.

Fig. 2 : Identification of the DLC coating endurance in the low pressure domain (p_{max} < 650 Mpa)

3:10pm **B4-3-4 Time- and Space-resolved High-throughput Characterization of Stresses during Sputtering and Thermal Processing of Al-Cr-N Thin Films**, ***D. Grochla*** *(dario.grochla@rub.de)*, Ruhr-Universität Bochum, Germany

Mechanical stresses (extrinsic or intrinsic) are a crucial feature of thin films. The mechanical behaviour of thin film-substrate combinations are strongly affected by internal stresses, especially with respect to the adhesion, durability and tribological performance. Thus, gaining a better understanding of stress-inducing mechanisms is an important concern for surface engineering. Interfacial stress components due to lattice mismatch or different thermal expansion coefficients contribute to the overall film stress as well as dislocations, impurities, voids and grain boundaries. To gain closer insight into the mechanisms of stress development and relaxation, real-time measurements during film growth are necessary. Furthermore, it is of interest to correlate the stresses to the chemical composition and the corresponding microstructure. This is possible in composition spread type materials libraries, where thin films of different compositions are fabricated simultaneously. In order to understand the stress development during sputtering and annealing as a function of composition, high-throughput measurement methods are needed which are both time-resolved and space-resolved.

$(Al_{100-x}Cr_x)N$ thin film materials libraries were fabricated on micro-machined cantilever arrays, in order to simultaneously investigate the evolution of stresses during film growth as well as during thermal processing by analyzing the changes in cantilever curvature. The issue of the dependence of stress in the growing films on composition, at comparable film thicknesses, was investigated. Among the various experimental parameters studied, it was found that the applied substrate bias has the strongest influence on stress evolution and microstructure formation. The compositions of the films, as well as the applied substrate bias, have a pronounced effect on the lattice parameter and the coherence length. For example, applying a substrate bias in general leads to compressive residual stress, increases the lattice parameter and decreases the coherence length. Moreover, bias can change the film texture from [111] orientation to [200]. Further detailed analysis using X-ray diffraction and transmission electron microscopy clearly revealed the presence of a [111] highly textured fcc (B1 type) Al-Cr-N phase in the as deposited state as well as the coexistence of the hexagonal [110] textured Cr_2N phase, which forms in the Cr-rich region. These results show that the combinatorial approach provides insight into how stresses and compositions are related to phases and microstructures of different Al-Cr-N compositions fabricated in the form of materials libraries.

3:30pm **B4-3-5 Mechanical Properties and Microstructures of Cr-O-N Coatings Deposited by Arc Ion Plating Method**, ***T. Minami*** *(t-minami@kanefusa.co.jp), S. Nishio,* Kanefusa Corporation, Japan, *Y. Murata*, Nagoya University, Japan

Using AIP (Arc Ion Plating) method, Cr-O-N coatings with different O contents, and CrN coating were prepared in a gas mixture of N_2 and O_2. Their mechanical properties and microstructures were investigated.As the Oxygen flow rate increased, the O content in the coatings also increased. X-ray diffraction measurements revealed that Cr-O-N coatings have the NaCl type cubic CrN phase until the oxygen flow rate increased to 20%, and other phases such as oxides were not detected. The diffraction peaks of the cubic CrN phase became broad and shifted to a lower angle in proportion to the O content. As the amount of O increased, hardness of the Cr-O-N coatings increased because the grain sizes became smaller and the compressive residual stresses increased.FE-SEM observations revealed that the CrN coating has a columnar structure, while the Cr-O-N coatings have very fine microstructure and nm-scale periodic layered structures regardless of their O content. We have found that the period of the lines depends on the rotation speed of the substrate holder in the PVD equipment. Microstructures of the Cr-O-N coatings were also investigated by TEM to find the details of the periodic lines. TEM observations clearly showed that the Cr-O-N coating has the fine periodic layered structure. It was also found by STEM/EDS analysis that the oxygen concentration at the periodic lines is higher than in other areas. Furthermore, we have examined reasons why fluctuation in oxygen concentration occurs during a coating process.

3:50pm **B4-3-6 Effect of Bias Voltage on the Mechanical-tribological Properties of AlCrN Coatings**, ***F. Lomello*** *(fernando.lomello@cea.fr)*, DEN/DANS/DPC/SEARS/LISL CEA Saclay, France, *A. Billard*, IRTES-LERMPS-UTBM, France, *F. Sanchette*, LRC CEA-ICD LASMIS, Nogent International Center for CVD Innovation (Nicci), France, *F. Schuster*, CEA Cross-Cutting Programme on Advanced Materials, France, *M. Tabarant*, DEN/DANS/DPC/SEARS/LISL CEA Saclay, France

In recent years, the application of AlCrN-type coatings in processes which involve attrition, chipping and/or cracking due to the impacts, such as the industrial metal forming has increased [1]. The cutting edge of coated tools may exceed 1000°C, therefore the oxidation resistance is a very important issue [2]. The oxidation resistance and high temperature mechanical properties of AlCrN are improved comparing with other ternary nitride such as AlTiN [3]. Furthermore, it presents good tribological properties up to 500°C, since a low friction coefficient is generally found even at high temperatures [4].

In this study, AlCrN coatings were prepared by vacuum cathodic arc deposition (CAD). This technique has been chosen due to its versatility, allowing an easy industrial up-scaling.

The correlation of processing parameters was focused on the influence of bias voltage on the resulting mechanical-tribological properties. Indeed, it was demonstrated that the variation of bias voltage by means of the *ion peening effect* has an important role in modifying the morphological properties - such as surface roughness, crystallite sizes and the associated residual stresses which influences the final properties.

Interesting mechanical properties such as hardness were measured. These properties were strongly affected by the combination of the grain size (*Hall-Petch effect*) and the intrinsic residual stress.

The tribological behaviour was a consequence of the resulting properties, especially ruled by the H/E ratio.

References

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[4] R. Franz et al. Tribol. Lett. 23 (2006) 101.

4:10pm **B4-3-7 Influence of Substrate Bias on the Structure and Mechanical Properties of ZrN Thin Films Deposited by Arc Ion Plating**, ***M. Zhang*** *(m.zhang@live.com)*, Liaoning Normal University, China, *K. Kwang Ho*, Pusan National University, Republic of Korea, *H. Ye*, *H. Xiaogang*, *P. Yunli*, Liaoning Normal University, China

In this study, zirconium nitride thin films were fabricated using arc ion plating under different negative substrate biases. To enhance the adhesion property of ZrN films, at the first 15min of deposition process, nitrogen flow rate was zero to form a Zr interlayer with thickness of 120nm. The phase structure, composition, resistivity and mechanical properties of ZrN films, with respect to substrate bias, were studied by means of X-ray diffraction, electron probe microanalyzer, four point probe method, nanoindentation, and tribotester. Cubic ZrN and hexegenol Zr phases were formed in the films. The competition between surface energy and strain energy made the preferred orientation of ZrN films change from (111) to (200) and then back to highly (111) preferred orientation as a function of substrate bias. With the increase of bias voltage, the crystallite size of ZrN films decreases, resultantly the nanohardness of the ZrN films increases. Meanwhile, film microstructure evolves from an apparent columnar structure to a highly dense one, indicating that ion bombardment enhanced by substrate bias can suppress columnar growth in ZrN films. The deposition rate and impurity oxygen content of ZrN films were substantially influenced by the resputtering effects due to the ion bombardment on the film surface. The electrical resistivity of ZrN films ranges from 0.07 to 0.15 Ω•μm, and shows a slight increase with substrate bias.

4:30pm **B4-3-8 Effect of Cr/Al Content on Creep Resistance of AlCrN Coatings Applied by Reactive Magnetron Sputtering**, ***Z. Gasem*** *(zuhair@kfupm.edu.sa)*, *S. Alam*, King Fahd University of Petroleum and Minerals, Saudi Arabia, *A. Matthews*, University of Sheffield, UK

The main objective of this work is to characterize the creep resistance of reactive magnetron sputtered AlCr nitride coatings as influenced by the Cr/Al content. The coating composition was varied by using a pure aluminium target with variable number of Cr plugs inserted along the sputtering track. A comparative creep test has been carried out for high and low Cr/Al coating compositions sputtered on H13 tool steel substrates. Creep testing was carried out by applying a constant load for a short period of time and monitoring the extent of penetration in the coating over a range of temperatures (25-150^{o}C). The loads applied were 20 mN, 40 mN, and 60 mN with a fixed loading rate of 20 mN/min. The coatings were characterized in terms of their elemental composition, phase composition, mechanical, and tribological properties. Preliminary results indicate that the creep resistance of AlCrN based coatings is sensitive to CrN and AlN phase distribution. At low temperatures, creep resistance is higher for the high Cr/Al coating. As the temperature is increased, the creep resistance of AlCrN coatings demonstrates less sensitive response to the Cr/Al content. The dependence of the creep resistance behaviour of AlCrN coatings on the temperature level will be discussed in terms of the coatings phase character and distribution.

Hard Coatings and Vapor Deposition Technology
Room: Royal Palm 1-3 - Session B7-2

Computational Design and Experimental Development of Functional Thin Films

Moderator: B. Alling, Thin Film Physics Division, IFM, Linköping University, D. Holec, Montanuniversität Leoben, Austria

2:10pm **B7-2-1 On the Structure and Growth of Reactive Magnetron Sputtered Ta_2O_5**, ***R. Hollerweger*** *(robert.hollerweger@tuwien.ac.at)*, Christian Doppler Laboratory for Application Oriented Coating Development at Montanuniversitat Leoben and Vienna University of Technology, Austria, *M. Bartosik*, Vienna University of Technology, Austria, *M. Arndt*, *R. Rachbauer*, OC Oerlikon Balzers AG, Liechtenstein, *P. Polcik*, PLANSEE Composite Materials GmbH, Germany, *J. Paulitsch*, Vienna University of Technology, Austria, *D. Holec*, Montanuniversität Leoben, Austria, *P.H. Mayrhofer*, Vienna University of Technology, Austria

Especially due to its high relative permittivity and refraction index, Ta_2O_5 is frequently being discussed for electronically and optically applications. These properties are very sensitive on the atomic arrangement within the crystal structure as even slight variations could cause changes in the band structure resulting in e.g. conductivity or loss of transmittance. However, the arrangement of oxygen atoms in the a-b plane of the orthorhombic structured Ta_2O_5, but also the structure itself, can be controlled by varying the deposition conditions during reactive magnetron sputtering. Nevertheless, the formation energy of the amorphous and crystalline Ta_2O_5 is similar, which makes it challenging to synthesize crystalline Ta_2O_5 at moderate temperatures. Therefore, Ta_2O_5 films were deposited by reactive DC magnetron sputtering at 500°C using O_2/Ar flow rates (Γ) ranging from Γ = 50 to 100%. Our investigations indicate an amorphous interlayer, which decreases with increasing Γ before the crystalline oxide phase is formed. Simultaneously, the deposition rate decreases with increasing Γ from about 120 to 10 nm/min and the chemical composition ratio O/Ta increases from 2.33 to 2.5, respectively. This trend was also confirmed by nano-indentation as the hardness and Young's modulus increase from ~14 to 16 GPa and ~180 to 235 GPa, respectively. Nano-beam measurements across the whole substoichiometric Ta_2O_5 film thickness of 15 µm exhibit a highly texturized 110 / 200 growth and strained a and b, but hardly affected c lattice parameters.

Driven by these experimental results, a new orthorhombic pentoxide crystal structure was designed and calculated by the DFT-GGA ab-initio method yielding lattice parameters of a = 6.32, b = 3.73, and c = 3.96 Å, a band gap E_g of at least 2.5 eV, and energy of formation E_f = –3.158 eV/atom. Moreover, when oxygen is removed to reach an O/Ta ratio of 2.33 as obtained by the experiments, the energy of formation remains nearly constant (E_f = –3.134 eV/atom). These calculations support the here proposed structure for tantalum pentoxide, which is formed under non-equilibrium conditions of sputtering.

2:30pm **B7-2-2 Probing Temperature-induced Ordering in $Ti_{0.33}Al_{0.67}N$ Coatings**, ***C. Århammar*** *(cecilia.arhammar@sandvik.com)*, Sandvik Coromant R&D S-126 80 Stockholm, Sweden, *J. Endrino*, Instituto Abengoa Research S. L., Spain, *M. Ramzan*, Uppsala University, Sweden, *D. Horwat*, Université de Lorraine, Institut Jean Lamour, CNRS, Institut Jean Lamour, UMR 7198, Nancy, F-54000, France Division of Molecular and Condensed Matter, France, *A. Blomqvist*, Sandvik Coromant R&D, Sweden, *J-E. Rubensson*, *R. Ahuja*, Uppsala University, Sweden

Cubic TiAlN is one of the most common coatings used as a protective layer on cutting tools. The TiAlN structure and its evolution with temperature have been under careful study by techniques such as X-Ray Diffraction (XRD), Near Edge X-ray Absorption Fine-structure (NEXAFS) [1], Transmission Electron Microscopy (TEM), first principles and phase field modeling. Previous modeling has provided estimations of the thermodynamical, kinetic and mechanical driving force for spinodal decomposition of TiAlN. In this paper we instead interpret the measured spectral features directly by spectra calculated from first principles. The ordering of supersaturated cubic titanium aluminum nitride (c-$Ti_{0.33}Al_{0.67}N$) coatings is probed by its electronic structure from room temperature up to and above the point of spinodal decomposition, using X-ray Emission Spectroscopy (XES), NEXAFS, along with Density Functional Theory (DFT) and the G_0W_0-approach. A simple ordered c-TiAlN model structure along with a Special Quasi random Structure (SQS) were used to correlate measured spectral features to local changes in partial and orbital projected density of states. The N K edge spectra along with the calculated N p density of states suggest that non-bonding Ti t_{2g}-states, as well as anti-

bonding Ti e_g-states are of maximum intensity at room temperature as the random distribution of Al and Ti on the metal lattice is still kept. This proves the strong configurational sensitivity of the electronic structure of TiAlN that was previously suggested by Alling et al. [2]. As temperature is raised, ordering into cubic Al-rich and Ti-rich domains decreases the unfavorable antibonding states. The N p-Ti e_g, and to some extent the N p-Ti t_{2g} overlap remain almost constant with temperature, whereas hybridisation between N p and Al p increases considerably. A similar trend was found at the Al and Ti K-edges. This observation is in agreement with previous phase field simulations [3]. The N p spectra calculated from DFT were in good agreement with spectra calculated by the G_0W_0-approach. These results should be of use in the in-depth understanding of structural changes in TiAlN and provide proof from the electronic structure to experimental tests reported in the past.

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[2] B. Alling, Dissertation No. 1334, Department of Physics, Chemistry and Biology, Linköping University, Sweden.

[3] J. Ullbrand, LIU-TEK-LIC-2012:30, Department of Physics, Chemistry and Biology, Linköping University, Sweden.

2:50pm **B7-2-3 Lattice Ordering Effects on Toughness Enhancement in Transition Metal Nitride Thin Films**, *D. Sangiovanni, D. Edström, **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 have 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, which upon shearing, leads to the formation of alternating layers of high and low charge density oriented orthogonal to the applied stress, and ultimately allows a selective response to tetragonal and trigonal deformations.

Recently, these results have been validated experimentally [3]. Single-crystal $V_{0.5}Mo_{0.5}N$/MgO(001) alloys, grown by dual-target reactive magnetron sputtering together with VN/MgO(001) and TiN/MgO(001) reference samples, exhibit hardness >50% higher than that of VN, and while nanoindented VN and TiN reference samples suffer from severe cracking, the $V_{0.5}Mo_{0.5}N$ films do not crack. However, as there is no evidence of Cu-Pt ordering in the synthesized $V_{0.5}Mo_{0.5}N$ films, 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, which are all predicted to have significantly enhanced toughness. 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.

[1] D. G. Sangiovanni et. al. Phys. Rev. B 81 (2010) 104107.

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[3] H. Kindlund et. al, submitted to Nature Materials.

3:10pm **B7-2-4 Plasticity in Complex Crystals**, ***C. Walter** (cwalter@gmx.com)*, University of Cambridge, UK, *J. Wheeler, R. Raghavan, J. Michler*, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland, *W. Clegg*, University of Cambridge, UK **INVITED**

Deformation in virtually all materials occurs by the movement of dislocations. However, there are crystals with unit cells that are sufficiently large for the misfit energies of dislocations to be very high. Despite this, such materials are known to be plastic above a ductile-brittle temperature, typically 0.5 – 0.75 of the melting point and deformation under these conditions has been associated with dislocation motion.

The aim of this paper is to investigate how such materials deform at temperatures below the ductile-brittle transition temperature. The low temperature deformation behaviour of an orthorhombic $Al_{13}Co_4$ and a cubic $Mg_{17}Al_{12}$ have been studied at temperatures using micropillar compression. This allows cracking to be suppressed by making the sample sufficiently small, in this case a few microns in diameter.

We combine the micropillar compression experiments with indentation and finite element simulations to understand which mechanisms might allow such large unit cell materials to deform plastically at temperatures below the ductile-brittle transition temperature.

3:50pm **B7-2-6 Oxygen-deficient Zirconia Thin Films Synthesized by Reactive Magnetron Sputtering**, ***S. Konstantinidis** (stephanos.konstantinidis@umons.ac.be), G. Geumez, T. Van Regemorter, J. Cornil, R. Snyders*, University of Mons, Belgium

Zirconium oxide (ZrO_x) thin films were synthesized by DC reactive magnetron sputtering. A 3 cm- in diameter zirconium target was sputtered in Ar/O_2 atmospheres (10mTorr). During the deposition process, the oxygen flow was controlled by means of a Plasma Emission Monitoring (PEM) device (speedflo, Gencoa Ltd.) by monitoring the Zr I lines. PEM allowed growing ZrO_x films inside the so – called metal-oxide transition.

X-Ray Photoelectron Spectroscopy data revealed that the films synthesized in the transition region are oxygen-deficient: ~10% of oxygen vacancies are incorporated in these films. The X-Ray Diffraction (XRD) patterns of these films exhibit reflections related to the high-temperature tetragonal and/or cubic phase of ZrO_2. In contrast, XRD patterns of the stoichiometric films deposited in the fully oxidized regime present reflections emanating from the low-temperature stable monoclinic phase. Our data reveal that the film chemistry, especially the incorporation of oxygen vacancies, is a key feature for controlling the phase constitution of zirconia thin films. Quantum-chemical calculations based on the Density Functional Theory method are consistent with these experimental observations. As oxygen vacancies are introduced in the ZrO_2 cell, the cubic phase is stabilized (by 20 meV/at. with ~10% of O vacancies in the cell) at the expense of the monoclinic structure. Finally, the oxygen-deficient 100 nm-thick films were annealed in air for 2 hours. It was found that the tetragonal/cubic phase was preserved up to 600°C.

Fundamentals and Technology of Multifunctional Thin Films: Towards Optoelectronic Device Applications
Room: Sunset - Session C5-1

Thin Films for Active Devices
Moderator: F. Tasnadi, Linköping University, S. Moram, Imperial College London

2:10pm **C5-1-1 Investigation on Plasma Treatment in Transparent Al-Zn-Sn-O Thin Film Transistor Application**, ***C.H. Chang**, P.T. Liu (ptliu@mail.nctu.edu.tw), Y.T. Wu, C.S. Fuh*, National Chiao Tung University, Taiwan, Republic of China

Recently, the thin film transistors (TFTs) with a-IGZO thin film as active layer perform higher mobility and better reliability than conventional hydrogenated amorphous silicon TFT (a-Si: H TFT). In addition, the uniformity of a-IGZO TFT is also superior to low temperature polycrystalline silicon TFT (LTPS TFT). Therefore, the a-IGZO TFTs have been widely considered to be the most promising candidate for the next generation display technology. a-IGZO TFTs showed good electrical performance, however, containing the rare-dispersive elements(In, Ga), will be an important issue for the long-term application. In this work, we developed rare elements-free oxide semiconductors--- amorphous Al-Zn-Sn-O thin film transistor (a-AZTO TFT).

We investigated on the physical characteristics and electrical performance of a-AZTO TFT under temperature effect of annealing process and plasma post treatment. The higher annealing temperature could strengthen the oxygen bonding, therefore the quality of the a-AZTO film improves. The electrical performance enhanced under high temperature of annealing process, as well. Moreover, O_2 and N_2O plasma could oxidize the AZTO film and eliminate some of the oxygen deficient. As a result, the reliability of the devices under GBS improved significantly after O_2 and N_2Oplasma post treatment. The optical energy gap of a-AZTO films untreated and with O_2 or N_2O plasma treatment were about 3.5 eV which indicated that all of the a-AZTO films were insensitive to visible light.These results showed the application potentials of a-AZTO TFT device on flat panel display technology.

2:30pm **C5-1-2 IGZO Deposition - Sputtering Technologies Comparison**, *P. Ozimek*, ***W. Glazek*** *(wojciech.glazek@pl.huettinger.com), A. Klimczak, P. Rozanski*, Huettinger Electronic, Poland

In the paper are compared results of sputtering of indium gallium zinc oxide by DC, pulsed DC, but also by MF and Bipolar - dual magnetron industrial sputtering technologies. Comparison including detailed results such as process parameters stability, deposition rates, and coatings quality are compared for full range of industrially available high rate sputtering deposition technologies.The sputtering technologies presented in the publication are realized by new range of power supplies equipped with advanced process stabilization solutions, ultra-fast arc management characterized by very low stored energy (in range down to 0.1mJ/kW) , and digital control platform enabling highly flexible software algorithms design, all this with intention to improve overall result of the process.

2:50pm **C5-1-3 Low Temperature Electrochemical Hydrocarbon Sensor Based on Reactive Magnetron Co-sputtering Deposited Layers**, ***E. Dereeper*** *(eloi.dereeper@utbm.fr), P. Briois, A. Billard*, IRTES-LERMPS-UTBM, France

Hydrocarbon vapours released by car exhausts or industrial activities can be either irritating or carcinogenic, flammable or explosives. Their monitoring thus relates to health and security issues. Electrochemical sensors are widely studied for the detection of oxidizable gases in an atmosphere: they are easy to miniaturize and exhibit good response time and sensitivity. However, oxide-based sensors generally require a rather high working temperature (600°C) to enable ionic conductivity through the electrolyte. The work presented here is about the fabrication of a hydrocarbon sensor able to work at lower temperature of about 300°C in ambient air. In a first step, attention has been paid to the synthesis of BITAVOX solid state electrolyte ($Bi_2Ta_xV_{1-x}O_{5.5}$), which makes oxide ion conduction possible at this temperature. It has been deposited on alumina pellets and on MSP 769 commercial sensor platform. The influence of tantalum substitution rate on the conduction performance of the material has been assessed by electrochemical impedance spectroscopy. Then, lanthanum perovskite and platinum have been sputtered to play the role of electrodes. The impact of deposition parameters on their microstructure and on the electrode / electrolyte interface has been assessed by X-ray diffraction and SEM observations. Finally, the sensor performances are investigated via four probe measurements under air-HC mixtures.

3:10pm **C5-1-4 Growth of Carbon Nanotubes/ Diamond Double Layers for High Stable Field Electron Emission**, ***L. Yang***, *C. Zhang, Y. Li, Q. Yang (qiy866@mail.usask.ca)*, University of Saskatchewan, Canada

Thin films of Diamond and carbon nanotubes (CNTs) are promising candidates as cold cathode field electron emitter. However, because of the poor electrical conductivity, diamond emitters usually present a high turn-on field. CNTS emitters fail with high emission current due to the heat accumulation at the contact surface caused by a poor contact to substrate. To improve the emitter's stability with better emission properties, a double-layered nanostructure consisting of a layer of vertically aligned CNTs and a layer of diamond has been synthesized on silicon substrate by hot filament chemical vapor deposition (HFCVD). The synthesis was achieved by firstly depositing an inner layer of diamond on silicon then a top layer of vertically aligned carbon nanotubes by applying a negative bias on the substrate holder. The growth of CNTs was catalyzed by a thin layer of spin coated Iron nitride. The morphology and structure of the CNT/diamond double layered material were characterized by Scanning Electron Microscope, X-ray diffraction, Transmission Electron Microscope and Raman Spectroscopy. The field electron emission properties were measured by KEITHLEY 237 high voltage measurement unit. This double layered material has a direct C-C bonding between vertically aligned CNTs and diamond and shows better field electron emission properties than single layered diamond films, and higher stability than CNT films. The high density CNTs arrays supply high emission density and large field enhancement factor while the diamond layer enhances the emission stability due to its high thermal conductivity.

3:30pm **C5-1-5 The Effect of Moisture on Oxygen Adsorption of InGaZnO Thin Film Transistors under Bias Stress**, ***Y.C. Chen*** *(oa_ccc@hotmail.com), T.C. Chang*, National Sun Yat-Sen University, Taiwan, Republic of China

This paper investigates the asymmetric degradation behaviors of amorphous InGaZnO thin film transistors (TFTs) in oxygen and moisture ambient under gate bias stress. In InGaZnO TFTs, the electrical characteristic of passivation-free device is a strongly function with the ambient gas, however, the influence combined with moisture and oxygen (O_2/H_2O) on the bias-induced instability of amorphous InGaZnO TFTs is studied rarely. Experimental results show the threshold voltage shifts of devices under positive and negative gate bias stress are increased and suppressed in O_2/H_2O ambient, respectively, when compared to that in only oxygen or moisture ambient . A physical model is proposed to explain the the dynamic relationship between the electrical instability of TFTs and ambient O_2/H_2O in environment, which may provide a better understanding of the adsorbed/desorbed gas phenomenon of the IGZO TFTs in atmospheric ambient .

Tribology & Mechanical Behavior of Coatings and Engineered Surfaces
Room: Golden West - Session E1-3

Friction, Wear, and Lubrication; Effects & Modeling

Moderator: V. Fridrici, Ecole Centrale de lyon, O. Eryilmaz, Argonne National Laboratory, US, S.M. Aouadi, University of North Texas

2:10pm **E1-3-1 Tribological Behavior of Multilayered Ti-Si-B/Zr-based Thin Film Metallic Glass Coatings with Various Si Contents**, ***H.W. Chen***, *Y.C. Chan*, National Tsing Hua University, Taiwan, Republic of China, *J.-W. Lee*, Ming Chi University of Technology, Taiwan, Republic of China, *J.G. Duh (jgd@mx.nthu.edu.tw)*, National Tsing Hua University, Taiwan, Republic of China, *J.S.C. Jang*, National Central University, Taiwan, Republic of China

This study aimed to investigate the Si effects on wear properties of both monolayered (Zr53Cu30Ni9Al8)100-ySiy and multilayered (TiB2)100-xSix/(Zr53Cu30Ni9Al8)100-ySiy coatings. The periodic (TiB2)100-xSix and (Zr53Cu30Ni9Al8)100-ySiy thin film metallic glass (TFMG) coatings were deposited by radio frequency magnetron sputtering of composite targets including TiB2 and Zr53Cu30Ni9Al8 in an argon atmosphere. The crystallography and chemical state were identified by X-ray diffraction and electron spectroscopy for chemical analysis (ESCA). The structure and surface morphology were studied by scanning electron microscope (SEM), transmission electron microscopy (TEM), and atomic force microscopy (AFM). It was observed that Ti-Si-B/TFMG with higher Si contents exhibited smoother morphology and lower friction coefficient, respectively. The mechanical properties analyzed by nanoindentation and nanoscratch revealed significant improvements in hardness, plastic deformation resistance, and adhesion for Ti-Si-B/TFMG with Si addition. It was demonstrated that Si incorporation effectively enhanced the coating performance and wear resistance due to structure refinement and self-lubricated characteristic.

2:30pm **E1-3-2 A Simple In-situ Method of AFM Calibration for Tribological Characterization of Ultra-thin Transfer Films**, ***D Burris*** *(dlburris@udel.edu), H. Khare*, University of Delaware, US **INVITED**

Solid lubricants are unusual in their ability to provide low friction and wear in otherwise unlubricated sliding conditions. In almost every case, thin (10-100nm) and well-adhered transfer films accompany low friction and wear during dry sliding and there is increasing evidence that the transfer films are responsible for the friction and wear reductions. Further elucidating the role of these transfer films in tribology requires direct studies of their tribological properties. Unfortunately, films of this scale are extremely challenging to probe with forces and contact areas that are sufficiently small to isolate their properties from those of the bulk. While the atomic force microscope is uniquely able to probe tribological surfaces in a wear-free single-asperity contact, instrument calibration challenges have limited the usefulness of this technique for quantitative tribological studies. A number of AFM calibration techniques have been proposed and used, but none has gained universal acceptance due to limitations or significant potential error sources. This paper describes a simple 'in-situ method' of calibrating AFM friction coefficients which: (1) allows simultaneous calibration and measurement for a given configuration of the AFM system, thus eliminating tip damage and confounding effects of instrument setup adjustments; (2) is insensitive to adhesion, PSD cross talk, transducer/piezo-tube axis misalignment, and shear-center offset; (3) is applicable to integrated tips and colloidal probes since 'calibration' is performed on the very substrate for which the friction coefficient is determined; (4) is applicable to any reciprocating friction coefficient measurement.

3:10pm **E1-3-4 Precession Electron Diffraction Studies to Determine Wear-induced Texture Formation and Grain Refinement in Tribological Coatings and Engineered Surfaces**, *H. Mohseni, J.-E. Mogonye, R. Banerjee, P. Collins*, ***T. Scharf*** *(scharf@unt.edu)*, University of North Texas, US

Transmission electron microscopy (TEM) coupled with selected area electron diffraction are capable of identifying nanoscopic phases in tribological contacts. However, interaction of the TEM's high energy

electron beam with the specimen can potentially cause non-systematic dynamic scattering and lead to an uneven distribution of the diffracted intensities. This severely limits the reliability of the nanostructural analysis. In addition, electron backscatter diffraction (EBSD) cannot resolve orientation and texture of tribologically-induced near surface ultrafine grain (<50 nm) structures. To circumvent these issues, precession electron diffraction (PED) was used in conjunction with TEM to investigate worn solid lubricants, such as Laser Engineered Net Shape (LENS) deposited graphite in a TiC/Ni matrix, and engineered surfaces, such as LENS nitrided Ti alloys (α+β Ti-6Al-4V, Ti64 and β Ti-35Nb-7Zr-5Ta, TNZT). In the case of the graphite/TiC/Ni composite, low friction (μ~0.1) was observed with the presence of amorphous carbon (a-C) on the surface with texture evolution in (010) Ni elongated grains, while higher friction was due to the absence of a-C. For the Ti-alloys, nitrided Ti64 exhibited brittle fracture (shear bands) while the nitrided TNZT exhibited plastic deformation (nanocrystalline grain refinement). Precession–orientation imaging phase maps were used to determine the orientation and percentage of α and β-Ti in nitrided TNZT on the surface and sub-surface regions responsible for improved friction and wear.

3:30pm **E1-3-5 Dry Friction Between Laser-patterned Surfaces: Role of Alignment and Structural Wavelength**, ***A. Rosenkranz*** *(a.rosenkranz@mx.uni-saarland.de), C. Gachot,* Saarland University, Germany, *N. Prodanov, M. Mueser,* Supercomputing Centre Juelich, *F. Muecklich,* Saarland University, Germany

Friction and related tribological phenomena play a decisive role in technological systems. For many years, a lot of research groups have sought to understand the origin of friction and to enhance the tribological performance of rubbing surfaces. The ability to modify frictional forces on different scales is of utmost importance. There are several techniques that offer the possibility to tailor the contact area thus leading to an improvement in the tribological behaviour. The laser interference metallurgy (LIMET), which is one possible approach of laser surface texturing, is used to produce a well defined surface topography with line-like pattern on both contacting surfaces. Commercial stainless steel and titanium samples were irradiated with a high power pulsed solid state laser (pulse duration of 10 ns and wavelength of 355 nm). The laser experiments were performed using a two beam interference configuration resulting in line-like patterns with three different structural wavelengths. Furthermore, a detailed study of the chemical and microstructural state before and after laser texturing was conducted. The tribological testing was done using a ball on disk configuration (ball material: 100Cr6 steel) in linear oscillating test conditions. In order to control the involved contact geometries and the frictional response, *both* contacting bodies were structured with the same structural wavelength.

The tribological tests demonstrate that the LIMET is a powerful tool to create a well defined surface topography and to design the contact area of rubbing surfaces. Furthermore, it can be stated that depending on the relative alignment and the structural periodicity, geometrical interlocking between the contacting bodies is possible thus leading to modified frictional properties and enhanced run-in behaviour. It could be shown that dry friction between two laser-patterned solids depends not only on the wavelength of the structuring but also on the relative orientation between the patterns.

3:50pm **E1-3-6 Influence of Aspect Ratio of Silicon Patterned and Coated Surfaces on Wetting and Tribological Characteristics**, *S. Piao, N. Machavallavan,* KIST, Republic of Korea, *K.Y. Jhang,* Hanyang University, Republic of Korea, ***E.-S. Yoon*** *(esyoon@kist.re.kr),* KIST, Republic of Korea

Technologically, majority of the MEMS/NEMS devices which are made out of silicon based materials have inferior tribological characteristics. The present work investigates the influence of aspect ratio on wetting and tribological characteristics of silicon patterned surfaces. Silicon surfaces were photo-lithographically patterned on circular pillar patterns with diameter of 3 μm, pitch of 6 μm, and different aspect ratio ranging from 0.06 to 8.33. Also, patterned silicon surfaces are modified with thin film layer of low surface energy materials such as PTFE to observe its secondary effect. First, wetting behavior of all patterned samples is characterized using Water Contact Angle measurement (WCA). Secondly, Tribological behavior is characterized using Atomic Force Microscopy. We observed that WCA of silicon patterned surfaces under low aspect ratio is decreased with roughness factor, which is good agreement with the Wenzel prediction. Wetting characteristics is changed with the aspect ratio. In case of hydrophobic PTFE surfaces, their trend follows Wenzel prediction. Tribological studies show that there is not much difference in adhesion & frictional behavior although aspect ratio and roughness factor of surfaces are varied. It is explained based on concept of contact area. Our experimental observations show that thin film layer of PTFE coating enhances the hydrophobicity & tribological characteristics of silicon surfaces.

4:10pm **E1-3-7 Laser Interference-induced Microstructural Architectures and Topographies in Gold Thin Films and their Effect under Dry Sliding Conditions**, ***C. Gachot*** *(c.gachot@mx.uni-saarland.de), A. Rosenkranz, F. Muecklich,* Saarland University, Germany

Numerous electrical contacts worldwide are exposed to sliding motion. Commonly conductor materials are gold and copper. Very often, electrical contacts are gold plated.

A basic understanding of the fundamental aspects during film growth and methods for a subsequent optimization or tailoring of the film microstructure and surface topography is absolutely essential for improving the physical properties of the as-deposited films. Independent of the deposition technique used (e.g. sputtering or electron beam evaporation), metallic thin films exhibit an amorphous or a polycrystalline microstructure when deposited under typical conditions, such as no or only a moderate substrate heating. In the latter case, films are mainly characterized by a logarithmic normal grain size distribution with randomly oriented grains. As far as technical applications are concerned, microstructural randomness leads to highly inhomogeneous and non-optimized device characteristics. Consequently, circumventing the random grain alignment by a laser-interference induced recrystallization for example with specified threshold energies results in a control of nucleation sites and grain orientations and thus superior properties.

In this context, gold thin films with a nominal thickness ranging between 300 and 700 nm were deposited on Si-substrates by electron beam evaporation. Subsequently, the as-deposited films were laser-patterned by a novel interference technique allowing for long-range ordered and periodic grain architectures and topographies (e.g. line-, dot- and cross-like patterns) on the micron-scale. Depending on the used laser energy density and the number of interfering laser beams, novel engineered microstructures and surfaces appear with beneficial properties.

The resulting tailored gold films were analyzed by high resolution techniques such as electron backscatter diffraction and transmission electron microscopy concerning the microstructure and correlated with thermal simulations. Moreover, detailed studies of the achieved topography after the laser treatment were performed by white light interferometry.

Finally, the results of the sliding tests under dry friction conditions will be presented showing a 40 % reduction of the friction coefficient and an enhanced wear resistance compared to the pristine sample state. Additionally, a Greenwood-Williamson approach is used to explain the tribological findings.

4:30pm **E1-3-8 Stress Analysis of WS2 Coatings Using Scratch Testing and Raman Spectrocopy**, ***J. Restrepo*** *(johansrestrepo@hotmail.com),* Universidad Nacional Autónoma de México, Mexico, *J.M. Gonzalez,* Universidad Del Valle, Colombia, *S. Muhl,* Universidad Nacional Autónoma de México, Mexico, *F. Sequeda,* Universidad Del Valle, Colombia

Tungsten disulphide coatings were deposited using a magnetron sputtering technique at different voltage biases. The films were characterized by X-ray diffraction, perfilometry and Nanoindentation. The tribological properties of the coatings were evaluated using scratch testing without causing severe cracking or total spallation, using two counter materials (1/16" balls of 100CR6 and Al_2O_3). To study the plastic deformation caused by the application of load during the scratch measurements we used 3d profilometry. Finally, micro-Raman spectroscopy was employed to study any deformation-induced chemical reaction with the ball at different loads for both coating materials. The results showed that the contact pressure caused a lattice deformation in the tungsten disulphide coatings with both type of test balls, but this deformation was larger for the Al_2O_3 balls. The Raman analysis showed that with the 100CR6 steel balls an oxide layer was formed whilst no such layer was observed for the Al_2O_3 balls. Finally, optical microscopy and Raman analysis of the two types of balls was performed to investigate the details of the tribological phenomenon that occurred during the scratch testing.

4:50pm **E1-3-9 Investigation of the Tribological Behavior of Electrocodeposited Ni-MoS_2 Composite Coatings**, *E. Saraloglu Guler (esaraloglu@gmail.com), İ. Karakaya,* Middle East Technical University, Turkey, *E. Konca,* Atilim University, Turkey, *A. Ozturk,* ***M. Erdoğan***, Middle East Technical University, Turkey

Molybdenum disulfide is regarded as one of the most widely used so lid lubricants. One of the application methods of MoS_2 on substrates is the electrodeposition in metal matrix. Ni–MoS_2 composite coatings were developed on AISI 304 stainless steel substrates by electroplating from Watts bath containing suspended MoS_2 particles. The effects of three types

of surfactants; depramin C, ammoniumlignosulfonate, sodiumlignosulfonate and the MoS_2 concentration on the tribological behavior and particle distribution of electrocodeposited Ni-MoS_2 composite coatings were studied by pin on disc tribometer and a scanning electron microscope. Addition of 10 g/l MoS_2 (1.2 micron average particle size) into the Watts bath, decreased the friction coefficient of nickel coatings from 0.75 to 0.45. The use of sodiumlignosulfonate and ammoniumlignosulfonate were more effective in homogenously distributing MoS_2 particles in nickel matrix and reducing the friction as compared to Depramin C. Moreover, increasing the MoS_2 content to higher levels caused further reductions in the friction coefficient.

5:10pm **E1-3-10 Fretting Wear Behaviour of Ti-TiC Composite Alloys: Influence of the TiC Concentration**, ***J. Duhart*** *(jeremy.duhart@ec-lyon.fr)*, *S. Fouvry*, Ecole Centrale de lyon, France

Metal matrix composites (MMCs) based with aluminium alloys are widely used in aeronautical industries, for small loading and low temperatures conditions. Different studies confirm that the wear resistance of aluminium alloys, reinforced with SiC particles, is improved significantly due to particle addition [1]. However these aluminium composites are no longer convenient for severe stressing and temperature conditions like observed in engine parts. New material structures involving titanium matrix reinforced with TiC particles have developed to palliate such limitations. These composites are realized by powder metallurgy, which have considerable potential for use in aerospace applications due to their high specific mechanical properties [2].

In this study, three composites, titanium grade 2 based with different particle rates, were tested under fretting wear conditions. The fretting wear analysis was performed under gross slip regime, for several pressures and sliding conditions. Both friction and wear rates responses have been investigated. Like for aluminium composite, it is shown the TiC particle concentration highly influences of the wear resistance. Various hypothesis including oxidation mechanisms and micro-cracking of TiC particules are discussed.

[1] R.N. Rao, S. Das; Materials and Design 31 (2010); 1200–1207

[2] D.B. Miracle, Compos. Sci. Technol. 65 (2005) 2526–2540

New Horizons in Coatings and Thin Films
Room: Sunrise - Session F2-2

High Power Impulse Magnetron Sputtering
Moderator: J. Sapieha, Ecole Polytechnique de Montreal, D. Lundin, Université Paris-Sud 11, France

2:10pm **F2-2-1 High Power Pulse Plasma Systems for the Reactive Deposition of Thin Films at Low Substrate Temperature**, ***Z. Hubicka*** *(hubicka@fzu.cz)*, *M. Cada*, *S. Kment*, Institute of Physics of the ASCR, v.v.i., Czech Republic, *P. Ksirova*, *J. Olejnicek*, Institute of Physics ASCR, v.v.i., Czech Republic, *T. Kubart*, Uppsala University, Sweden, *V. Stranak*, Insitute of Physics ASCR, v.,v.,i., Czech Republic **INVITED**

Semiconductor oxide thin films of Fe_2O_3, TiO_2 and WO_3 were deposited by reactive sputtering in various high power pulse plasma systems and their properties were investigated for photocatalytic water splitting applications. TiO2 represents semiconductor typically used for this purpose. Fe_2O_3 and WO_3 provide a potential means to capture a relatively significant portion of the available solar light, due to their lower band-gap energies. A nanocrystalline WO_3 film on a conducting glass electrode also provides high IPCEs for photoelectrochemical water decomposition under visible light. The first system used in this study was high power pulsed magnetron sputtering system (HIPIMS) employing metallic targets and working in a gas mixture of Ar and O_2 . The influence of different magnitudes of the applied pulsed power and pulsing frequency on the formation of crystalline structure, physical properties and photocatalytical properties was investigated. The next system, hybrid pulsed magnetron working in combination of simultaneous HIPIMS discharge generation and medium frequency (MF) plasma generation with MF frequency f=350 kHz, was investigated for the depositions of these coatings. Effect of the applied MF power on physical and photocatalytical properties and on the deposition rate was evaluated. Finally, the oxide thin films were deposited by a DC pulsed hollow cathode system with additional RF field. Two metallic hollow cathodes were sputtered in argon plasma flow and reactive gas was supplied directly to the reactor. The hollow cathode discharges were supplied from the DC pulsed power supply connected in parallel with the RF power source working at frequency 13.56 MHz. The main advantage of this system was the high deposition rate which was nearly independent on the amount of used oxygen in the plasma. Deposited films were more porous from the hollow cathode system in comparison with dense and flat films deposited usually by pulsed HIPIMS magnetron. A plasma diagnostics was carried out in all the investigated systems. The most important was emission spectroscopy, Langmuir probe measurement and the investigation of ion velocity distribution function by retarding field analyzer or by energetically resolved mass spectrometry. Various forms of quartz crystal microbalance QCM with several types systems of grids were used to determine ionization fraction of sputtered and reactively sputtered particle fluxes to the substrate under different deposition conditions of these oxide thin films.

2:50pm **F2-2-3 Mo_2BC a Stiff and Moderately Ductile Tool Coatings – from Ab Initio Predictions to HPPMS Synthesis in an Industrial Deposition System**, *H. Bolvardi*, *J. Emmerlich*, *D. Music*, RWTH Aachen University, Germany, *M. Arndt*, *H. Rudigier*, OC Oerlikon Balzers AG, Liechtenstein, ***J. Schneider*** *(jochen.m.schneider@googlemail.com)*, RWTH Aachen University, Germany

The elastic properties of Mo2BC were studied using ab initio calculations. The calculated bulk modulus of 324 GPa is 45% larger than that of Ti0.25 Al0.75 N and 14% smaller than that of c-BN, indicating a highly stiff material. The bulk modulus (B) to shear modulus (G) ratio is 1.72 at the transition from brittle to ductile behaviour. This, in combination with a positive Cauchy pressure (c12 − c44), suggests moderate ductility. When compared with a typical hard protective coating such as Ti0.25Al0.75N (B = 178GPa; B/G = 1.44; negative Cauchy pressure), Mo2BC displays considerable potential as protective coating. This prediction was critically evaluated by structural and mechanical characterization of combinatorial grown Mo2BC thin films on sapphire substrates at a substrate temperature of ∼900 °C. The calculated lattice parameters are in good agreement with values determined from x-ray diffraction. The measured Young's modulus values of ∼460 ± 21 GPa are in excellent agreement with the 470 GPa value obtained by calculations. Structural and mechanical characterization of coatings deposited in an industrial deposition system by HPPMS also result in excellent agreement with the ab initio predictions. The reduction in synthesis temperature of 300 °C compared to the combinatorial deposition described above illustrates the applicability of this coating system on technologically relevant substrates for protective coatings and underlines the relevance of the here implemented quantum mechanically guided materials design approach for application.

3:10pm **F2-2-4 Influence of HPPMS Pulse Length and Inert Gas Mixture on the Properties of (Cr,Al)N Coatings**, *N. Bagcivan*, *K. Bobzin*, Surface Engineering Institute - RWTH Aachen University, Germany, *G. Grundmeier*, *C. Kunze*, University of Paderborn, Technical and Macromolecular Chemistry, Germany, ***R.H. Brugnara*** *(brugnara@iot.rwth-aachen.de)*, Surface Engineering Institute - RWTH Aachen University, Germany

Injection moulding and extrusion are effective techniques for mass production of high value plastic products. However, during production of these products adhesion and abrasion wear as well as corrosion take place in the moulding tools. Limited tool life of moulding tools represents an issue for mass production especially of plastic products with complex geometries. Concerning this, ternary nitride coatings such (Cr,Al)N deposited via physical vapor deposition (PVD) have good potential to be used as protective coatings on injection and extrusion tools. For an effective protection of coated tools a uniform layer of coating material is also required. In this regard, the HPPMS (high power pulse magnetron sputtering) technology offers possibilities to improve coating thickness uniformity as well as to adapt the chemical and mechanical properties. The present work deals with the investigation of influence of HPPMS pulse length and argon/krypton ratio on the (Cr,Al)N coating properties. For this reason, (Cr,Al)N coatings were deposited with HPPMS pulse length of 40, 80 and 200 µs at constant Ar/Kr ratio (120/80 sccm). The results of these coatings were compared with a coating deposited with DC Magnetron Sputtering (DC-MS) with the same Ar/Kr ratio. Afterwards, (Cr,Al)N coatings were deposited with constant pulse length (200 µs) in pure argon atmosphere. The chemical composition of the coatings as well as the inert gas incorporation in the samples was determined using XPS (X-ray Photoelectron Spectroscopy). Mechanical properties, morphology, phase composition and lattice parameters were analyzed by means of Nanoindentation, SEM (Scanning Electron Microscopy) and XRD (X-ray Diffraction) measurements, respectively. It can be shown that the deposition rate of the HPPMS process reduces with decreasing pulse length. Nevertheless, short HPPMS pulse leads to an increase of the hardness from 27 GPa to 34 GPa while the DC-MS coating displays a hardness of 18 GPa. Further improvement of the hardness was also indentified in the coating deposited using argon instead of mixture of argon and krypton. In addition, EIS (electrochemical impedance spectroscopy) was employed to determine the charge carrier density, which was correlated to the defect structure of the coatings.

3:30pm **F2-2-5 Ultra-thin Poly-crystalline TiN Films Grown by HiPIMS on MgO(100) - *in-situ* Resistance Study of the Initial Stage of Growth**, ***S. Shayestehaminzadeh*** *(ses30@hi.is)*, *T.K. Tryggvason*, University of Iceland, Iceland, *F. Magnus*, Uppsala University, Sweden, *S. Olafsson*, University of Iceland, Iceland, *J.T. Gudmundsson*, University of Michigan-Shanghai Jiao Tong University Joint Institute, China

TiN thin films have various applications in microelectronics and coating technology. In microelectronics, it is commonly used as an adhesion layer and diffusion barrier due to high thermal stability and low bulk electrical resistance. It has also been offered as a gate metal on high-κ dielectrics in metal oxide field effect transistors (MOS) technology [1]. One of the potential high-κ candidates is MgO as it has higher dielectric constant than SiO_2 [2]. Earlier we have demonstrated that films grown by high power impulse magnetron sputtering (HiPIMS) [3] exhibited higher density, lower roughness than dc magnetron sputtered films and a growth rate that was roughly constant for all temperatures [4]. Such high-quality and low-resistance films are desirable for low-temperature device manufacturing which lead to avoid post-annealing or substrate biasing. Here, we discuss the properties of ultra-thin TiN films grown by HiPIMS on single-crystalline MgO(100) substrates at growth temperatures ranging from 30 to 600 °C. The resistance of the TiN films was measured *in-situ*, during growth, in order to determine the coalescence thickness and film continuity at the initial stage of growth. The film grown at room temperature coalesced at 0.92 ± 0.06 nm and became structurally continuous at 2.7 ± 0.1 nm. At 600°C, the coalescence and continuity thicknesses decreased to 0.21 ± 0.04 nm and 0.58 ± 0.05 nm, respectively. X-ray reflectivity (XRR) measurements revealed that the growth rate of the films was roughly constant for all growth temperatures. The films density increased slightly up to 5.3 g/cm^{-3} at 600 °C and the surface roughness of the films decreased from 1 nm to 0.3 nm while the growth temperature increased from 30 to 600 °C. For the low-temperature grown films, grazing incident X-ray diffraction (GI-XRD) measurements showed the presence of [111], [200] and [220] crystallites in all growth temperatures. The grain size of [111] crystallites slightly reduced by increased growth temperature. The minimum [220] crystallites appeared at 400 °C while the maximum [200] grain size occurred at 400°C. It was also observed that the majority of grains corresponded to the [200] direction, which is similar to substrate orientation.

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[2] L. Yan, C.M. Lopez, R.P. Shrestha, E.A. Irene, A.A. Suvorova, M. Saunders, Appl. Phys. Lett. 88 (2006) 142901.

[3] J. T. Gudmundsson, N. Brenning, D. Lundin and U. Helmersson, J. Vac. Sci. Technol. A, 30 (2012) 030801.

[4] F. Magnus, A.S. Ingason, S. Olafsson, J.T. Gudmundsson, Thin Solid Films 519 (2011) 5861-5867.

3:50pm **F2-2-6 Influence of Ion Bombardment Energy on the Growth of CrN Films by Reactive Magnetron Sputtering and High Power Impulse Magnetron Sputtering**, ***A.P. Ehiasarian*** *(a.ehiasarian@shu.ac.uk)*, Sheffield Hallam University, UK, *B. Howe*, Air Force Research Lab, US, *I. Petrov*, University of Illinois at Urbana-Champaign, US

Production of transition metal nitrides with dense structures in industrial relevant conditions well below the homologous temperature requires assistance by ion bombarding flux and ion energy additional to that of a sputter process. In conventional direct current magnetron sputtering (DCMS) the metal species remain in a non-ionised state and have low energies. Thus, even at high ion-to-neutral ratios of 30, microstructures can be porous. Recently, fully dense CrN films have been deposited at low temperature without substrate bias by high power impulse magnetron sputtering (HIPIMS) technology which ionizes the metal flux and dissociates reactive nitrogen molecules within its plasma.

It is not clear if the additional ionization provided by HIPIMS can outweigh a simple addition of energy by substrate biasing in DCMS. Therefore we compare floating and biased growth of CrN films by DCMS and HIPIMS technologies.

Mass spectroscopic analyses showed that HIPIMS deposition produces a factor of 10 higher flux of dissociated N^{1+} compared to DCMS. A ratio of N^{1+} : N_2^{1+} = 0.4 in the HIPIMS plasma is factor 5 greater than in DCMS.

The crystallinity of the DCMS layers improved with ion energy to a certain extent. However, a step change was observed when ionization degree increased in HIPIMS-process. The texture evolved from random towards (200) as energy and ionisation increased. (220) growth was eliminated altogether.

HIPIMS layers had a laterally-homogeneous texture as observed by transmission electron microscopy. Nucleation and competitive growth were resolved very quickly and the film structure was very dense. HIPIMS deposition on top of DCMS layers resulted in fast closure of voids and establishing of a fully dense structure within 50 nm.

Growth of DCMS layers on HIPIMS layers was unable to sustain textured growth because of the low ionization of the DCMS process. Island coalescence was poor resulting low boundary density.

Results from DCMS-deposited films indicate that ion energy alone may be insufficient to promote a dense structure and a dominant (200) texture if N^{1+} : N_2^{1+} ratio is too low. The HIPIMS results show that elevating the N^{1+} : N_2^{1+} ratio to a moderate amount promotes the growth of (100) surfaces. Complementing this with moderate ion energy produces highly textured films with a fully dense structure.

4:10pm **F2-2-7 Properties of $Ti_{1-x}Si_xN$ Films Grown in Hybrid HIPIMS-DCMS Configuration**, ***G. Greczynski*** *(grzgr@ifm.liu.se)*, *J. Lu*, *J. Jensen*, Linköping University, 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, Sweden

$Ti_{1-x}Si_xN$ alloy thin films are grown by high-power pulsed magnetron (HIPIMS) and dc magnetron (DCMS) co-sputtering. Elemental Ti and Si targets are operated in HIPIMS and DCMS, co-sputtering mode. The properties of resulting films are analyzed by x-ray diffraction, scanning electron microscopy, transmission electron microscopy, x-ray photoelectron spectroscopy, elastic recoil detection analysis, and nanoindentation. Ion fluxes at the substrate position are determined using time-resolved in-situ mass spectrometry. The distinctly different flux distributions obtained from targets driven in HIPIMS *vs.* DCMS modes allow the effects of Si^+/Si^{2+} and Ti^+/Ti^{2+} ion irradiation on resulting film properties to be investigated separately. [1] Interesting results are presented showing the dependency of coating microstructure, phase composition, hardness, elastic modulus, residual stresses and others from process parameters and silicon content.

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[1] G. Greczynski, J. Lu, M. Johansson, J. Jensen, I. Petrov, J.E. Greene, and L. Hultman, "Role of Ti^{n+} and Al^{n+} ion irradiation (n = 1, 2) during $Ti_{1-x}Al_xN$ alloy film growth in a hybrid HIPIMS/magnetron mode", *Surf. Coat. Technol.* 206 (2012) 4202

4:30pm **F2-2-8 A Comparative Study of AlN Films Deposited by Deep Oscillation Magnetron Sputtering and Pulse DC Magnetron Sputtering**, ***B. Wang***, Colorado School of Mines, US, *I. Dahan*, Ben Gurion University of the Negev, Israel, *J. Moore*, Colorado School of Mines, US, *W. Sproul*, Reactive Sputtering, Inc., US, *J. Lin (jlin@mines.edu)*, Colorado School of Mines, US

Nanocrystalline aluminum nitride thin films were deposited on various substrates by sputtering an aluminum target in an Ar+N_2 mixture by deep oscillation magnetron sputtering (DOMS) and pulse DC magnetron sputtering (PDCMS) at different working pressures. Deep oscillation magnetron sputtering (DOMS) is an alternative high power pulsed magnetron sputtering technique which can achieve virtually arc free deposition for reactively deposition of insulating films. The structure, mechanical, optical and electrochemical corrosion properties of the AlN films deposited by these two techniques have been studied and compared. The results show that the AlN films deposited using DOMS exhibited a much stronger (0002) texture as compared to those deposited by PDCMS with the same film thickness. Additionally, the films prepared by DOMS exhibited denser microstructure and finer grain size, indicating MPP is a promising process for preparing high quality textured AlN films. The thermal stability of the AlN films obtained by DOMS and PDCMS has also been investigated by in-situ X-ray diffraction.

4:50pm **F2-2-9 Characterization of Hard Coatings Deposited by Constant Voltage HIPIMS and MPP Sputtering System and their Cutting Performance**, ***T. Sasaki*** *(tomoya_sasaki@hitachi-tool.co.jp)*, *K. Inoue*, *S. Abusuilik*, Hitachi Tool Engineering, Ltd., Japan

High Power Impulse Magnetron Sputtering (HIPIMS) has been of interest over the past decade owing to its ability to ionize sputtering materials at higher ionization energy. It is possible to modify coating properties in ways that are not easily possible with DC sputtering due to the higher ionization of HIPIMS. Therefore, HIPIMS technology is expected to be of interest applicable in the field of hard coatings for cutting tools. However, it was reported that the deposition rate in HIPIMS is lower than the DC sputtering rate. The low deposition rate in HIPIMS has been explained in terms of ions attraction back toward the target and ion capture by the negative potential on the cathode. In recent years, an alternative HIPIMS technique known as Modulated Pulse Power (MPP) has been developed to overcome the rate loss problem with a high degree of ionization of the sputtered material. The aim of this work is to study the effect of deposition parameters of coatings

applied by constant voltage HIPIMS and MPP sputtering systems and to study its applicability in the field of cutting tools.

In this study, bias voltage during coating was investigated in details. In the same regard, chemical composition, morphology and crystal structure of coatings were analyzed using Electron Probe Micro Analyzer (EPMA), Scanning electron microscope (SEM) and X-Ray Diffraction (XRD) under different deposition parameters. Furthermore, cutting tests were made with different deposition parameters. Both of them coatings made by constant voltage HIPIMS and MPP sputtering systems showed better cutting performance than the coatings made by DC sputtering. Coatings deposited by HIPIMS and MPP sputtering systems showed good possibility of application in the field of cutting tools.

5:10pm **F2-2-10 Performance of RMS vs. HPPMS Cr/Cr_2O_3 Films in Protection against Metal Dusting**, *M. PÉREZ, O. Salas (osalas@itesm.mx)*, ITESM-CEM, Mexico, *J. Lin*, Colorado School of Mines, US, ***J. Oseguera***, *D. Melo-Maximo*, ITESM-CEM, Mexico, *R. Torres*, PUCPR, Brazil, *C. Lepienski*, UFPR, Brazil, *R. De Souza*, Usp, Brazil

Cr/Cr_2O_3 thin films have been deposited on 304 stainless steel substrates via reactive magnetron sputtering (RMS) and high power pulsed ma gnetron sputtering (HPPMS) to compare their performance in metal dusting atmospheres. The processing conditions in each method were selected to produce films with similar architectures. In each deposition method, the effect of the partial pressure of oxygen as well as the application of a bias voltage was investigated. The structure of the resulting films was characterized by optical microscopy, scanning electron microscopy + energy dispersive analysis, and their adhesion by scratch testing. Their performance in metal dusting conditions was evaluated by thermogravimetric analysis in a carburizing atmosphere at high temperature.

New Horizons in Coatings and Thin Films
Room: California - Session F3-1

New Boron, Boride and Boron Nitride Based Coatings
Moderator: H. Hoegberg, Linkoeping University, A. Inspektor, Kennametal Incorporated, USA

2:10pm **F3-1-1 Exploring New W-B Coating Materials for the Aqueous Corrosion-wear Protection of Stainless Steels**, ***P. Dearnley*** *(p.dearnley@soton.ac.uk)*, University of Southampton, UK, *B. Mallia*, University of Malta, Malta

The present paper explores the viability of using W based coatings super saturated with varying levels of boron and reports their performance when applied to implant grade austenitic stainless steel and subjected to reciprocation sliding contact tests (against aluminium oxide) in an aqueous 0.9%NaCl solution under a normal force of 1N. The electrode potential and corrosion current was monitored (where possible) throughout the tests. As the boron content of the coatings was raised they changed from being nano-crystalline into "X-ray amorphous" materials. Coating compositions on either side of the crystalline to amorphous transition provided excellent corrosion-wear protection to the stainless steel surfaces (comparable to CrN). Basic static corrosion tests revealed the W-B based coatings to provide a significant improvement in crevice corrosion resistance compared to uncoated stainless steel substrates.

2:30pm **F3-1-2 Exploring Coating Materials Based on the Cr-B-N System for the Corrosion-wear Protection of Stainless Steels**, *P. Dearnley (p.dearnley@soton.ac.uk)*, University of Southampton, UK, *M. Stüber*, Karlsruhe Institute of Technology, Germany, ***B. Mallia***, University of Malta, Malta

The corrosion-wear material loss of metallic surfaces is a serious concern in many application sectors, ranging from bio-medical implants to marine, oil and gas field components to transport vehicle and nuclear reactor devices. To date little effort has focused on developing specific coating materials to combat corrosive-wear processes. The present paper explores the viability of using Cr-B-N based coatings and reports their performance when applied to a grade of super austenitic stainless steel and subjected to reciprocation sliding contact tests (against aluminium oxide) in an aqueous 0.9%NaCl solution under a normal force of 1N. (Super austenitic stainless steels are widely used in the oil & gas sector as well as in the nuclear and bio-medical device industries) The electrode potential and corrosion current was monitored (where possible) throughout the tests. Whilst in principle the formation of low friction layers based on BN was considered probable, in practice this did not happen, instead relatively high friction layers were produced. On the whole, increasing the N content of the coatings caused a deterioration in hardness and corrosion-wear resistance. In fact the best corrosion-wear protection was offered by Cr-B coatings containing no additions of N. The same coatings have also shown useful performance for the protection of ferritic stainless steel internal combustion engine piston rings in elevated temperature (circa 190˚C) high speed organic fluid lubricated reciprocation sliding contact tests.

2:50pm **F3-1-3 Magnetron Sputtering of Me-B-C coatings**, ***U. Jansson*** *(ulf.jansson@kemi.uu.se)*, *N. Nedfors*, Uppsala University, Sweden, *L. Wang*, Lanzhou Institute of Chemical Physics, China **INVITED**

Thin Me-B-C coatings (Me = early transition metal) have interesting mechanical and tribological properties. Only one ternary phase, Mo_2BC, is known and predicted to exhibit a unique combination of stiffness and ductility [1]. The stability of this ternary structure is considerably less for other Me-B-C systems and some explanations for this trend will be discussed. The thermodynamically most stable phase combination in most Me-B-C systems is therefore a mixture of binary phases. During magnetron sputtering at lower temperatures, the high quenching rate combined with low diffusion rates make it difficult to form the crystalline binary phases and amorphous growth is therefore frequently observed. A general overview of this behaviour will be discussed for different early transition metals. Some general trends in the correlation between materials properties and composition will be discussed with a special emphasis on the Cr-B-C system. Magnetron sputtering of Cr-B-C coatings using targets of CrB_2 and graphite leads in general to films with a B/Cr ratio < 2. With increasing carbon content the

coatings become amorphous. X-ray photoelectron spectroscopy (XPS) suggests a mixture of Cr-B, B-C and C-C bonds. The friction and wear of this material is dependent on the carbon content and a reduced friction coefficient is observed at higher carbon contents. The tribological behavior is, however, strongly dependent on the humidity. Finally, the possibility for formation of low friction boron oxide tribofilms on this type of materials will be discussed.

[1]. J. Emmerlich et al., J. Phys. D. Appl. Phys. 42 (2009) 185406

3:30pm **F3-1-5 Synthesis of Very Thick PVD Boron Carbide Films for Potential Fusion Targets**, ***P. Mirkarimi*** *(Mirkarimi1@llnl.gov)*, *K. Bettencourt, N. Teslich, K.J. Wu, M. Wang*, Lawrence Livermore National Laboratory, US, *H. Xu*, General Atomics, Inc.,US, *G. Randall, Nikroo*, General Atomics, Inc., US

There is significant interest in inertial confinement fusion (ICF) and one of the institutions where research is being performed is the National Ignition Facility in Livermore. Thick film ablators serve a critical role in the targets and historically Plastic, Beryllium, and Diamond, have been considered as potential ablators. For Beryllium and Diamond, films several tens to hundreds of microns thick, are typically deposited on a spherical substrate that is subsequently removed to leave a hollow capsule that is filled with a deuterium-based gas. Due in part to the challenges in achieving ignition, there is a strong desire to have an alternative ablator candidate. And due to the fact that the film needs to be of a high quality and deposit uniformly on a small spherical capsule, PVD methods are usually preferred.

Based on simulations a new and potentially very promising ablator material is Boron Carbide. One challenge in employing this material as an ablator is that PVD Boron Carbide typically has a high film stress which limits the thickness achievable before delamination occurs. We have used a PVD process, e-beam evaporation, to deposit Boron Carbide films up to and exceeding 100 microns thick, which to our knowledge may be a record thickness for PVD deposited Boron Carbide. We shall briefly discuss efforts to use our Boron Carbide films for preliminary high pressure experimental studies at the Omega facility. We shall also discuss the process research/development that lead to these very thick films as well as present metrology results on the structure and properties of the films; for example, results showing that the Boron Carbide films were very hard.

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344

3:50pm **F3-1-6 Influences of Boron Contents on the Microstructure and Mechanical Properties of Ti-Zr-B-N Thin Films Deposited by Pulsed DC Reactive Magnetron Sputtering**, ***W.S. Lai***, National Taiwan University of Science and Technology, Taiwan, Republic of China, *J.-W. Lee (jefflee@mail.mcut.edu.tw)*, Ming Chi University of Technology, Taiwan, Republic of China, *C.J. Wang*, National Taiwan University of Science and Technology, Taiwan, Republic of China

A series of Ti-Zr-B-N films with various zirconium and boron additions were deposited by a pulsed DC reactive magnetron sputtering. The effects of Zr and B contents were investigated in relation to the microstructure, adhesion, tribological and mechanical properties of thin films. The chemical

composition, phase composition and microstructure of thin films were determined by Electron Probe for Microanalyzer (EPMA), X-ray diffraction (XRD), field-emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM), respectively. It was found that the coating hardness increased with decreasing boron content. The maximum hardness of 34.6 GPa was achieved when the B content was 0.79 at.%. The addition of B element to the Ti-Zr-B-N films showed significant influence on the microstructure and mechanical performance. A proper chemical composition of Ti-Zr-B-N films was proposed in this work.

4:10pm **F3-1-7 Boron-10-Based Thin Films for the Next Generation of Neutron Detectors**, ***C. Höglund*** *(carina.hoglund@esss.se)*, European Spallation Source ESS AB/Linköping University, Sweden **INVITED**

Lately, the demands for ^{3}He have increased, mainly due to the U.S. Homeland Security programs. At the same time the production of this rare gas has decreased since the end of the cold war, due to the main source being the radioactive decay of tritium. This had led to an urgent need for alternatives to ^{3}He-based neutron detection techniques at large-scale neutron research facilities. New large area neutron detectors, including the ones that will be built at the European Spallation Source (ESS), or radiation scanners at, e.g., airports, would require much more than the complete U.S. supply of ^{3}He.

We present a new generation of neutron detectors that use ^{10}B-containing thin films as the neutron-absorbing material instead of ^{3}He. The detectors comprise thin films of $^{10}B_4C$, which are deposited onto Al-blades or Si-wafers. A full-scale detector needs in total ~1000 m^2 of two-side coated Al-blades with ~1 µm thick $^{10}B_4C$ films. Tough demands on film purity and thickness uniformities make it a big challenge to upscale such a process (total need > 7000 m^2) to fulfill the demands of the ESS.

DC magnetron sputtering (PVD) in an industrial deposition system, from $^{nat}B_4C$ and $^{10}B_4C$ targets has been used for coatings on flat surfaces. For detector designs that need films on irregularly shaped substrates, chemical vapor deposition (CVD) is preferred. Since the substrate is Al, the temperature shall not exceed 600 °C, which is why both thermally activated and plasma enhance CVD are of interest.

The coatings have been characterized with scanning electron microscopy, elastic recoil detection analysis, X-ray reflectivity, and neutron scattering. Substrate temperatures of 400 °C result in PVD films with a density close to bulk values and good adhesion to film thicknesses above 3 µm. The ^{10}B content is close to 80 at.%, i.e. full isotope enrichment, with impurity levels of less than 1 at.% of H, N, and O. Various relevant properties, including stress in the coatings and neutron radiation damage, have been looked into. Simulations to predict detector performance and optimal thin film properties have been supporting the experimental work.

Detector prototypes with $^{10}B_4C$ thin films have been tested for their neutron performance and compared with existing flagship instruments, like the IN6 at the ILL in France. The prototypes yield a neutron detection efficiency of ~50%, which is in general agreement with simulated results. These new $^{10}B_4C$ thin film based neutron detectors have a potential to replace most ^{3}He-containing detectors. The development will continue far into the ESS construction phase, which lasts until ~2025.

4:50pm **F3-1-9 Tailoring the Mechanical and Tribological Properties of Boron Carbide Films by Adjusting the BC_x Stoichiometry**, ***J.C. Qian***, *Z.F. Zhou, C. Yan*, City University of Hong Kong, Hong Kong Special Administrative Region of China, *D.J. Li*, École Polytechnique de Montréal, Canada, *M. Azzi*, Notre Dame University, US, *K.Y. Li*, *W.J. Zhang, I. Bello*, City University of Hong Kong, Hong Kong Special Administrative Region of China, *L. Martinu*, École Polytechnique de Montréal, Canada, *J.E. Klemberg-Sapieha (jsapieha@polymtl.ca)*, Ecole Polytechnique de Montréal, Canada

Boron carbide (BC_x) coatings appear very attractive due to their high hardness and interesting tribological properties. In the present work, we systematically studied the effect of stoichiometry of BC_x films ($0 < x < 1$) as a means to tailor their hardness (*H*) and Young's modulus (*E*) as well as the wear coefficient and corrosion resistance. The BC_x films were deposited on Si (100) and M2 high speed steel substrates using a pilot-scale closed-field unbalanced magnetron sputtering system equipped with one graphite and two boron targets. Different compositions were obtained by tuning the graphite target current. We found that the hardness of the BC_x films (measured on Si) decreases from 28 GPa to 18 GPa as the carbon content [C] increases from 22.1 at.% to 65.3 at.%, but it increases again up to ~22 GPa when reaching [C] = 82.0 at.%. The hardness variation is explained by changes in the film microstructure, namely formation of a nanocomposite structure formed by BC_x nanocrystals dispersed in an amorphous BC_y/a-C matrix as confirmed by a combination of XRD, TEM XPS, micro-Raman and ERD measurements. The friction coefficient of the BC_x films with a 200 nm TiB_2 interlayer on the high speed steel substrates decreased from 0.7 to 0.2, and the wear rate against alumina ball (6 mm diameter) decreased from 6.4×10^{-5} mm^3/N-m to 1.3×10^{-7} mm^3/N-m as [C] was increased. Subsequent surface analyses clearly indicated that improvement of the tribological properties of the BC_x films is primarily due to the formation of a graphitic tribolayer that acts as a solid lubricant during the wear process. Application of the BC_x coating possessing a high hardness (28 GPa) and 22.1 at.% of carbon improved the corrosion resistance of the M2 steel substrate by four orders of magnitude, documented by a decrease of the corrosion current from 3×10^{-6} A/cm^2 to 8×10^{-10} A/cm^2.

5:10pm **F3-1-10 Modification of Multi-walled Boron Nitride Nanotubes by Metal Ion Implantation**, ***D. Shtansky*** *(shtansky@shs.misis.ru)*, *E. Obraztsova, A. Sheveko, A.M. Kovalskii*, National University of Science and Technology "MISIS", Russian Federation, *M. Yamaguchi, D.V. Golberg*, National Institute for Materials Science, Japan

Recent progress in boron nitride nanotubes (BNNTs) syntheses opened new possibilities for utilization of the attractive combination of their excellent mechanical characteristics and superb thermal and chemical stabilities for the creation of new structural and functional reinforced materials. In this work we have applied metal ion implantation to prepare novel BNNTs/metal matrix composites. The resulting structures have thoroughly been studied by high-resolution transmission electron microscopy and Raman spectroscopy. The obtained results show that by changing the ion implantation parameters it is possible to fabricate BNNT/metal composites with different contents of BNNT crystalline phase and controlled morphologies, structures, and volume fractions of metal phase additives. Such novel composite nanomaterials are envisaged to be attractive for many structural and functional applications, in particular for reinforcing ultralight Al-based alloys.

Hard Coatings and Vapor Deposition Technology
Room: Royal Palm 4-6 - Session B2-1

CVD Coatings and Technologies
Moderator: E. Blanquet, CNRS, France, S. Ruppi, Walter AG, Germany

8:00am **B2-1-1 New Developments in the Field of CVD Hard Coatings**, ***I. Endler*** *(Ingolf.Endler@ikts.fraunhofer.de)*, Fraunhofer IKTS, Germany **INVITED**

Since 40 years CVD hard coatings have been applied widely as wear-resistant coatings for cutting tools. After an intensive development of new CVD coatings in the first years the research activities declined in the nineties. The research shifted more and more to the development of novel PVD coatings as TiAlN and nanocomposite coatings. However CVD coatings still dominate as wear-resistant coatings for hard metal cutting tools on the market. Due to the increase of high speed and dry cutting as well as emerging new workpiece materials the metalworking industry has a growing demand on high performance tools. This fact has also been favoring an increase in the research and development of new CVD hard coatings in the last years. There are complex requirements to hard coatings because of high thermal and mechanical loads at the cutting edge of the insert. Modern hard coatings must offer high hardness as well as high oxidationn resistance and they should be inert to the workpiece material at elevated temperatures. First the state of the art of CVD methods and coatings is considered. Following novel CVD coatings are presented and also research trends. New CVD coatings with a high application potential are aluminum-rich TiAlN and TiAlCN as well as TiSiCN nanocomposite coatings. These novel CVD coating types exhibit a high hardness between 30 GPa and 40 GPa and an oxidationn resistance up to 900°C. Furthermore the progress in the development of alumina coatings will be described. Finally the potential of these new coatings for the design of new CVD coating systems will be shown.

8:40am **B2-1-3 CVD $Ti_{1-x}Al_xN$ Coatings for Mass Production**, ***H. Holzschuh*** *(helga.holzschuh@sucotec.ch), W. Buergin*, SuCoTec AG, Switzerland

Over the last 20 years $Ti_{1-x}Al_xN$ coatings were the domain of PVD.

Published in 2008 the first cubic $Ti_{1-x}Al_xN$ coatings containing high Al (x>0.8) were developed in a lab scale CVD system. Remarkable wear behavior and properties were reported. In 2011 a tool manufacturer succeeded to develop an in house CVD process to produce CVD $Ti_{1-x}Al_xN$ coated inserts. They reported high Al-content (>70%), high hardness, a phase mixture of cubic and hexagonal and excellent cutting results.

We now report on $Ti_{1-x}Al_xN$ results achieved with the first commercially available CVD systems SCT600 and SCT400 which can coat up to 15'000, respectively 8'000 pcs. ½"inserts per batch . The newly developed NH_3 module proved its capability to coat homogenously single phased cubic $Ti_{1-x}Al_xN$ in medium temperatures and Al contents >70%. By varying the gas parameters phases of the $Ti_{1-x}Al_xN$ coatings could be tailored (pure cubic, mixed cubic and hexagonal) while keeping the Al-content high. The coated samples were characterized in terms of structure, composition, physical and mechanical properties.

9:00am **B2-1-4 The Development of a CVD Material for Thermally Oxidative Environments with High Hydrophobicity and Oleophobicity, and Good Wear Resistance with a Low Friction Coefficient**, ***D. Smith*** *(david.smith@silcotek.com), J. Mattzela, P. Silvis*, SilcoTek Corporation, US

There is a significant need within a variety of applications for surfaces that exhibit and maintain high hydrophobicity, oleophobicity and good wear resistance with a corresponding low coefficient of friction after exposure to environments of high thermal stress in oxidative environments. Examples include areas such as fuel delivery and exhaust systems, and heat transfer systems. With modifications of a commercially available CVD process, a new material is being evaluated for the above characteristics, before and after exposure to 450°C in air. A variety of surface evaluation methods will be discussed, including the use of tensiometer and goniometer data for contact angle analysis, surface FT-IR microscopy and X-ray photoelectron spectroscopy for material composition analysis, potentiometric information for electrochemical and corrosion resistance analysis, and pin-on-disc data for wear resistance and friction coefficient evaluation. The method of deposition will also be discussed, as it allows for the deposition on to complex three-dimensional configurations, in bulk quantities, and on to parts of significant size.

9:20am **B2-1-5 Phase Selective Deposition of α-Al_2O_3 by Thin Layers of TiO_2**, *B.E. Boman (mats.boman@kemi.uu.se)*, ***D. Fondell***, *S. Munktell*, Uppsala University, Angstrom Laboratory, Sweden, *O. Alm, T. Larsson*, Seco tools AB, Sweden

The industry of metal cutting is under constant development. New machines with higher cutting speed and new materials that require more advanced cutting tools are two reasons for this. A cutting tool needs to be tough, wear resistant, deformation resistant and stable at high temperatures. Today most cutting tools for different kinds of steels and other types of metals are constructed with a hard but tough bulk material and a multilayer coating of hard and stable ceramics. Often a bulk material of cemented carbide and coatings of titanium carbon-nitride and aluminum oxide are used. To further enhance the properties multilayer coatings are deposited on the tool.There are two different techniques often used to create these kinds of hard coatings; chemical vapour deposition (CVD) and physical vapor deposition (PVD). CVD is used to deposit the titanium carbonnitride and the aluminum oxide coatings.

A material that has proven useful in the harsh environment of metal cutting is aluminium oxide. Aluminum oxide shows great properties in wear resistance, toughness and deformation resistance at high temperatures. The most common phases of aluminium oxide usually obtained in the CVD process are α-Al2O3 and κ-Al2O3. The thermodynamically stable phase is α-Al2O3. If a cutting tool is coated with κ-Al2O3 the film may undergo phase transformation during the cutting process which could reduce the durability of the tool coating and therefore α-Al2O3 is the desired phase. Aluminum oxide is usually combined with layers of titanium carbonitrides. Ti(C,N) which has complementary wear properties to aluminum oxide making it widely used on metal cutting tools. It has proven to be a difficult task to deposit α-Al2O3 on Ti(C,N) with CVD as the phase obtained is mainly κ-Al2O3.

In this investigation phase selective growth of α-Al2O3 is demonstrated by thin interlayers of TiO2 deposited by atomic layer deposition.

9:40am **B2-1-6 Influence of the N/Al Ratio in Gas Phase on the Crystalline Quality of AlN Grown by HTCVD on c-sapphire.**, ***R. Boichot*** *(raphael.boichot@phelma.grenoble-inp.fr), N. Coudurier*, Grenoble INP, France, *E. Blanquet, M. Pons*, CNRS, France

The availability of industrial-grade quality and cheap AlN templates is currently a major concern for optoelectronic industry. A solution could be to produce epitaxial AlN layers by high temperature chemical vapor deposition (HTCVD) directly grown on c-sapphire, one of the cheapest UV/visible transparent substrate. The main difficulty is that in addition to the fact that the lattice mismatch between c-sapphire and AlN is high (13.3 %), leading to strain and cracks in the grown layer, the initial sapphire surface is not stable in HTCVD conditions (H2 etching or NH3 nitridation at temperature above 1200°C).

Many studies attempted to optimize epitaxial growth of AlN on sapphire c-plane using AlCl3 and NH3 as precursors. The most promising way is to protect the sapphire surface with a controlled nucleation/nitridation layer grown at low temperature (below 1200°C) and low growth rate [1] prior the deposition at high temperature (typically 1500°C). Another solution is to control precisely the N/Al ratio in the gas phase during growth. Previous studies [2] concluded that the optimal N/Al ratio in gas phase for AlN epitaxial growth on various substrates was about 1.5. The main issue is that in all previous experiments, the N/Al ratio influence was investigated whereas growth rate and layer thickness also varied.

On the other hand, kinetic modeling of AlN growth rate is available [3], so that a study of the influence of N/Al ratio at constant thickness and constant growth rate is possible without any time-consuming growth rate calibration experiments. This study focuses on the influence of the N/Al ratio in gas phase at constant growth rate and thickness. The influence of layer thickness at constant growth rate and layer growth rate at constant thickness is also discussed. Finally, the addition of a protective by different ways (two steps growth or continuous growth) is studied.

This study leads to the synthesis of 5 µm AlN templates grown at 5 µm/h with a crystalline quality of 460 arcsec for the FWHM 0002 reflectivity, exhibiting no cracks on two inches sapphire wafers. The photoluminescence spectra and TEM interface image of some samples are also presented.

[1] M. Balaji, A. Claudel, V. Fellmann, I. Gélard, E. Blanquet, R. Boichot, A. Pierret, B. Attal-Trétout, A. Crisci, S. Coindeau, H. Roussel, D. Pique, K. Baskar, M. Pons, Journal of Alloys and Compounds 526 (2012) 103.

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[3] R. Boichot, A. Claudel, N. Baccar, A. Millet, E. Blanquet, M. Pons, Surface and coatings Technology, 205 (2010) 1294.

10:00am **B2-1-7 Growth of HfC and Nanostructured Multilayer HfC/SiC Coatings by DLICVD**, *G. Boisselier*, ***F. Maury*** *(francis.maury@ensiacet.fr)*, CIRIMAT, France, *F. Schuster*, CEA-Saclay, France

Nanostructured refractory multilayer coatings exhibit high protective performances under extreme environment. They are deposited by different processes in alternating the growth of each layer. To develop CVD processes industrially viable 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. Thus the key point is to select molecular precursors which decompose under identical conditions. On the other hand, the pulsed direct liquid injection (DLI) of precursors is an emerging technology to feed with high vapor flow rate CVD reactors, which offers new opportunities for metallurgical coatings. Recently (ICMCTF 2012), SiC coatings were grown by DLICVD starting with a solution of polysilaethylene (PSE) in toluene as single-source precursor. The growth was achieved in the temperature range 700- 800 °C at a total pressure of 50 Torr. These ceramic coatings were amorphous, very dense and exhibited an Si:C atomic ratio close to 1:1. As salient feature, the coatings had many microcracks through the coating to the substrate of graphite or Si. The microcracks resulted from high tensile intrinsic stresses induced by the growth mechanism that was essentially a densification with hydrogen release from the growing layer. Here, in the same hot-wall reactor and using comparable conditions, HfC coatings were deposited by injection of a solution of Cp_2HfMe_2 in toluene under H_2 partial pressure. These coatings are very dense, crack-free, nanocrystalline and C-rich. They exhibit a very smooth surface morphology (Ra < 6 nm) and the growth rate can reach 5 µm/h. HfC/SiC multilayer coatings were deposited at 750 ° C by combining alternatively both chemical systems. Coatings with a thickness of approximately 5 µm have been prepared and characterized. Each HfC and SiC layer had the same thickness and the bylayer period was varied between 400 and 100 nm, which corresponded to a number of individual layers between 26 and 100, respectively. In this last case, a nanostructuration of the coating was achieved since the thickness of each individual layer was only 50 nm. Interestingly, a self-healing of SiC cracks occurs during the growth of the multilayer coating as a result of a good infiltration and conformal coverage of HfC and other layers within cracks until clogging. Preliminary properties are also reported and discussed.

10:20am **B2-1-8 Industrial Scale Production of HFCVD Diamond Coatings**, *O. Lemmer*, *C. Schiffers*, ***M. Frank*** *(Martin.Frank@CemeCon.de)*, *B. Mesic*, CemeCon AG, Germany, *M. Rüffer*, DiaCCon GmbH, Germany, *S. Rosiwal*, University Erlangen-Nürnberg, Germany

The extraordinary properties of diamond coatings produced by hot filament chemical vapor deposition (HFCVD) make it suitable for a broad spectrum of applications. A unique coating machine allows deposition of diamond coatings with different properties and numerous types of substrates in an industrial scale. This is achieved by highly versatile filament arrays, substrate fixtures and process parameters.The polycrystalline and nanocrystalline diamond coatings on cutting tools are well established not only for machining graphite, printed circuit boards (PCB) and extremely abrasive aluminum-silicon and titanium-aluminum alloys but also for machining of challenging composite materials such as carbon fiber reinforced plastics (CFRP) for aerospace applications. Nanocrystalline diamond is one of the most interesting materials for micro-mechanical systems and MEMS devices. Large scale deposition of diamond films on silicon and on wear parts in an industrial scale have been developed. Boron doped diamond coatings can be used as electrode material for different electrochemical applications such as electrochemical synthesis or waste water treatment. Homogenous large area electrodes were produced using the same set up. Nanocrystalline self-supporting diamond foils, e.g. for erosion protection, were produced on appropriate templates and afterwards stripped-off. Despite the pure covalent bond and highest hardness the diamond foil is very flexible and easy to handle. This enables the application of diamond coating on temperature sensitive substrates.

10:40am **B2-1-9 Gradient of Tribological and Mechanical Properties of Diamond-like Carbon Films Grown on Ti6Al4V Alloy with Different Condition of Interlayer Preparation**, ***P. Silva***, *G. Martins*, *J. Machado*, *E. Corat*, Instituto Nacional de Pesquisas Espaciais (INPE), Brazil, *V. Trava-Airoldi (patricia.engpro@gmail.com)*, Instituto Nacional de Pesquisas Espaciais (INPE, Brazil

Ti6Al4V alloy are used on advanced aerospace systems, as a biomaterials, etc., because of their properties like high strength to weight ratio and excellent corrosion resistance and biocompatibility compared to many other metal alloys. In order to improve such applications, it is necessary to improve its tribological and mechanical properties and a good choice is the deposition of diamond-like carbon (DLC) coating with very high adhesion. DLC films are well known for their low friction, high hardness and good wear resistance. The adhesion between a DLC coating and Ti6Al4V alloy can be enhanced by the application of an interlayer of diverse materials. In this work, it was used a silicon interlayer that was deposited with different controlled ion energy, generating singular ion subimplantation profiles on the titanium alloy substrate. The DLC films were deposited using a modified PECVD pulsed-DC discharge under controlled conditions to obtain maximum hardness, minimum stress and maximum deposition rate. Tribological and mechanical tests were made to observe the friction and wear gradient of the samples. The tribometer was adjusted for ball-on-plate mode, in the reciprocating manner, in a humidity of 26 ± 2% RH and a temperature of 25 ± 1 ºC. The scratching tests were made in order to study the adhesion of DLC coatings on Ti6Al4V alloy as a function of silicon interlayer parameters of obtaining. The samples were also characterized by micro and nano-identation to observe the hardness profile, and Raman spectroscopy to verify the structural arrangement of carbon atoms. It was observed that the adhesion between DLC film and substrate is strongly related to gradient of mechanical and tribological properties of the substrate from the bulk to the surface.

Tribology & Mechanical Behavior of Coatings and Engineered Surfaces
Room: Golden West - Session E2-4

Mechanical Properties and Adhesion

Moderator: M.T. Lin, National Chung Hsing University, Taiwan, R. Chromik, McGill University, D. Bahr, Washington State University

8:00am **E2-4-1 3D Micro Scratch Tests in Combination with a Comprehensive Stress Analysis – a New Tool for the Understanding of Surface Failures**, ***T. Chudoba*** *(t.chudoba@asmec.de)*, ASMEC Advanced Surface Mechanics GmbH, Radeberg, Germany, *N. Schwarzer*, Saxonian Institute of Surface Mechancis, Germany, *A. Gies*, OC Oerlikon Balzers AG, Liechtenstein

Beside the Rockwell adhesion test, the scratch test is the standard tool for the investigation of adhesion properties of thin hard coatings. Typically such tests are carried out using a Rockwell C indenter with a tip radius of 200 µm and relatively high forces in the range between 10N - 100 N. However, the results are difficult to compare since they depend on substrate material, film thickness, scratch speed, perfectness of the tip and other parameters (see [1]). Generally, such tests allow mostly a ranking of different coating systems but no analysis of failure reasons.

In the last years modifications of the scratch test have been developed which are mainly designed for the micro range with forces up to 2N. Tips with a radius of typically 10 µm or smaller and precise displacement measurements with nanometer resolution allow a scan of the surface before and after the test with the scratch tip itself. These scans can give valuable information about the surface profile which influences the local stresses and about the remaining surface failures, especially the elastic – plastic transition. The measurement of the depth under load allows an estimation of the elastic and plastic deformation energy, introduced into the material, and allows often detecting the point of abrupt coating failure.

However, all these data are not sufficient to understand the reason of coating failures and their localization and to use this knowledge for the design of better coating systems. This requires a comprehensive analysis of the local stresses [2]. The elastic parameters of all layers and the substrate, the area function of the tip, the accurate lateral position of the tip in relation to the rough surface and the tilting moment of the shaft, holding the tip, have to be known for the calculation. It is further an improvement when not only the surface profile within the scratch track is considered but the full 3D surface topography in a certain range around the track.

Using a variety of coatings on different substrates such 3D stress analysis will be presented and it will be shown how it can be used for failure analysis.

[1] REMAST, A certified reference material for the scratch test, European project SMT3-CT98-2238, Final technical report, February 2002

[2] N. Schwarzer, Q.-H. Duong, N. Bierwisch, G. Favaro, M. Fuchs, P. Kempe, B. Widrig, J. Ramm, Optimization of the Scratch Test for Specific Coating Designs, Surface and Coatings Technology, volume 206, issue 6, year 2011, pp. 1327 - 1335

8:20am **E2-4-2 A New Dynamic Impact and Sliding Wear Testing Method for the Tribological Evaluation of Treated Surfaces**, ***P. Epaminonda***, *C. Rebholz (claus.rebholz@yahoo.com)*, University of Cyprus, Cyprus

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 of a new Dynamic Impact and Sliding Test (DIST) for the tribo-mechanical evaluation of surfaces under complex loading conditions is presented, where the surfaces are simultaneously subjected to sliding and impact loading. 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. Instruments and techniques for combined loading situations (such as the proposed DIST) offer a feasible way for fast, economical and reliable evaluation of complex tribo-systems with high practical and industrial interest. 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 characteristics of the DIST (e.g. combined impact and sliding 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) are described and discussed, and also the evaluation method of the expected results and possible limitations and difficulties.

8:40am **E2-4-3 Laser Shock Adhesion Test (LASAT) of EB-PVD TBCs: Towards an Industrial Application**, ***G. Bégué*** *(geoffrey.begue@mines-paristech.fr), V. Guipont, M. Jeandin*, Mines-ParisTech, France, *P. Bilhe, J.Y. Guédou*, Snecma, SAFRAN Group, France

The assessment of the adhesion strength of yttria (7%wt.)-stabilized (7YSZ) EB-PVD TBC is a key issue to better understand the life duration before spallation of coated turbine blades. Laser Shock Adhesion Test (LASAT) consists in focussing a pulsed nanosecond laser on the metallic side (MS) of a coated plate. Using different laser power densities permits to achieve different levels of tensile stress at the interface that could lead to the coating debonding. Two methods were previously developed to measure the interface strength on TBCs. First, adhesion threshold could be determined by LASAT-1D through the searching of a "LASAT threshold" that is the lowest laser energy to debond the coating. The LASAT-2D method consists in measuring the evolution of the interfacial crack diameter when increasing the laser power density. On TBCs the crack diameter is easily revealed by the presence of a white spot due to change of optical properties of the debonded ceramic. The conventional configuration to test TBC coupons by LASAT involves a laser shock applied on the metallic side (MS) with water as a confinement media. Unfortunately, in case of industrial turbine blades, the substrate cannot be reached by the laser beam. In this paper we introduce a new and fully original configuration (Snecma/Armines patent FR 1157284) by implementing the laser shock onto the ceramic side (CS). MS and CS LASAT-2D configurations are compared experimentally through the observation of the interfacial damaging and numerically by implementing the calculation of shock wave propagation for different substrate thicknesses. TBC as-coated plates (50×30×2 and 50×30×1 mm^3) of a nickel-based superalloy (AM1) with a (Ni,Pt)Al bond-coat and EB-PVD 7YSZ top-coat were used as samples. The CS configuration required a laser absorbing black tape and a transparent adhesive as confinement media to replace water (Fig. 1). The resulting shock wave that propagated through the TBC was monitored using photonic Doppler velocimetry (PDV) to calibrate the pressure profile. A similar change of optical properties was also obtained with CS-LASAT (Fig. 2). Laser-shocked interfaces were thoroughly observed and evolution of the interfacial crack diameter was studied (Fig. 3). This allowed introducing successfully the LASAT-2D applied to TBC involving the CS configuration. A numerical FEM Abaqus simulation considering the 2D propagation of the shock wave was implemented to calculate the temporal profile pressure and the maximum stress at the interface. In the near future, the LASAT-2D with CS configuration could be applied on turbine blades with TBCs to control the adhesion in a non destructive manner.

9:00am **E2-4-4 Self-organized Thin Film Buckling Patterns**, ***S. Grachev*** *(s.grachev@inbox.com), J.-Y. Faou*, Saint-Gobain Recherche, France, *G. Parry*, SIMaP, France, *E. Barthel*, Saint-Gobain Recherche, France

Thin films may spontaneously buckle under compression forming blisters of various shapes. When attached to a substrate, the buckling phenomenon is restricted by adhesion to the substrate. The interplay between the driving force to buckle and the counter-force of adhesion often results in formation of periodic patterns, as telephone-cord-like blisters. On one hand, the film buckling is described by the non-linear Föppl–von Kármán equations and has been well reproduced by finite element method (FEM) simulations. On the other hand, the delamination process involves the fracture of the interface under a mixed mode loading (both with normal and shear forces), which influences the energy needed to crack the interface, that is the interfacial toughness. Recently we have shown the importance of taking into account both these phenomena [Faou et.al., Phys.Rev.Lett. v.108, 2012]. In the current work we make a step further and study the critical conditions for the blisters to branch and to form periodic two-dimensional patterns. The parameters space was thoroughly studied by coupled buckling and mixed mode adhesion model FEM simulations. We show that the period of the blisters rather than their width is defined by the parameters of the system (stress, thickness, materials properties). The branching and the formation of patterns can occur in a certain area of the parameter space, and their period can be predicted. The results of simulations are confirmed by experimental observations of buckling of the sputter-deposited films. In particular, the self-organized hexagonal network was both simulated and observed experimentally with the period of the features of ~10 μm. We anticipate that such patterns can be scaled down to the nano-scale.

9:20am **E2-4-5 Determination of the Young´s Modulus of Hard Coatings on Soft Polymer Substrates**, ***T. Sander*** *(sander@mfk.uni-erlangen.de), S. Tremmel, S. Wartzack*, Friedrich-Alexander-University Erlangen-Nuremberg, Germany

The knowledge of the Young´s modulus for both, coating and substrate material is essential for an accurate numerical simulation or the calculation of stresses from measured displacements. While measuring the modulus of elasticity of the substrate material is state of the art, the determination for the coating is often difficult. Although several measurement methods for the elastic properties of coatings exist, the application on a compound of a polymer substrate and a hard coating is still a major challenge. The influence of the very soft polymeric substrate material on a nanoindentation of a thin hard layer is significant. Other measurement methods like tensile testing, resonance method or cantilever method require highly accurate sample geometries or lengthy preparations. The presented method uses both, experimental and numerical results. The indentation depth is measured by spherical indenters. Compared to a Berkovich or Vickers indenter the spherical indenters are less sensitive to the surface roughness and allow higher indentation loads without plastification or even coating failure. In addition to the experimental results, the test is simulated with FEM models and varying parameters such as coating thickness, Young´s modulus of substrate and coating, radius of the indenter or applied load. Knowing the coating thickness and the Young´s modulus of the substrate, the Young´s modulus of the coating can be determined by matching the indentation depth of the experimental measurements with the numerical results. The influence of the substrate is considered. In order to save time during the characterization of the coated samples, the parametric FEM simulations are carried out previously according to a statistically based sampling plan. After the experimental measurement, the results can be directly received from the data pool using a meta model (e.g. the response surface methodology). Time consuming subsequent simulations can be avoided. The results are shown for different polymeric substrate materials and thin hard coatings. However, the method can also be used for other substrate materials.

9:40am **E2-4-6 Nanoscale Mechanical Mapping at a Wide Range of Deformation Rates with AFM**, ***B. Pittenger*** *(bede.pittenger@bruker-nano.com), S. Minne, C. Su*, Bruker Nano Surfaces Division, US

Atomic force microscopes (AFM) can measure and map mechanical properties of materials with very high resolution. Over the years, the methods of mechanical mapping have evolved from slow force volume to multiple-frequency based dynamic measurements using TappingMode and contact resonance.

Recently, real-time control of the peak force of the tip-sample interaction has led to a fundamental change in AFM imaging, providing quantitative mapping of mechanical properties at unprecedented resolution. During material property mapping, the time scale of tip-sample interaction now spans from microseconds to seconds, tip sample forces can be controlled from piconewtons to micronewtons, and spatial resolution can reach sub-nanometer. AFM has become a unique mechanical measurement tool having large dynamic range (1kPa to 100GPa in modulus) with the flexibility to integrate with other physical property characterization techniques in versatile environments.

This presentation will review this recent progress, providing examples from a wide range of fields that demonstrate the dynamic range of the measurements, and the speed and resolution with which they were obtained. Additionally, the effect of time dependent material properties on the measurements will be explored.

10:00am **E2-4-7 The Effective Indenter Concept and its Extension into the Time Domain**, ***N. Bierwisch*** *(n.bierwisch@siomec.de)*, *N. Schwarzer*, Saxonian Institute of Surface Mechanics, Germany

It's well known that the theoretical basis of the standard analysis method for nanoindentation measurements, the Oliver & Pharr method [1], is the concept of the effective indenter. This concept was introduced by Bolshakov et al in 1995 [2]. Since then many papers have appeared demonstrating that it is not used only in analysing nanoindenation curves. It's applicable to more complex mechanical contact experiments on layered materials for normal and multi-axial loading conditions [3,4] too.

Within this work the concept will be applied to materials with time dependent behaviour, coated and microstructured systems. In addition its possible to determine correct generic material parameters like Young's modulus (time dependent if neccessary) and yield strength.

[1] W. C. Oliver, G. M. Pharr, J. Mat. Res. 7 (1992) 1564-1583.

[2] A. Bolshakov, W. C. Oliver, G. M. Pharr, MRS Symp. Proc 356, p 675 (1995)

[3] N. Schwarzer, Phil. Mag. 86 (33-35) 21 Nov – 11 Dec 2006, 5153 – 5767

[4] N. Schwarzer, J. Mater. Res., Vol. 24, No. 3, March 2009, 1032 - 1036

10:20am **E2-4-8 Determining Average Effective X-ray Elastic Constant (AEXEC) of Hard Coatings by Combining $\cos^2\alpha$ $\sin^2\psi$ X-ray Diffraction and Laser Curvature Methods**, ***A. Wang***, *G.P. Yu, J.H. Huang (jhhuang@ess.nthu.edu.tw)*, National Tsing Hua University, Taiwan, Republic of China

The X-ray elastic constants (XECs) are the major sources of experimental error in stress measurement for thin films and coatings. The selection of XEC is usually problematic and often leads to an undesirable error. To improve the accuracy in stress measurement, it is necessary to acquire reliable elastic constants. In this study, we proposed a new X-ray elastic constant for hard coatings named AEXEC (average effective X-ray elastic constant) that can be determined by combining $\cos^2\alpha\sin^2\psi$ X-ray diffraction and laser curvature methods. TiN hard coating on Si (100) substrate was selected as our model system, where the residual stress was determined by two techniques, namely, laser curvature technique using Stoney's equation and $\sin^2\psi$ XRD methods accompanying with AEXEC. Since the residual stress obtained by laser curvature technique (ORS) covers the entire thickness, ORS can be regard as the bulk average stress of the film. The elastic constant ($E/1+\nu$) can be calculated by substituting the ORS into the slope of strain vs. $\cos^2\alpha\sin^2\psi$ plot acquiring from grazing incident X-ray diffraction, where the corresponding penetration depth of X-ray must encompass the coating thickness. The effective elastic constant (EXEC), $E/1+\nu$, can be used for X-ray stress measurement without knowing the individual values of E and ν. However, the XECs are usually sampled from one specific diffraction direction with a few groups of grains, which may have statistical fluctuation at different rotational angles (Φ). The AEXEC (average effective X-ray elastic constant) is the average value of EXEC at several rotational angles, which can increase the sampling volume and reduce the statistical fluctuation. By comparing the AEXEC of TiN coating with different elastic constants, the AEXEC is comparable to the elastic constants determined from nanoindentation and $\sin^2\psi$ XRD method. Furthermore, applying AEXEC in the conventional $\sin^2\psi$ XRD stress measurement gave an acceptable deviation from ORS, ranging from 0% to 17%. The results indicated that AEXEC effectively reduced the statistical fluctuation in the stress measurements. Therefore, the proposed method provides a nondestructive technique to acquire reliable XECs in hard coatings, and the values are comparable to those determined by nanoindentation.

10:40am **E2-4-9 Fatigue Property Enhancements of Crystalline Metallic Substrates by Coating Thin Film Metallic Glasses**, ***C.H. Chang***, *J.P. Chu (jpchu@mail.ntust.edu.tw), C.M. Lee*, National Taiwan Univ. of Sci. and Tech., Taiwan, Republic of China

Zr-based thin film metallic glasses (TFMGs) are deposited on the crystalline metallic substrates by magnetron sputtering. Four-point-bending fatigue tests are conducted on those coated materials. It has been found that fatigue properties of materials can be considerably improved, and the enhancements varied with the maximum applied stresses. 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 TFMGs, are the major factors for the fatigue properties enhancements. The effects of TFMGs on fatigue properties of alloy substrates will be discussed.

11:00am **E2-4-10 Bending Ductility Enhancement of Bulk Metallic Glass by Surface Treatment s**, *J.P. Chu (jpchu@mail.ntust.edu.tw)*, ***C.C. Yu***, National Taiwan Univ. of Sci. and Tech., Taiwan, Republic of China

Bulk metallic glasses (BMGs) are normally fractured with very limited plastic strain at room temperature, severely restricting their application as engineering materials. Since deformation in BMGs is accommodated by shear bands and surface offsets, it is important to promote homogenous formation and propagation of shear bands in order to obtain measureable plastic strains.

In this study, artificial scratches are generated on tensile surface and then annealed by rapid thermal annealing below T_g, followed by magnetron sputter coating of a layer of thin-film metallic glass. The surface modifications result in increasing of bending plastic strain and more homogeneous shear band formed. The effects of surface treatments on the mechanism of shear band formation and multiplication as well as the bending plasticity will be discussed.

11:20am **E2-4-11 Crystal Orientation Effect on the Mechanical Behaviour of Al_2O_3 Coatings at Ambient Temperature**, *V. Bhakhri (v.bhakhri@imperial.ac.uk)*, Imperial College London - South Kensington Campus, UK, *R. Msaoubi*, Seco tools AB, *F. Giuliani*, Imperial College London - South Kensington Campus, UK, ***E. Bouzakis***, Fraunhofer Project Center for Coatings in Manufacturing (PCCM), Greece

Micro-pillar uni-axial compression testing provides a way to study the mechanical behaviour of materials in a much simpler stress state and plastic flow in individual slip system can be studied. This technique is employed to investigate in to the room-temperature plasticity of otherwise brittle 10mm thick Al_2O_3 coatings. Two different surface orientation coatings, (001) and (012), preferably oriented for Prismatic and Basal slips respectively, were deposited by chemical vapour deposition (CVD) technique on WC-Co cemented carbide substrates. Micro-pillars with approximate dimensions of 0.4mm in diameter and 1.5mm in height were fabricated with-in a single grain on these coating surfaces. These structures were then subjected to compression using a flat-punch indenter tip at a constant loading rate of 0.15mN/s. The estimated critical resolved shear-stress (CRSS) was found to be of the order of 11.5GPa for Basal slip and 4.0GPa for prismatic slip. These results are consistent with the data obtained by Lagerlof & Heuer [1] for these two slip orientations at elevated temperatures. Higher CRSS for Basal slip in Al_2O_3 is attributed to the splitting of a dislocation into two non-colinear partials separated by high-energy stacking faults. While, the dislocation structures in Prism slip were shown to dissociate into three collinear partials separated by low-energy stacking faults resulting in lower CRSS. (1) K.P.D. Lagerlog & A.H. Heuer; J. Amer. Ceram. Soc. 77[2]: 385-97 (1994).

New Horizons in Coatings and Thin Films
Room: Sunrise - Session F4-1

New Oxynitride Coatings
Moderator: W. Kalss, OC Oerlikon Balzers AG, Liechtenstein, S. Ulrich, Karlsruhe Institute of Technology

8:00am **F4-1-1 Oxynitride Coatings by Reactive Arc Evaporation**, ***D. Kurapov*** *(denis.kurapov@oerlikon.com)*, OC Oerlikon Balzers AG, Liechtenstein **INVITED**

The oxygen containing coatings are well established products on the cutting tools market. Recently, commercially available PVD oxide coatings have been developed. In spite of growing importance of oxide containing wear protective coatings, there is only minor information available about their growth mechanism as well as their properties and cutting performance.

This paper gives an overview about the progress in the development of oxygen containing coatings using industrial scale PVD equipment. The advantages and the flexibility of the reactive arc evaporation for the coatings design are emphasized.

The deposition experiments were performed in a cathodic arc production system. The target composition was changed in order to influence the chemical composition of the coatings. Different coating stoichiometry was obtained through the variation of oxygen flow, while keeping nitrogen pressure constant. The correlation between the coating stoichiometry, phase formation and coating properties is presented. Finally examples for application of the oxyntiride coatings are given.

8:40am **F4-1-3 Nitride and Oxy-Nitride Coatings for Application on Injection Moulding Tools**, ***N. Bagcivan*** *(bagcivan@iot.rwth-aachen.de)*, *K. Bobzin*, Surface Engineering Institute - RWTH Aachen University, Germany, *C. Hopmann*, Institute of Plastics Processing - RWTH Aachen University, Germany, *R.H. Brugnara*, Surface Engineering Institute - RWTH Aachen University, Germany

Injection and extrusion moulding is used to produce plastic parts for a wide variety of applications. In 2006 nearly 245,000 kt of plastics products were produced by means of extrusion and injection moulding. Due to rapidly increasing demands on individualized products, higher process stability and lower amounts of rejects new material concepts have to be developed. Especially, production of high precision lenses leads to high requirements for the production process. Every source of defects while processing has to be eliminated. For processing transparent polymers injection molding machines are most commonly used. While processing optical polymers like polycarbonate (PC) and polyether sulfone (PES) defects are produced by the plasticizing unit. Therefore, coatings for injection molding machines were developed by physical vapor deposition (PVD) in order to reduce the polymer defects as well as to protect the coated toll against wear and corrosion. All investigations were carried out on plasma nitrided ASTM A355 (X34CrAlNi7, 1.8550). TiN, (Ti,Al)N, (Ti,Al)ON, CrN, (Cr,Al)N and (Cr,Al)ON were deposited with Arc PVD. For all coatings a good adhesion to the substrate could be achieved. The adhesion affinity of the polymers to the coating surface was measured using high temperature contact angle measurements. With the PVD-coating (Cr,Al)ON the lowest adhesion of the polymers to the surface was achieved. This coating was applied on screw tips and tested in injection moulding experiments at different process parameters. After the tests, the produced parts were investigated regarding the defects on the polymer surface. The application of (Cr,Al)ON on the tools leads to reduction of defects on the polymer surface. The analysis of the coated parts showed that the tools could be cleaned much easier from the polymers after the experiments without delamination of the coating, so that the reduced adhesion was also confirmed in field tests.

9:00am **F4-1-4 Effects of Si and Y in Structural Development of (Al,Cr,Si/Y)O_xN_{1-x} Thin Films Deposited by Magnetron Sputtering**, ***H. Najafi*** *(hossein.najafi@epfl.ch)*, *A. Karimi*, *D. Alexander*, Ecole Polytechnique Fédérale de Lausanne, Switzerland, *P. Dessarzin*, *M. Morstein*, PLATIT AG, Switzerland

Silicon (Si) and Yttrium (Y) are believed to have a strong influence on functional properties of hard thin films due to their effects in the growth process and incorporation in solid solution phases. It is worthwhile noting that even very low concentrations of these elements may be active for controlling structural evolution during the growth. The aim of this work is to systematically study the microstructural development and mechanical properties of (Al,Cr,Si/Y)O_xN_{1-x}oxynitride films as a function of Si and Y contents. Our results show that Si and Y have a different mechanism for incorporation into the oxynitride films. According to the TEM, XRD, and XPS results, substitutional role of yttrium is suggested for investigated coatings, whereas silicon tends to form an amorphous glassy phase. Such oxynitride layers meet an enhanced phase stability by the incorporation of both silicon and yttrium. As a result, nitride growth regime is extended in the range of $O/(O+N) \leq 0.80$ with cubic (B1)-structured (Al,Cr,Si/Y)O_xN_{1-x}. However, on the other hand, Si and Y hinder the formation of corundum phase α-$(Al,Cr,Si/Y)_{2+\delta}(O_x,N_{1-x})_3$ in the predominant oxide regime ($O/(O+N) \geq 0.98$) suggesting retarded diffusional processes with the presence of such minor alloying elements in the deposition flux. Additionally, the Y-containing oxynitrides demonstrate a greater nano-hardness for all growth regimes.

9:20am **F4-1-5 Two-phase Single Layer Al-O-N Nanocomposite Films with Enhanced Resistance to Cracking**, ***R. Jilek***, *J. Musil (musil@kfy.zcu.cz)*, *T. Tolg*, *R. Cerstvy*, University of West Bohemia, Czech Republic

The article reports on dc pulsed reactive sputtering of *two-phase single layer* Al-O-N nanocomposite films using dual magnetron in a mixture of N_2 + O_2 with pulsed inlet of oxygen. Two kinds nanocomposite films were sputtered: (1) nc-AlN/a-(Al-O-N) and (2) nc- (γ-Al_2O_3)/a-(Al-O-N) nanocomposite films; here nc- and a- denotes the nanocrystalline and amorphous phase, respectively. The transition from the nc-AlN/a-(Al-O-N) nanocomposite to the nc-(γ-Al_2O_3)/a-(Al-O-N) nanocomposite was controlled by the length of the period of oxygen pulses T_{O2}. It was found that both nanocomposites are highly elastic films with relatively high hardness H = 15 to 20 GPa, low effective Young's modulus E^* satisfying the condition that the ratio $H/E^* > 0.1$, high elastic recovery $W_e > 60$ % and high resistance to cracking in bending. Correlations between the film structure and its mechanical properties are discussed in detail.

9:40am **F4-1-6 Phase Formation of TiAlNO Thin Films**, ***M. to Baben*** *(to_baben@mch.rwth-aachen.de)*, *F. Kruschewski*, *M. Hans*, *J. Schneider*, RWTH Aachen University, Germany

In literature, studies on phase formation of transition metal oxynitrides are rare. It has been proposed that the defect structure is important for NaCl structured CrAlSiNO and CrAlNO [1-4] and TiAlNO [5, 6]. While the formation of metal vacancies is commonly accepted for CrAlNO, it is not clear what defects occur in TiAlNO and if the properties are influenced.

Here, we study phase formation of TiAlNO by high power impulse magnetron sputtering in an industrial deposition system. With a N_2:O_2 flow ratio of 15:1, NaCl structured TiAlNO is detected with a (200) fibre texture exhibiting a lattice spacing of d_{002} = 2.138 Å, which corresponds to a 0.4 % larger lattice spacing than TiAlN deposited under the same conditions, without intentional oxygen addition. The cause for the lattice spacing expansion will be discussed. Additionally, the influence of N_2:O_2 flow ratio on phase formation will be presented.

[1] Karimi A, Morstein M, Cselle T. Surf. Coat. Technol. 2010;204:2716.

[2] Najafi H, Karimi A, Dessarzin P, Morstein M. Thin Solid Films 2011;520:1597.

[3] Stueber M, Diechle D, Leiste H, Ulrich S. Thin Solid Films 2011;519:4025.

[4] Khatibi A, Sjölen J, Greczynski G, Jensen J, Eklund P, Hultman L. Acta Mater. 2012;in press.

[5] Sjölen J, Karlsson L, Braun S, Murdey R, Hörling A, Hultman L. Surface and Coatings Technology 2007;201:6392.

[6] to Baben M, Raumann L, Schneider JM. Journal of Physics D-Applied Physics 2012;accepted.

10:00am **F4-1-7 Thermodynamic Modeling in the Materials System Ti-Al-O-N**, ***H.J. Seifert*** *(hans.seifert@kit.edu)*, Karlsruhe Institute of Technology, Germany

Thermodynamic modeling and calculations using CALPHAD methods (computer coupling of phase diagrams and thermochemistry) support the understanding of engineering materials and corresponding coatings formation. A key task in this approach is the modeling of stable and metastable solid solution phases under varying physico-chemical conditions by taking into account their crystal chemistry and amorphous states, respectively. Sublattice models expressed in the so-called compound energy formalism can be used to develop analytical descriptions for the Gibbs free energies of individual phases. Experimentally determined phase diagrams and thermochemical data such as enthalpies of formation, heat capacities and chemical potentials are key input data for the development of the descriptions for all system phases. Based on these data, multicomponent multiphase calculations for different thermodynamic conditions can be performed by extrapolations. Examples for modeling and calculations will be presented for binary and ternary subsystems in the quaternary materials system Ti-Al-O-N. The binary subsystem Ti-Al is of metallic nature, the other systems are of ceramic (Ti-O, Ti-N, Al-O, Al-N) and "gaseous" (O-N) nature, respectively. One of the challenges in modeling is the selection of suitable phase descriptions, reference states and compatibility approaches to combine such different types of systems. It turns out that also the ternary subsystems (Ti-Al-O, Ti-Al-N, Ti-O-N, Al-O-N) have to be treated by advanced solution modeling to cover extended homogeneity phase ranges including order-disorder and metastable states. The state-of-the-art for thermodynamic calculations of metastable states in this system will be especially discussed.

10:20am **F4-1-8 Design of Thermal Conductivity of Hard Oxynitride Coatings**, ***M. Böttger*** *(phmb@mat.ethz.ch)*, *V. Shklover*, ETH Zurich, Department of Materials, Switzerland, *E. Lewin*, *J. Patscheider*, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland, *D. Cahill*, University of Illinois at Urbana-Champaign, US, *M. Sobiech*, OC Oerlikon Balzers AG, Liechtenstein

With the development of new alloys for the aerospace and energy industries, such as Ni- and Ti-based superalloys, comes the need for new high heat resistant tool coatings which are able to ensure process productivity during machining of these difficult-to-cut materials. Hardness, oxidation resistance and thermal stability are important optimization parameters for tool coatings operating at high temperatures. Moreover, in the case of machining difficult-to-cut materials, the design of thermal conductivity of the hard tool coating is also of particular significance.

Against the above background this talk will discuss the interrelations between microstructure, thermal conductivity and cutting performance of coatings in machining operation by cutting with defined cutting edge. Time-domain thermoreflectance measurements of thermal conductivity in arc-evaporated Ti-O-N and Cr-O-N coatings are presented, where thermal conductivity could be adjusted in a wide range (2 to 35 W/m·K) while

keeping mechanical and oxidation performance unchanged. The obtained results fit a newly developed model based on constant phonon scattering cross section of the introduced oxygen. On this basis it will be discussed how to use the knowledge about thermal conductivity in order to create high-performance coatings for machining of difficult-to-cut materials.

10:40am **F4-1-9 Oxides, Nitrides and Oxinitrides of Silicon on Non-silicon Substrates with Tailored Mechanical, Optical, Electrical and Chemical Properties**, ***U. Beck*** *(uwe.beck@bam.de), A. Hertwig, M. Griepentrog, M. Weise*, BAM Berlin, Germany

Silicon oxide on silicon as electrical insulator in microelectronics was probably the first really nano-scaled thin film system manufactured on an industrial scale. This dates back almost 50 years. However, there are plenty of applications beyond microelectronics where silicon oxides, nitrides and oxinitrides meet manifold requirements on very different substrate materials rather than silicon.

These applications cover mechanical, optical, electrical and chemical functionalities such as plasto-elastic properties, interfacial stress and adhesion, wear and tribological properties, refractive index and extinction coefficient, reflectivity and transmissivity, breakdown voltage and leakage current, corrosion protection and barrier features, wet and plasma etching behaviour as well as and environmental durability. Typical substrate materials for these applications are glass, ceramics, polymers, metals and steel.

In particular by means of PVD- and CVD-processes, both the stoichiometric silicon oxide (SiO_2) and the silicon nitride (Si_3N_4) can be deposited by fully reactive processes. For the majority of applications, it is very beneficial that almost all of the silicon oxinitrides (SiO_xN_y) can deposited within the same deposition chamber and with the same technology in a sufficiently stable way by partially bi-reactive processes. In principle, this allows a property tailoring from the pure oxide to the pure nitride mode with almost any intermediate state in between.

In addition to a short overview regarding the possible property range of mechanical, optical, electrical and chemical quantities, at least one application example of each major field of application is discussed in more detail. The interdependence of process characteristics, film properties and functional features is demonstrated. It has been shown that various plasma processes even at lower temperatures are available to meet the needs of advanced surface finishing. Moreover, vacuum-based plasma-processes provide cheap cleanroom-like conditions even under robust industrial environments.

11:00am **F4-1-10 The Consequence of Different Sputtering Parameters on Optical, Wettability and Structural Characterization of Chromium Oxynitride Thin films**, *S. Rawal (sushant2713@gmail.com),* Indian Institute of Technology Roorkee and Charotar Univ. of Science and Tech., India, *A. Chawla,* University of Petroleum and Energy Studies, India, *R. Jayaganthan,* Indian Institute of Technology Roorkee and Indian Institute of Technology, India, ***A. Joshi***, G.H. Patel College of Engineering & Technology, India, *R. Chandra*, Indian Institute of Technology Roorkee, India

In the current paper we have studied effect of different sputtering parameters such as nitrogen flow rate, deposition time and sputtering pressure on chromium oxynitride films. The X-ray diffraction studies show presence of Cr_2O_3 and Cr_2N phases with various textures depending upon the sputtering parameters. The stress are compressive and maximum stress (-4.5GPa) is observed for films deposited at 70sccm of nitrogen flow rate, the compressive stress (-0.2 to -5.3GPa) increases with deposition time but the stress is tensile (0.5 to 3.6GPa) and increases with sputtering pressure. The maximum contact angles observed are 102° for 70sccm nitrogen flow rate, 108.7° for deposition time of 140 minutes and 97.4° at sputtering pressure of 6Pa. The chromium oxynitride films are hydrophobic and can have potential applications as water repellent surfaces for self cleaning purpose. The transmission and absorption curves of chromium oxynitride films were recorded by UV-Vis-NIR spectrophotometer. The band gap of deposited chromium oxynitride films decreases with increase in nitrogen flow rate, deposition time while it increases with sputtering pressure.

Keywords: Chromium oxynitride, Sputtering, X-ray diffraction, Optical properties, Wettability

Applications, Manufacturing, and Equipment
Room: California - Session G6-1

Advances in Industrial PVD & CVD Deposition Equipment

Moderator: N. Bagcivan, RWTH Aachen University, Germany, M. Schuisky, Sandvik Machining Solutions

8:40am **G6-1-3 Recent Developments in Pulsed I-PVD Technology for Sputtering Thin Films of Oxides, Nitrides and DLC for Tribological, Optical, Electrical and other Applications**, ***R. Chistyakov*** *(rchistyakov@zpulser.com),* Zpulser LLC, US **INVITED**

Magnetron sputtering technology is widely used for the deposition of thin films for different applications. Thin films can be metals, non-metals (carbon), metal nitrides, metal oxides or their combinations. The properties of the sputtered films depend on magnetron plasma density during the deposition process. In conventional magnetron sputtering the target power density during the deposition process is in the range of 10-50 W/cm2 that gives low plasma density and therefore small fractions of the ions.

In 1995 -1999 a new way of magnetron sputtering was introduced. It was HIPIMS (high power impulse magnetron sputtering). The main idea of this approach is to apply short (~ 50-100 µs) high power pulses with target power density during the pulse around 1-3 kW/cm2. High power pulses generate high density magnetron plasma with high fraction of ions that allows significantly improve and control properties of the films for tribological, optical, electrical or other applications. Significant effort in terms of hardware (high power pulse plasma generators) design, plasma research of pulsed magnetron discharge and pulsed thin film deposition was applied during the last 15-20 years in order to bring this technology to a commercial level. Still there is a problem for HIPIMS reactive sputtering to generate a stable arc free (or near arc free) magnetron discharge particular for deposition of non-conductive films. The arc appears due to formation of the insulating layer on the target surface due to re-deposition. There are different ways to control arcs during the reactive HIPIMS process that depend on HIPIMS plasma generator design and capabilities.

The biggest applications of pulsed I-PVD technology could be directional sputtering processes to deposit metal (oxides, nitrides) into different sized high aspect ratio features (trenches, vias and etc.) for integrated circuit fabrication. For this application control of the ratio of neutral sputtered atoms to metal ions is very important.

The influence of the voltage pulse shape, duration and frequency generated by HIPIMS plasma generator on the process stability and properties of thin films for tribological, optical, electrical, semiconductor and other applications will be discussed

9:20am **G6-1-5 Optical Emission Spectroscopy of HiPIMS Coatings at Industrial Scale**, ***R. Cremer***, *T. Takahashi (takahashi@kcs-europe.de),* KCS Europe GmbH, Germany, *S. Hirota*, Kobe Steel Ltd., Japan

We have developed a sputtering process at industrial scale based on High Power Impulse Magnetron Sputtering (HiPIMS). In contrast to a conventional DC magnetron sputtering, the HiPIMS process provides a higher degree of sputtered metal species, enabling the deposition of dense hard coatings with superior mechanical properties. The better understating of the plasma properties and the comparison thereof with other deposition techniques, e.g. DC-sputtering and arc ion plating, contribute towards the optimization and the further improvement of the process.

In this work, different types of nitride coatings including TiN and TiAlN were deposited by our industrial HiPIMS-based technique, and the plasma characteristics were analyzed using Optical Emission Spectroscopy (OES). A high degree of metal ionization was clearly confirmed by the OES. The relative intensity of Ti-ion to neutral is increased as the peak discharge current is increased. The degree of ionization in the HiPIMS can be achieved even to a level of those of arc ion plating. Our HiPIMS-based process provides an opportunity to vary the plasma properties ranging from the less ionized DC-like plasma up to the highly ionized arc-like plasma depending on applications. The results of the OES measurements were also correlated with the resulting coating properties.

9:40am **G6-1-6 Advances in Process Technology and Deposition Equipment for HiPIMS Coatings for Cutting Tools**, ***C. Schiffers***, *T. Leyendecker (toni.leyendecker@cemecon.de), O. Lemmer, W. Kölker*, CemeCon AG, Germany

HiPIMS is characterised by short power pulses with an extremely short signal rise time. The design of the coating equipment need to take this characteristic into account with regard to feeding the electrical energy into the sputtering cathodes and finally into the plasma. This paper will present

recent results on the correlation of the hardware design of the machine and the coating process. Fundamental research about the efficiency of the pulse transfer and about methods to transmit an undistorted pulse shape and wave form into the process was done.

The end user of a cutting tool sets its focus to the properties of the coating and, most important, to the machining characteristics of the film. Examples and field data will show how the most up-to-date HiPIMS coatings boost both productivity and quality.

SEM images reveal a dense morphology of HiPIMS coatings. To this feature can be attributed that HiPIMS films combine high hardness and a relatively low Young's modulus indicating a high coating toughness in a way most favourable for metal cutting.

Super smooth coatings, free from any droplets, and low compressive stress are the most beneficial characteristics of sputter coatings for cutting tools. The effective bombardment of the growing film with highly ionized species further improves the surface of HiPIMS coatings.

10:00am **G6-1-7 QuadCoatings$^{4®}$, a New Generation of PVD Coatings for High-Performance Cutting Applications**, ***A. Luemkemann***, *M. Morstein (m.morstein@platit.com), P. Dessarzin, T. Cselle*, PLATIT AG, Switzerland, *B. Torp*, PLATIT Inc., US, *M. Jilek jr.*, PLATIT Pivot a.s., Czech Republic

This contribution introduces a new generation of Physical Vapor Deposition (PVD) coatings, deposited by cylindrical rotating arc cathodes technology. Based on the TripleCoatings$^{3®}$ concept widely used for cutting tools since its introduction in 2007, the new QuadCoatings$^{4®}$ combine the advantages of both conventional and nanocomposite high-performance coatings, using a novel unified architecture containing at least four coating zones.

The new high tech industrial coatings are applicable for a wide range of high-performance cutting tools dedicated to particular applications, yet provide an unmatched performance even in in difficult-to-cut materials.

Using the new high-power coating unit π^{411}, QuadCoatings$^{4®}$ can be produced quickly and economically even for small batches. One of the unit's main advantages is the ability to produce QuadCoatings$^{4®}$ at a high degree of productivity running all of the unit's four cyclindrical rotating arc cathodes at the same time. In a configuration using preferentially pure metallic LARC®- and CERC®- targets, adjustments in coating architecture within the four layer zones, such as microstructure or stoichiometry, can easily be realized through the user-friendly π^{411} software interface. In adition, a superior coating adhesion is reached by combining the tube and virtual shutters to form the new LARC-GD® option. This technology provides a very efficient plasma etching before coating starts, even on highly three-dimensional tool geometries.

Applications of several members of the new concept coating family will be presented, ranging from productive general milling to high-performance gear cutting, which was optimized using fast feedback from a model fly cutting test. Another case study will show how tool productivity can be increased by a dedicated QuadCoating$^{4®}$ with carbon-containing top layer, successfully used for thread forming and tapping.

10:20am **G6-1-8 About the Novel HI3 Deposition Technique**, ***O. Jarry*** *(olivier.jarry@sulzer.com), G. Erkens, J. Vetter, J. Mueller, T. Krienke*, Sulzer Metaplas, Germany

Manufacturers and end users are constantly confronted with complex problems that require more than a standard solution. Using novel technologies and processes, unique and dedicated solutions for current and future challenges can be provided. One novel holistic approach to tailored solutions is the use of the HI3 (High Ionization Triple) PVD process technology. HI3 combines several processes for the generation of layer-forming particles in a single coating system. HI3, the combination of HIPAC (High-Ionization Plasma Assisted Coating) sputtering technology, APA-Arc technique (Advanced Plasma Assisted) and AEGD (Arc Enhanced Glow Discharge) represents a hybrid holistic approach to fascinating new coating designs and architectures. The present work will highlight the HI3 deposition technique to apply novel and tailored micro alloyed hybrid coatings. Such coatings were analyzed by SEM, EDX, nano-indentation hardness measurement and tribological tests were performed. Oxidation tests were carried out at elevated temperatures. The HI3 films illustrate the technical potential for those applications where high thermal stability, high oxidation resistance and low friction are pre-dominant requests.

10:40am **G6-1-9 New Arc Evaporation Technology CARC^{+}: High Performance Coatings Deposited at High Deposition Speeds**, ***M. Eerden*** *(meerden@hauzer.nl), F. Papa, D. Derckx, T. Krug*, Hauzer Techno Coating, BV, Netherlands

Hauzer's new arc evaporation technology CARC^{+} offers the advantage of producing smooth, high-performance arc coatings at very high deposition rates, leading to low coating costs. The new technology combines speed and performance while keeping the flexibility, known for Hauzer systems. Moreover, the technology has been designed with easy maintenance and robustness as one of the most important design criteria. Target lifetime has been improved to further reduce the coating costs. Data for deposition rates, coating characteristics and cutting performance will be shown as well as cost-of-ownership considerations.

11:00am **G6-1-10 The LAM Family – Tools for Production of ta-C Coatings with Excellent Properties**, ***M. Falz*** *(michael.falz@vtd.de), M. Holzherr, K.-D. Steinborn, T. Schmidt*, VTD Vakuumtechnik Dresden GmbH, Germany, *H.-J. Scheibe, A. Leson, V. Weihnacht*, Fraunhofer-Institut für Werkstoff- und Strahltechnik, IWS Dresden, Germany

Hydrogen-free amorphous carbon coatings are characterized by the potential of extreme high hardness in combination with low friction coefficients of less than 0.1. Laser-controlled pulsed arc evaporation has been proven as a suitable technique for stable deposition of such ta-C films at high deposition rates. This technique was realized in the Laser-Arc Module (LAM) concept as an external evaporation source for industrial coating machines. Several LAM sources were developed for different deposition hights: LAM 400, 500 and 850. They were optimized for the production of exceptional ta-C films under industrial conditions. These modules operate with Nd-YAG laser, pulsed power supplies and an automatic control system. Arc pulse currents up to 1600 A and pulse frequencies up to 300 Hz allow deposition rates of 2 µm/h and more in double rotation can be obtained. The combination of the LAM sources with a new developed filtering system reduces the rate only by about 40 % and allows coating at industrial acceptable deposition rates. Film properties of such coatings on real components and the influence of the coating parameters will be shown and discussed.

Topical Symposia
Room: Royal Palm 1-3 - Session TS2-1

Advanced Characterization of Coatings and Thin Films

Moderator: S. Korte, University of Erlangen-Nürnberg, Germany, M. Sebastiani, University of Rome "Roma Tre", F. Giuliani, Imperial College London - South Kensington Campus, UK

8:00am **TS2-1-1 Correlative Analysis of Phase and Microstructural Evolution of Rapidly Solidified Metallic Multilayers by Transmission Electron Microscopy and Atom Probe Tomography**, ***P. Leibenguth*** *(p.leibenguth@matsci.uni-sb.de), I. Schramm, F. Mücklich*, Saarland University and Materials Engineering Center Saarland, Germany

Understanding the processes taking place at the interfaces of heat treated multilayered thin films requires high spatially resolved information on local chemical composition and phases present. By this, the explanation of the microstructural modifications resulting from the treatment can be facilitated. Especially the combination of structural and compositional data on the submicron and nano-scale can yield valuable insights. To this end, correlating selected area diffraction in a transmission electron microscope (TEM) and near-atomically resolved atom probe tomography (APT) is a powerful approach for such examinations.

Our study is focused on demonstrating the benefits of the combined use of these complementary techniques in elucidating the microstructural modification of binary metallic multilayers induced by ns-pulsed-laser treatment (Laser Interference Metallurgy). As material combination, technically and thermodynamically well-known binary systems, namely Ni/Al, Ti/Al and Ni/Ti were chosen.

Depending on substrate material and local stoichiometry in the heat affected zones, different crystalline and amorphous metastable phases were formed and could be kept frozen-in to room temperature. Even long-range ordered intermetallics were observed, which is in accordance with literature on pulsed-laser induced rapid solidification and partitionless transformations from the melt. The combination of site-specific crystallographic analyses by TEM and compositional data gained by APT with finite element based thermal simulations proved useful in clarifying the processes of phase selection and microstructure formation during the pulsed laser processing of multilayered thin films.

8:20am **TS2-1-2 *In situ* Transmission Electron Microscopy Studies of Metal Diffusion on Ceramic Coatings**, *I. Jouanny, C. Ngo,* University of California, Los Angeles, US, *J. Palisaitis,* Linköping University, Sweden, *P.H. Mayrhofer,* Vienna University of Technology, Austria, *L. Hultman, P. Persson,* Linköping University, Sweden, ***S. Kodambaka*** *(kodambaka@ucla.edu),* University of California, Los Angeles, US

Using *in situ* transmission electron microscopy (TEM), we investigated the diffusion kinetics of metals on ceramic coatings. All our experiments were carried out in 200 kV CM20 and 300 kV Titan^3 TEMs using sputter-deposited polycrystalline, 50-nm-thick, ZrB_2 films on Al_2O_3(0001). A cross-sectional TEM sample was prepared via focused ion beam (FIB) milling using Ga ions. In this process, an amorphous carbon film is first deposited on the ZrB_2 surface to serve as a protective layer and the sample is attached to a molybdenum TEM grid by depositing Pt at one end of the sample. During annealing at temperatures < 500 ^{o}C, we observed the formation and Ostwald ripening of liquid Ga droplets, formed due to the FIB, on the surface of carbon layer. From the measured rates of coarsening/decay of Ga droplets, we determine that surface diffusion is the rate-limiting mechanism. At temperatures > 800 ^{o}C, we observed a diffusion front moving unidirectionally along the ZrB_2 film from the end attached to the TEM grid. Using energy dispersive spectroscopy, we identify the diffusing material to be a $Pt_{0.95}Mo_{0.05}$ alloy, presumably formed due to the intermixing of the FIB-deposited Pt and the Mo from the TEM grid. We followed the diffusion of this alloy front as a function of annealing time and temperature. From the measured rates of diffusion as a function of temperature, we extract an activation barrier of 3.8±0.5 eV.

8:40am **TS2-1-3 Advanced Transmission Electron Microscopy Methods: Going beyond Imaging**, ***C. Scheu*** *(christina.scheu@cup.lmu.de),* LMU Munich, Germany **INVITED**

Advanced transmission electron microscopy (TEM) is a powerful tool to investigate thin films and coatings where the grain size, type of phases present and their spatial distribution play an important role and where the constituents often possess nanometer dimensions. In addition, such nanostructured materials possess numerous interfaces which determine the functionality and which require atomic scale characterization.

High-resolution TEM (HRTEM) and so called Z-contrast images (Z stands for the atomic number) using a scanning TEM (STEM) allow to study the atomic structure of nanometer-sized grains and interfaces and these are well established methods in thin film and nanostructured materials analysis. However, besides the atomic arrangement, the chemical composition of individual nanometer-sized grains and interfaces is of great interest and this can be studied by analytical TEM measurements such as energy dispersive X-ray spectroscopy (EDX) and electron energy-loss spectroscopy (EELS). In addition to the chemical composition, EELS measurements can also be used to determine optical properties and to get insight into the electronic structure down to the nanometer regime or even below. These information are obtained by analyzing the spectral features occurring in the low-loss region (up to energy-losses of around 50 eV) or with the help of the element-specific ionization edges which are found in the core-loss region (above 50 eV). To investigate locally the optical properties such as the dielectric function or the band gap, a high energy resolution is required in the low loss region which can be realized by using a monochromator or advanced deconvolution methods. The ionization edges in the core-loss EELS region can be used to determine both, the chemical composition and the electronic structure of interfaces and nanostructures. This latter information is obtained by analyzing the electron energy-loss near-edge structure which is associated with each element-specific edge and which contains information on e.g. bonding characteristics and nominal oxidation states of the probed atoms. The data can be interpreted applying a fingerprint method or by performing ab-inito calculations.

In this talk, examples for the different techniques will be presented and discussed, which show that advanced TEM studies can provided information beyond imaging.

9:20am **TS2-1-5 *In Situ* Transmission Electron Microscopy Studies of Thermochemical Stability of TiO_2/C Core/Shell Nanocrystals**, ***I. Jouanny*** *(isabellejouanny@ucla.edu), S. Kodambaka*, University of California, Los Angeles, US

We studied the thermal stability and the effect of electron beam irradiation during annealing of TiO_2/C core/shell nanocrystals up to 900 °C by *in situ* transmission electron microscopy (TEM). All of our experiments were carried out in a FEI Titan 300 kV S/TEM using rutile-structured TiO_2 nanocrystals encapsulated in 5-10 nm thick carbon shells. Upon heating, we observed several interesting phenomena. At temperatures above 600 °C, we find that the carbon shells become more graphitic; the graphene layers become highly-ordered and appear to align along the surface facets of the TiO_2 cores. The shape and size of the TiO_2 cores change with increasing time and temperature. At temperatures above 800° C, we observed the formation of hollow core graphitic shells due to the disappearance of the TiO_2 particles. Our observations indicate that the core/shell structure and composition are sensitive to electron beam dose and annealing temperature. In our experiments, electron irradiation at doses above 10^5 A/m^2 induce damage in the core/shell particles at room temperature. At temperatures above 600 °C, 10^5 A/m^2 dosage leads to hollow core formation. At doses > $1.15.10^6$ A/m^2, carbon shells reconfigure into onion structures, consistent with previous reports.

9:40am **TS2-1-6 Evaluation of Laboratory and Synchrotron Nanobeam X-Ray Diffraction Methods for the Characterization of Residual Stress Gradients in Hard Coatings**, ***M. Stefenelli*** *(mario.stefenelli@mcl.at),* Materials Center Leoben Forschung GmbH, Austria, *R. Daniel,* Montanuniversität Leoben, Austria, *A. Riedl,* Materials Center Leoben Forschung GmbH, Austria, *M. Bartosik,* Montanuniversität Leoben, Austria, *M. Burghammer,* European Synchrotron Radiation Facility, France, *C. Mitterer, J. Keckes,* Montanuniversität Leoben, Austria

Nanocrystalline hard coatings usually exhibit pronounced depth gradients of microstructure and residual stress which decisively predefine their function and properties. The residual stress gradients are routinely evaluated using laboratory X-ray diffraction techniques in reflection geometry utilizing varying penetration depths of the X-ray beam, thus generating a stress profile in Laplace space. Inverse Laplace transformation is applied to refine unknown strain profiles in real space. Recently, however, a new synchrotron approach of stress gradient characterization based on cross-sectional synchrotron X-ray nanobeam diffraction was proposed [1]. The new approach allows the stress characterization directly in the real space. In this contribution, both laboratory and the new synchrotron approaches are evaluated when analysing monotonous and non-monotonous residual stress depth gradients in representative hard coatings based on TiN and CrN. The results reveal that the approaches based on the Laplace transformation are limited to a relatively simple stress depth profiles. On the other hand, the X-ray nanobeam approach provides excellent resolution even for very complex stress profiles, but is connected with more experimental effort and sophisticated data treatment.

[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 Mat. 67 (2012) 748.

10:00am **TS2-1-7 Cross-Sectional X-ray Nanodiffraction on a Graded Multiphase Cr-N Thin Film**, ***M. Bartosik*** *(matthias.bartosik@tuwien.ac.at),* Christian Doppler Laboratory for Application Oriented Coating Development at Montanuniversitat Leoben and Vienna University of Technology, Austria, *J. Keckes, R. Daniel, C. Mitterer,* Montanuniversität Leoben, Austria, *M. Burghammer,* European Synchrotron Radiation Facility, France, *L. Zhou,* Vienna University of Technology and Montanuniversität Leoben, Austria, *D. Holec,* Montanuniversität Leoben, Austria, *P.H. Mayrhofer,* Vienna University of Technology, Austria

Wide angle X-ray nanodiffraction performed along the cross-section of nano-crystalline thin films allows for in-depth characterization of microstructure and residual strain with submicron resolution along the film-growth direction [1]. The position-resolved analysis is performed using synchrotron X-ray nanobeams with diameters focused down to 100 nm.

Here, we demonstrate that the nanodiffraction approach opens the possibility to analyze not only single-phase but also complex multiphase coatings with gradients in phases, microstructure and strain at the sub-micron scale along the growth direction when using cross-sectional investigations. The new position resolved technique [1] allows for a simultaneous evaluation of depth gradients of X-ray elastic strain, lattice parameters, microstructure and phases as performed and demonstrated on 6 µm thick Cr-N films consisting of hexagonal Cr_2N and nonstoichiometric cubic CrN_x. The studies are furthermore corroborated by ab inito investigations. Cross-section transmission and scanning electron microscopy were additionally applied for comparison and complementation of the results obtained from the nanodiffraction experiments. The results reveal how growth conditions and chemical composition correlate with structural gradients. The new approach represents a significant step forward in depth-resolved microstructural characterization of thin films.

[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 (2012) 748.

10:20am **TS2-1-8 Smart Approach of Surface Characterizations of Engineered Diamond-like Carbon (DLC) Coatings**, *D. Caschera, **B. Cortese** (barbara.cortese@ismn.cnr.it), G. Gigli, A. Mezzi, M. Brucale, G.M. Ingo, T. De Caro, G. Padelletti*, CNR, Italy

The ability to control the specific wettability, mechanical stability and bio-inertness of Diamond-like Carbon (DLC) films is of increasing awareness in both academic sciences and industrial technologies. Tuning of growth parameters and incorporated hydrogen and oxygen, influences the amount of sp^2/sp^3 electronic hybridizations imparting attractive properties such as extreme hardness, low friction coefficients and high corrosion resistance. We report the deposition of DLC films by Plasma Enhanced Chemical Vapour Deposition (PECVD) on different substrates. The influence of different precursors plasma pre-treatments of H_2, Ar or O_2 on the properties of DLC coatings is evaluated and analysed in terms of structure and mechanical properties. The electronic configuration of the DLC specimen are investigated combining Raman and XPS measurements. The $I_{(D)}/I_{(G)}$ ratio, the *disp(G)* and the FWHM of G band have been calculated using a micro-Raman apparatus. The sp^2/sp^3 ratio was calculated using the first derivative of C KLL spectra by means of an ESCALAB apparatus. Contact angle (CA) measurements were measured and compared. Based on roughness measurements, the differences in the pre-treatment of the substrate showed an influence on the hydrophilic/hydrophobic behaviour as well as mechanical properties of the DLC functionalized substrates. Additionally, the use of the different reactive elements in the pre treatment coating was investigated, demonstrating the flexibility and viability of this low cost coating concept.

10:40am **TS2-1-9 Multi-scale Residual Stress Analysis of AlN on (100)Si Substrate Deposited at Different Biases**, ***M. Renzelli** (mare@stm.uniroma3.it), E. Bemporad, M. Sebastiani*, University "Roma Tre" Rome, Italy

The aim of the present work was to investigate the effect of substrate bias on AlN residual stress state at the micro and macro scale.Reactive magnetron sputtering with ion plating was used to coat silicon substrates with AlN. The applied bias on the substrates was changed in order to obtain different residual stress levels in the resulting film due to ion pinning of the growing surface. Several techniques have been used like wafer curvature method, TEM investigation, XrD and a recently developed focused ion beam (FIB) micron-scale ring-core method [1]. The effect of residual stress has been compared with mechanical properties such as adhesion and apparent elastic modulus by micro scratch, nano scratch and nanoindentation.In this way, the correlation between the micro- and macro-stress distributions with the adhesion of the coatings can be quantitatively assessed and related to the observed microstructure and growth mechanisms. The results clearly showed an effect of the surface defects and other microstructural features on the local residual stress field, thus confirming that a structured information can be achieved by the use of a multi-scale approach for residual stress assessment.A correlation between the macro and micro-stress in the coatings with the adhesion and observed failure modes during scratch is finally proposed. [1] Sebastiani, M., Eberl, C., Bemporad, E., Pharr, G.M. (2011) Materials Science and Engineering A, 528 (27), pp. 7901-7908.

11:00am **TS2-1-10 Focused Ion Beam Milling for Localized Stress Measurement on Thin Films**, ***M. Krottenthaler** (markus.krottenthaler@ww.uni-erlangen.de), F. Haag, C. Schmid, K. Durst, M. Göken*, University Erlangen-Nuremberg, Germany

Focused ion beam (FIB) milling methods can be used for measuring residual stresses in thin films which has been shown in the literature for several coating systems. By FIB milling stresses are relaxed and the resulting displacement are tracked by means of digital image correlation (DIC), based on this deformation and by using finite element analysis (FEA), the residual stress can be reconstructed.

A newly developed geometry in form of an H-bar, as it is commonly used for transmission electron microscopy sample preparation, is used for analyzing the residual stress. The geometry has the distinct advantage that it can be adjusted by means of FEA to obtain a uniaxial relaxation and thus for the calculation of the residual stress only the relaxation strain and Young's modulus are required.

To verify this new method, relaxation measurements were performed on a bending stage in a scanning electron microscope on bulk metallic glass (BMG). The BMG sample was loaded by four point bending and H-bars were cut on the compression side as well as on the tension side of the specimen. By using the bending beam theory, the residual stress is evaluated and used as a reference for the FIB-DIC analysis. Prior to the measurements platinum nanoparticles were sprayed onto the sample for surface patterning. The bar's relaxation displacement was tracked by DIC and Hooke's law is used to calculate the stress from the relaxation strain. The resulting relaxation strain and stress over the cross section of the beam were in good correlation with the bending beam theory. The results can be used to further verify the sensitivity of the different approaches. Further, the FIB-DIC analysis was successfully applied to measure the residual stresses of an a-C:H coating system.

11:20am **TS2-1-11 A New Methodology for the Analysis of Fracture Toughness and Residual Stress in Thin Hard Coatings**, ***M. Sebastiani** (seba@stm.uniroma3.it), E. Bemporad*, University of Rome "Roma Tre", Italy, *EG. Herbert, GM. Pharr*, University of Tennessee, US

In this work, the effect of residual stress on fracture toughness and deformation modes of CAE-PVD TiN and CrN based coatings is analyzed and discussed.

A novel characterization methodology for the determination of surface elastic residual stress and fracture toughness in thin films is described. The new methodology is based on nanoindentation testing on focused ion beam (FIB) milled micro-pillars.

Finite element modeling (FEM) of strain relief after controlled material removal demonstrates that progressively increasing relaxation of pre-existing residual stress state can be achieved by milling of annular trenches of increasing depth and size at specimen surface, where the stress-free state is approached when the depth of the trench approaches the diameter of the remaining pillar.

Basing on FE modeling, the average residual stress present in the coating can be calculated by comparing the different sets of load-depth curves: the first obtained at the center of stress-relieved pillars, the second on the undisturbed (residually stressed) surface.

The implementation of in-situ SEM nanoindentation tests, using both a Berkovich and cube corner indenters, allowed to realize controlled fracture tests on the stress relieved pillars, thus giving quantitative information on fracture toughness by the use of analytical and numerical models, and allowing for the detailed analysis of the influence of the compressive residual stress on the mechanical behavior of the coating.

The proposed methodology can give further insights into the actual mechanisms that regulate deformation and fracture behavior of highly stressed ceramic coatings.

Hard Coatings and Vapor Deposition Technology
Room: Royal Palm 4-6 - Session B2-2

CVD Coatings and Technologies
Moderator: E. Blanquet, CNRS, France, S. Ruppi, Walter AG, Germany

1:30pm **B2-2-1 Residual Stress and Crystallographic Texture in CVD Zirconia Thin Films**, ***V. Ji*** *(vincent.ji@u-psud.fr), M. Andrieux, N. Prud'Homme*, Université Paris-Sud 11, France **INVITED**

Film crystalline growth and associated microstructure can been largely influenced by CVD (Chemical Vapor Deposition) process parameters. Residual stress can then be generated due to film growth and also due to thermomechanical phenomena during sample cooling. In present study, several-microns-thick Zirconia films have been obtained on Si (001) single crystal, using MOCVD method, with different process conditions (various precursor flows, different partial O_2 and N_2 pressures and various substrate temperatures). Crystalline phase identification on film layer, crystallographic texture and residual stress in quadratic ZrO_2 phase has been carried out by X-ray diffraction method. FEG-SEM technique has been used for film morphology study and for film thickness evaluation on cross-section observation. The relationship between MOCVD process parameters, crystalline texture effect and residual stress level in ZrO_2 films has been discussed.

2:10pm **B2-2-3 The Deposition of Hydrogenated Silicon Films under Different H_2 and Ar Flow Rates by an ICP CVD System**, *C. Li (cli10@yahoo.com)*, National Central University, Taiwan, Republic of China, *J.H. Hsieh*, Ming Chi University of Technology, Taiwan, Republic of China, ***K.L. Huang***, National Central University, Taiwan, Republic of China

Amorphous hydrogenated silicon (a-Si:H) films were deposited on quartz substrates in an ICP-CVD (inductive coupled plasma-CVD) system with four internal low inductance antennas (LIA) units. Different Ar and hydrogen flow rates were tested for their influences on the structures of deposited films. For monitoring purposes, Langmuir probe and optical emission spectrometer (OES) were installed to detect the variation of electrical field in plasma during deposition. After deposition, the films were examined by XRD, Raman spectrometer, FTIR, FE-SEM and UV-visible-NIR spectrometer for their microstructures, surface morphologies, optical absorption and band gap. Results indicate that under the supply of pure Ar flow, the deposition rate can reach 3.5nm/sec and amorphous films were formed on quartz substrates. While with the supply of mixed hydrogen and argon the deposition rate can be even higher. Although it is known that a high supply of H_2 helps the formation of micro-crystalline silicon, these hydrogenated Si films were confirmed to be amorphousness under various ranges of Ar and H_2 flow rates.

2:30pm **B2-2-4 High-rate PECVD with Metal Strip Magnetron for Hard and Other Functional Coatings**, ***C. Metzner*** *(christoph.metzner@fep.fraunhofer.de), B. Scheffel, O. Zywitzki*, Fraunhofer FEP, Germany

Magnetron glow discharges have been used for a long time in a variety of different ways. They form the basis for a series of developments in the area of surface coating. Various methods for coating and reactive process control, a wide variety of magnetron sputter sources and pulsed power supplies for magnetron discharges have been and are being developed. Magnetron discharge is also used for pre-treating of metal strips. For this a magnetron discharge is applied to the surface of the metal strip to be cleaned. Due to the bombardment of the surface with argon ions and the sputtering effect, material is removed from the surface and this means a better surface is created for the adhesion of subsequently applied layers. There are novel opportunities for coating metal strips by using magnetron glow discharge in a PECVD. A precursor is fed into the plasma of the magnetron discharge. The process is set such that the ion bombardment does not lead to removal of material from the cathode surface, but rather assists the layer formation process. In this way, very dense, thin layers can be deposited on the cathode, namely the metal strip. If the metal strip has to be at earth potential, an anode box is used. The medium frequency pulse technique, which was developed for magnetron sputtering, can be advantageously used with the metal strip magnetron for the deposition of electrically insulating layers too. The fundamental characteristics of the novel process are being studied using acetylene und hexamethyldisiloxane (HMDSO) as precursors. The coating rate, due to reaction of the precursor, is closely linked to the plasma density in the discharge. For that reason, the circular magnetron discharge at the cathode can be depicted as layer formation on a stationary strip. The dynamic coating rate of 150 to 300 nm m/min is relatively high. Very dense and hard layers were deposited. For the layers which formed due to reaction of HMDSO, layer hardness in the region of 6 to 18 GPa were measured. The hardness and other layer properties can be customized by adding oxygen. In the case of the acetylene precursor, hydrogen-containing, amorphous, carbon layers were deposited with very high layer hardness of up to 40 GPa. Studies on the long-term stability of the discharge and the coating of strip edges will be investigated next. The application area for this method is limited to the coating of electrically conducting and not too thick ferromagnetic strip materials. A broad spectrum of applications is envisaged for metal strip treatment, due in particular to the high quality of the deposited layers and the expected low technological complexity of the method.

2:50pm **B2-2-5 Study of the Uniformity of SiO_2 Films Developed in Atmospheric Plasmas**, ***D. Pappas***, *J.H. Yim (jacqueline.h.yim.ctr@mail.mil), V. Rodriguez-Santiago, A. Bujanda, S.D. Walck*, US Army Research Laboratory, US

Plasma-enhanced chemical vapor deposition under atmospheric pressure conditions has been widely accepted as an industrially scalable, cost efficient method for the development of large scale coatings that does not require the use of vacuum equipment. However, treatment of large area substrates requires creation of considerable volumes of uniform plasma, which is not a trivial task at atmospheric pressure. Depending on the process parameters, stable non-filamentary discharge modes can be obtained, but the plasma uniformity does not necessarily guarantee film uniformity.

This study concentrates on the deposition of SiO_2 thin films using dielectric barrier discharges (DBD) under 1 atm from hexamethyldisiloxane (HMDSO). The effect of gas mixture composition, dissipated power, and operation frequency will be discussed. Preliminary results show that by changing the HMDSO/oxygen ratio in the gas mixture it is possible to tune the composition of the deposited film from organic polymerized HMDSO-like to inorganic silica-like coatings with negligible residual carbon content. The chemical uniformity of the grown films was studied through X-ray photoelectron spectroscopy (XPS), electron energy loss spectroscopy and attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR), while the surface morphology was investigated using scanning electron microscopy and atomic force microscopy. Moreover, the development of structures of gradient composition is feasible showing that these SiOxCy materials have the potential to be integrated in corrosion protection, optical and diffusion barrier applications.

3:10pm **B2-2-6 Semi-empirical Modeling of the Optical Gap of Plasma-deposited a-C:H:F, a-C:H:Cl and a-C:H:Si:O:F Films**, *A. Neto, T. Gonçalves, R. Turri*, UNESP, Brazil, *W. Schreiner*, UFPR, Brazil, *D. Galvão*, UNICAMP, Brazil, ***S. Durrant*** *(steve@sorocaba.unesp.br)*, UNESP, Brazil

Diverse amorphous hydrogenated carbon thin films also containing halogens were obtained by plasma deposition. The films were characterized by Fourier Transform Infrared Spectroscopy (FTIR) and X-ray Photo-electron Spectroscopy (XPS). Films with different degrees of halogenation were produced. Mean deposition rates were determined from the film thickness and deposition time. Optical properties such as the refractive index, n, absorption coefficient, $\alpha(E)$, where E denotes the photon energy, and the optical gap, E_g, were determined from spectra taken in the Ultraviolet-visible Near-Infrared part of the electromagnetic spectrum. The dependencies of E_g, determined using the Tauc method, on the degree of halogenation of the film, R_H, were determined. The trends in E_g as a function of R_H were modeled using Parametric Method 3 (PM3) to optimize the molecular geometry, and the ZINDO program to simulate the oscillator strengths. Film molecular structure was approximated from the results of the FTIR and XPS analyses. Although the approach adopted here cannot account for the absolute values of E_g, the trends in E_g as a function of R_H can be reproduced. To our knowledge, the E_g of the more complex films examined here have not previously been modeled.

3:30pm **B2-2-7 The $SiO_xC_yH_z$ Hydrophobic Film with Chemical and Mechanical Properties using PECVD by Controlling the Plasma Process**, ***J.S. Lee*** *(platinum87@skku.edu), S.B. Jin, Choi, Choi, Han*, Institute for Plasma-Nano Materials, Center for Advanced Plasma Surface Technology,Sungkyunkwan University, Korea

SiO_x films produced from octamethylycyclodisiloxane ($Si_4O_4C_8H_{24}$, OMCTS) with oxygen carrier gas have a low contact angle. The surface energy of the SiO_x films can be changed by controlling the Ar plasma. $SiO_xC_yH_z$ print films were deposited on glass substrates by plasma

enhanced chemical deposition (PECVD) using hexamethyl-disilazane (HMDS) precursor with hydrogen gas. The process parameters were Ar flow rate and RF power. They were changed to the surface energy, mechanical and chemical properties of the hydrophobic film. The plasma diagnostics, surface energy and surface morphology were characterized by residual gas analyzer (RGA), contact angle measurement and atomic force microscopy (AFM), respectively. The chemical properties of the coatings were examined by Fourier transform infrared spectroscopy (FT-IR). The surface energy of the $SiO_xC_yH_z$ films produced using a room temperature plasma process could be controlled by employing the appropriate intensity of excited neutrals, ionized atoms, molecules and energy (input rf power), as well as the suitable dissociation of HMDS. In addition, we tested the mechanical properties by rubber and hardness tester. Also chemical properties tested by salty boiling water and ethanol. The mechanical and chemical properties tested by water contact angle.

3:50pm **B2-2-8 Modeling Surface Processes and Kinetics of Compound Layer Formation during Plasma Nitriding of Pure Iron**, *F. Cazares, A. Jimenez-Cenisero,* ITESM-CEM, Mexico, *J. Oseguera (joseguer@itesm.mx),* ITESM-CEM,Mexico, ***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 into the material. During this process, the ion bombardment causes sputtering of the specimen surface.

This work presents a mathematical model of compound layer formation during plasma nitriding of pure iron. The model takes into account the erosion effect at the plasma-solid interface due to sputtering. This erosion effect is studied using mathematical simulation of the ion bombardment on surface through HP TRIM package. The model is related to a moving boundary diffusion problem, which considers the observed qualitative behavior of the process. Experimental research was conducted in order to gather data of pure iron nitriding, which are used in modeling the process. The results of the presented model are in good agreement with experiments. A comparison of this model with other kinetic models is made in order to determine its scope and relevance.

Tribology & Mechanical Behavior of Coatings and Engineered Surfaces
Room: Golden West - Session E3-1+G

Tribology of Coatings for Automotive and Aerospace Applications

Moderator: S. Dixit, Plasma Technology Inc., G.L. Doll, University of Akron, A. Gies, OC Oerlikon Balzers AG, Liechtenstein

1:30pm **E3-1+G-1 Friction Reduction Through Thermal Spray Coatings on Cylinder Running Surfaces of Internal Combustion Engines**, ***PE. Ernst*** *(peter.ernst@sulzer.com),* Sulzer Metco AG (Switzerland), Switzerland **INVITED**

More stringent environmental laws in the field of vehicle emissions such as nitrogen oxides, particulate matter and carbon dioxide increase the pressure on the internal combustion engine manufacturers to develop, validate and apply technologies, which contribute to a reduction in these emissions. As a result, the interest in low friction coatings for cylinder running surface has risen significantly over the past few years. Among others, the SUMEBore® coating solution from Sulzer Metco can provide such properties. Current commercial applications range from small 2-stroke engines for motorcycles and other leisure vehicules, (downsized) lightweight passenger car engines up to highspeed diesel truck and medium speed diesel engines for power generation, marine propulsion, locomotives, etc.SUMEBore coatings are applied by a powder based air plasma spraying (APS) process. The APS process is extremely flexible when it comes to freedom of materials choice and can also process materials to which wire-based coating methods – such at Plasma Transferred Wire Arc (PTWA) or Twin Wire Arc Spray (TWAS) - do not have access, particularly metal matrix composites (MMC) and pure ceramics.The compositions can be tailored to the specific challenges in an engine, e.g. reducing friction and excessive abrasive wear, addressing scuffing issues, corrosion attack caused by adulterated fuels, improve the heat transfer into the water jacket, etc. Up to date a number of engines have been tested successfully. Most of the tested engines achieved significant reductions in lubricant oil consumption (LOC), sometimes in excess of 75%, reduced fuel consumption, very low wear rates and corrosion resistance on the cylinder running surfaces. The paper will give an introduction into the APS coating application on cylinder running surfaces. It will be underlined with recent examples of engines that achieved significant reduction in friction and LOC and improved corrosion resistance. One specific example will be highlighted from the industrialization of the APS process on a 3-cylinder, 1.5l high performance engine for a leisure vehicle with start of industrial production (coating application) in September 2012.

2:10pm **E3-1+G-3 Thermal Treatment and Tribological Behaviour of Hybrid Coatings Deposited by Sol-gel Route on Martensitic Stainless Steel**, ***S. Rahoui*** *(rahoui@chimie.ups-tlse.fr), V. TURQ, J.P. Bonino,* Université Paul Sabatier, France

Stainless steels are widely used in the aeronautical field. Among these steels, the 15-5 PH martensitic stainless steel (X5CrNiCu15-5), known for high strength and good corrosion resistance, presents poor tribological behavior, particularly in high temperature environment. Moreover, in the field of surface treatments and coatings, recent environmental regulations encourage working on new non polluting process.

In this study, a process was developed to improve the tribological behavior of the martensitic stainless steel until 500°C. Organic-inorganic hybrid coatings were prepared via sol-gel route and deposited onto stainless steel by dip-coating technique.

The effects of an additional thermal treatment, under different temperatures and in air or in nitrogen atmospheres was then studied. Combined analysis was conducted by thermal analysis (DTA/TGA), Nuclear Magnetic Resonance (of ^{29}Si and ^{13}C) and Raman Spectroscopy on the xerogel and on the coating.

The mechanical properties and the tribological behavior (evaluated with a pin-on-disk tribometer) of the coated samples were also studied.

2:30pm **E3-1+G-4 Tribological Behavior of New Coatings for High Temperature Aeronautical Applications**, *M. Bernard,* ***V. Fridrici*** *(vincent.fridrici@ec-lyon.fr), P. Kapsa*, LTDS - Ecole Centrale de Lyon, France

In aeronautics tribology, mechanical parts are required to operate with increasing temperature. The increased functioning temperature (up to 700°C) of the contacts prone to friction and wear (such as bearings and other structural parts) is a direct consequence of the increasing power of jet engines. In the case of ball bearings, the substrate materials as well as the coating durability are affected by temperature. There is then a pressing need to introduce new coatings demonstrating effective tribological behavior at high temperature (e.g. 600°C instead of 150°C for some aeronautical joints), especially in order to replace silver coating used at normal temperature but that cannot work at higher temperature. In partnership with Airbus Aerospace and SKF Aerospace, the durability of ball bearings functioning under extreme conditions in terms of temperature and sliding friction was studied.

First, SEM/EDX analyses were done on the silver coating deposited in the contact between the ball bearings rings, in order to acknowledge the actual bearings surface damage. Tribological testing of the silver coating was then performed in a standard cylinder-on-flat configuration in order to compare in situ and experimental damages.

More than ten different coatings (both soft and hard coatings, with solid lubrication properties and/or wear resistance properties) were then tested in the same configuration and conditions as the silver coating. These tests allowed us to identify the best suitable coatings for the application. An original test rig was also designed in the lab, in order to better simulate the bearings functioning conditions. This tribometer makes it possible to perform tests in ring-on-flat configuration (close contact) and to simultaneously apply a normal force up to 50 kN and a reciprocating rotating motion. Using this tribometer, the final tests were conducted on the best candidates among the different coatings, in a configuration as close to reality as possible, with a hard coating covered ring and a soft coating covered flat, the contact between the two being greased. From these tests, mechanisms of solid lubrication were examined and typical tribological damages such as adhesion and abrasion were observed. Finally, several possible solutions were determined, for two different functioning temperatures: 200°C and 600°C.

2:50pm **E3-1+G-5 Thick TiSiCN-based Nanocomposite Coatings for Aerospace and Automotive Applications**, ***R.H. Wei*** *(ronghua.wei@swri.org),* Southwest Research Institute, US **INVITED**

This paper reviews the thick nanocomposite coating research conducted at Southwest Research Institute® (SwRI®). We have been developing thick TiSiCN-based coatings (20-500 µm) for severe environments including sand erosion, sand abrasion, water droplet erosion, heavy load sliding wear and corrosion. The SwRI process utilizes magnetron sputtering of Ti from all targets in a mixture of Ar, N_2 and TMS (trimethylsilane) to form the

TiSiCN-based coatings. TMS is much more user-friendly than SiH4 or SiCl4; therefore, the process is suited for large-scale coating production. To increase the coating quality, a plasma enhanced magnetron sputtering (PEMS) method is used. During the deposition, in addition to the magnetron plasma, a global plasma is generated using thermionic emission for the enhanced ion bombardment. The coatings thus produced have a dense structure, good adhesion to the substrate, low internal stress and superior mechanical properties compared to those obtained with the conventional magnetron sputtering. The coatings formed have a microstructure composed of nanocrystalline TiC_xN_{1-x} (x=0, 0.3 and/or 0.7) with the grain size of 4-10 nm in a matrix of amorphous SiC_yN_z, or nc-TiC_xN_{1-x}/a-SiC_yN_z. The microstructure of the coatings results in the super-hardness (up to 4600Hv). However, the internal stress was found to be less than 1 GPa, thereby allowing the deposition of ultra-thick coatings over 500 µm for a few specific applications. The coatings also have high toughness characterized by a high value of H^3/E^{*2}. The nanocomposite coatings have been found to significantly increase erosion resistance compared to uncoated alloy substrates including Ti-6Al-4V, Inconel 718, H-13, 17-4PH stainless steel (SS), Custom 450 SS, 304 SS, carbon steels and many others. When the coatings are prepared using specific precursors, a low coefficient of friction below 0.2 in dry sliding has been achieved. These coatings have many industrial applications including compressor blades or vanes for aero engines, cylinder liners for automotive, stamping dies, and cutting tools. In this paper we review the method for preparing these coatings, discuss their microstructural, mechanical and tribological properties, and present examples for practical applications.

3:30pm **E3-1+G-7 In-situ Real Time Solid Particle Erosion Testing Methodology for Hard Protective Coatings**, ***E Bousser***, *L. Martinu,* École Polytechnique de Montréal, Canada, *J.E. Klemberg-Sapieha (jsapieha@polymtl.ca),* Ecole Polytechnique de Montréal, Canada

Solid Particle Erosion (SPE) degradation of engine components in aircraft operating in harsh environments is a well known issue causing severe maintenance and reliability problems. In order to enhance the lifetime of engine components many different hard protective coatings have been developed over the last two decades. While these coating systems are mostly based on TiN/Ti multilayer microstructures, they present varying material removal mechanisms depending on the phase constitution and microstructure of the target, and on the erodent characteristics (particle size, speed, composition and shape). Studying these mechanisms in detail is quite challenging given that SPE testing is notoriously inaccurate due to its aggressive nature and its many methodological uncertainties. In this presentation we will outline the work recently performed at Polytechnique Montreal on the methodological aspects of gas-blast SPE testing of hard protective coatings.

We will first present our work with respect to "traditional" erosion testing by evaluating the volume loss from the tested samples in order to accurately compare the SPE performance of different coatings without the need of obtaining coating density which is rarely accurately known. In the second part of the presentation, we will demonstrate a new in-situ real time erosion testing methodology using a quartz crystal microbalance in order to study the SPE of different hard protective coating systems. Using the previous results by volume loss measurement, we validate and discuss the advantages and challenges related to such a method. Finally, this time-resolved technique enables us to discuss some transient events present during SPE testing of hard coating systems leading to new insights into the erosion process.

3:50pm **E3-1+G-8 Characterization and Tribological Investigation of $TiSi_xC_y$ Wear Protective Coatings**, ***J. Matthey*** *(joel.matthey@he-arc.ch),* Haute Ecole Arc Ingenierie, Switzerland

$TiSi_xC_y$ hard coatings have been deposited by magnetron sputtering from a composite target that was manufactured by powder technology. Other coatings were also obtained from a Unbalanced Magnetron Sputtering unit mounted with Ti and Si targets in partial acetylene atmosphere. The attained films are principally composed of TiC_x nano-crystallites and amorphous phases. Although the Ti_3SiC_2 phase has not been detected, the hard coating properties are yet interesting. Nanohardness values up to 1800 Hv could be obtained for coatings with friction values below 0.20 against steel in an unlubricated pin-on-disk setup. The main parameter, which governs mechanical and tribological properties, found to be the negative bias voltage applied to the substrates during the deposition process. Application of a negative bias voltage results in significant variation between the target and thin film composition. Material transfer, roughness reducing and tribo-chemical reactions between TiC_x and environmental gases caused interesting tribological behavior of biased $TiSi_xC_y$ thin films. A strong dependence on the adhesion layer hardness and the film tribological endurance has been demonstrated. Measurements showed a thermal stability up to 400°C. Additionally, recent works showed $TiSi_xC_y$ could be also use as an adhesion layer for DLC coatings. Coatings have been tested in industrial applications and have been found encouraging because, in certain cases such as cold stamping and watch mechanisms, the $TiSi_xC_y$ coatings can compete against those currently available on the market. Compared to some industrial processes, the benefit is that no reactive gas is needed. Consequently, it has a long-term stability. This present document reports the investigation of the morphology, structure and tribological behavior of Ti-Si-C hard coatings deposited from a composite target.

4:10pm **E3-1+G-9 Effects TiN and TaN Barrier Layers on the Rmergence of Ag and Cu Particles and the Subsequent Mechanical and Antibacterial Properties of TaN-(Ag,Cu) Nanocomposite Films**, *J.H. Hsieh (jhhsieh@mail.mcut.edu.tw),* ***Y.R. Cho***, *Y.T. Su,* Ming Chi University of Technology, Taiwan, Republic of China

TaN–(Cu,Ag) nanocomposite films were deposited by reactive co-sputtering on Si(001) and M2 tool steels. Prior to annealing, the films were deposited with a barrier layer of TiN or TaN (with various thickness) in order to control the amount of emerged Ag and Cu particles. As a result, the tribological and anti-bacterial behaviors can be controlled. The films were then annealed using RTA (Rapid Thermal Annealing) at 200 °C–400 °C to induce the nucleation and growth of metal particles. Thes films' structures, surface morphologies, and mechanical properties were analyzed. The samples were tested for their anti-wear and anti-bacterial behaviors against Gram-negative Escherichia coli, as function of barrier layer thickness. It is found that, through the application of diffusion barrier, the antibacterial efficiency against E. coli as well as the tribological properties can be changed and controlled, depending on the layer thickness of TiN and TaN. In general, the films with TiN layer tended to allow more Ag and Cu particles to form on the surface.

New Horizons in Coatings and Thin Films
Room: Sunrise - Session F5-1

Coatings for Compliant Substrates
Moderator: B Beake, Micro Materials Ltd., N. Moody, Sandia National Laboratories

1:30pm **F5-1-1 Deformation Domains of Nanostructured Metallic Thin Film onto Polyimide Substrate under Controlled Biaxial Deformation**, ***P.O. Renault*** *(pierre.olivier.renault@univ-poitiers.fr),* *E. Le Bourhis,* University of Poitiers, France, *D. Faurie,* University of Paris 13, France, *S. Djaziri, P.O. Goudeau,* University of Poitiers, France, *D. Thiaudière, C. Mocuta,* Synchrotron SOLEIL, France, *G. Geandier*, University of Lorraine, France

This paper reports on the mechanical behaviour of nanostructured W/Cu thin films deposited on a polyimide substrate under controlled biaxial loadings thanks to a biaxial testing device developed on DiffAbs beamline at SOLEIL synchrotron (Saint-Aubin, France). The elastic-plastic-failure behaviour of the composite metallic film - polymeric substrate can be investigated under equi-biaxial and non-equi-biaxial loading conditions. The in-situ tensile tests were carried out combining synchrotron X-ray diffraction (XRD) and digital-image correlation (DIC) techniques. The combination of these two techniques can accurately measure deformations at two different scales, namely the in- grain scale and the macroscopic scale. The results show that the two strain measurements, i.e. lattice strain in the crystalline part of the W component of the film measured by XRD and macroscopic strain in the substrate measured by DIC, match to within $1x10^{-4}$ in the linear elastic domain. This result clearly demonstrates that the applied strain in the elastic domain is transmitted unchanged through the film-substrate interface, and thus the W/Cu thin film elaborated by magnetron sputtering exhibit a good adhesion to the polymeric substrate without adhesion layer. The second part of the paper deals with higher strains response under equi-biaxial tensile tests. The elastic limit of the nanostructured W/Cu thin films was determined at the bifurcation point between the XRD lattice strain and the DIC macroscopic strain. Deformation mechanisms such as film fragmentation are proposed.

1:50pm **F5-1-2 Stress Measurement in Thin Films: Micro-focus Synchrotron X-ray Diffraction Combined with Focused Ion Beam Patterning for d_o Evaluation**, ***N. Baimpas*** *(nikolaos.baimpas@eng.ox.ac.uk),* University of Oxford, UK, *E. Le Bourhis,* Université de Poitiers, France, *S. Eve,* ENSICAEN, CRISMAT, France, *D. Thiaudière,* Synchrotron SOLEIL, France, *C. Hardie, A.M. Korsunky,* University of Oxford, UK

Nanocrystalline metallic coatings of sub-micron thickness are widely used in modern microelectronic applications. Their deformation properties differ considerably from those of thicker and more coarse-grained counterparts,

due to obstacles to dislocation motion presented by the grain boundaries, and the proximity of the free surface and the interface.

In X-ray diffraction experiments to determine both the residual and 'live' stresses in nanocrystalline coatings, one difficult challange that comes up invariably is the determination of the strain-free lattice spacing d_o. The present study addresses this challenge as described below.

Previously, detailed experimental analysis by Digital Image Correlation and Finite Element modelling have been used to demonstrate that Focused Ion Beam (FIB) ring-core drilling can produce full stress relief of circular and rectangular "islands" [1]. We used this approach to generate a built-in strain-free reference by patterning a $50\times50\mu m^2$ region of the coating by FIB milling to produce an array of small stress-relieved "islands" $\sim0.4\times0.4\mu m^2$ each.

Transmission X-ray diffraction setup was used for data collection at DIFFABS beamline (Synchrotron Soleil, France). A 400nm-thick nanocrystalline gold coating on PMMA substrate [2] and a 240nm-thick multi-layered W-Cu nano-composite thin films on Kapton substrate [3] were studied. The samples were loaded incrementally using a compact uniaxial loading device, and micro-beam diffraction data were collected on and away from the reference array. It was shown experimentally that the "island" array remained strain free throughout the experiment, providing an on-board d_o lattice spacing reference. The changing lattice spacing d in the coating was also monitored away from the array, to deduce the elastic strain evolution during deformation. The results and their implications are presented and discussed.

[1] Korsunsky, A.M., (2009), Materials Letters, Vol. 63, p.1961-1963.

[2] Girault, B. *et al.* (2011), J. of Applied Physics, (109) 014305.

[3] Eve, S. *et al.* (2011), Int. J. Theoretical and Applied Multiscale Mechanics, Vol. 2, No. 1, p.38–45.

Keywords: gold thin film, W-Cu, polymer substrate, stress relaxation, Synchrotron X-ray Diffraction, Focused Ion Beam

2:10pm **F5-1-3 Wrinkling and Delamination of Thin Films on Compliant Substrates**, ***R. Huang*** *(ruihuang@mail.utexas.edu)*, University of Texas at Austin, US **INVITED**

When the surface of a soft material is coated with a stiff thin film, compression induced buckling instability of the thin film results in surface wrinkles, and wrinkling of the thin film may lead to fracture and delamination. In this talk, I will present a study on the mechanics of wrinkling and buckle-delamination for an elastic film on a very compliant substrate. First, with no delamination to begin with, an analytical solution is developed to predict onset of wrinkling, which takes into account the effect of Poisson's ratio of the substrate. In comparison with a nonlinear finite element analysis, an approximate formula is derived to estimate the normal traction at the interface and to predict initiation of wrinkle-induced interfacial delamination. Next, with a pre-existing delamination, the critical strain for onset of buckling instability is predicted by finite element analysis, showing a smooth transition from wrinkling to buckle-delamination. For an intermediate delamination size, the critical compressive strain is found to be lower than previous solutions for both wrinkling and buckle-delamination. Post-buckling analysis by the finite element method shows a significant shear-lag effect with an effective load transfer length over three orders of magnitude greater than the film thickness. Finally, concomitant wrinkling and buckle-delamination is simulated to illustrate the interaction between the two buckling modes, and the results are discussed in view of predicting failure mechanisms as well as other applications of thin film materials.

2:50pm **F5-1-5 Interfacial Failure in a Model Polymer-metal Thin Film Structure**, ***R. Friddle*** *(rwfridd@sandia.gov), D. Reedy, E. Corona, D. Adams*, Sandia National Laboratories, US, *M. Kennedy*, Clemson University, US, *Cordill*, University of Leoben, Austria, *D. Bahr*, Washington State University, US, *N. Moody*, Sandia National Laboratories, US

Interfaces are the critical feature governing performance of polymer-metal thin film structures where differing properties between adjacent films can induce strong interlaminar normal and shear stresses and catastrophic failure. We are studying these effects in a model system created by spin coating PMMA films with thicknesses ranging from 10nm to 650nm onto copper coated silicon substrates followed with a sputter deposited overlayer of highly stressed tungsten. The high film stresses triggered spontaneous delamination and buckling along the PMMA-tungsten interface accompanied by intense deformation in the PMMA layers. In this presentation we will show recent AFM images that convey PMMA plastic deformation varied markedly between each system studied and from model elastic behavior. We will also show our recent AFM and nanoindentation work in understanding the mechanism of failure of the PMMA polymer near the tungsten interface. This work was supported by Sandia National Laboratories through USDOE NNSA under Contract DE-AC04 94AL85000.

3:10pm **F5-1-6 Fatigue-corrosion Behavior of Flexible Optoelectronic Device Electrodes**, ***T. Bejitual*** *(tbejitua@mix.wvu.edu), K. Sierros, D. Cairns*, West Virginia University, US

The electrical, optical, and structural integrity of flexible transparent electrodes is paramount in the design and fabrication of optoelectronic devices, such as organic light emitting diodes, liquid crystal displays, touch panels, solar cells, and solid state lighting applications. The electrodes may corrode due to acrylic acid containing pressure sensitive adhesives. In addition, structural failure may occur due to external applied loading. The combined action of mechanical loading and corrosion can aggravate the failure of the electrodes.

In this study we investigate the effects of acrylic acid concentration, film thickness, number of bending cycles, and applied strain on the electrical and structural integrity of carbon nanotube and indium tin oxide films on polyethylene terephthalate substrates.

In situ electrical resistance measurements are conducted during corrosion, bending, corrosion-bending, fatigue, and fatigue-corrosion experiments in order to determine the crack onset strain. Crack density calculation is performed on images acquired using optical microscopy. In addition, scanning electron microscopy is conducted in order to determine failure mechanisms.

3:30pm **F5-1-7 Load Bearing Capacity of Hydrogenated Amorphous Carbon Coatings on Ultrafine Grained Al Substrates**, ***C. Schmid*** *(christoph.schmid@ww.uni-erlangen.de), C. Schunk*, University of Erlangen-Nürnberg, Germany, *S. Meier*, Fraunhofer Institute for Mechanics of Materials, IWM, Germany, *M. Göken, K. Durst*, University Erlangen-Nuremberg, Germany

Thin hydrogenated amorphous carbon (a-C:H) coatings suffer from insufficient load bearing capacity for high load applications when they are deposited on relatively soft substrates like Al-alloys. In this work, the contact damage behaviour of an a-C:H coating system deposited on Al-alloy sheets was investigated by indentations with different indenter geometries and scratch tests. The investigated coating system consists of a silicon rich adhesion layer, an adjacent ramp layer with a graded chemical composition and a 2 µm thick a-C:H top coat deposited by PECVD. Using an accumulative roll bonding (ARB) process the flow stress as well as the grain size of the Al-alloy has been modified. Additionally shot peening was applied to increase the load strength and residual stresses in the Al-alloy sheet. Doing so, the mechanical properties of the substrate were varied systematically without changing its chemistry. The aim of this treatment was to enhance the load bearing capacity of the coating-substrate system. During indentation with a spherical tip, several discontinuities (pop-ins) occurred in each load displacement curve. Using Focused Ion Beam (FIB) cross-sections, these events were attributed to the formation of cracks in the coating allowing for an analysis of the fracture toughness of the a-C:H layer. The pop-in behaviour also depends on the mechanical properties of the substrate and reflects the different load bearing capacities. Finally, the concepts for increasing the load bearing capacity are discussed with the help of FE models.

3:50pm **F5-1-8 Three-dimensional Finite Element Analysis of Adhesive Failure on Coated Systems under Uniaxial Tensile Tests**, ***N. Fukumasu*** *(newton.fukumasu@gmail.com)*, University of São Paulo, Brazil, *F. Silva*, Federal University of ABC, Brazil, *R. Souza*, University of São Paulo, Brazil

Tensile tests are an important tool to improve the understanding of the mechanical behavior of coatings and their interaction with compliant substrates. When submitted to an increasing uniaxial tensile load, the coating presents nucleation and propagation of transversal cracks, up to a critical load in which the space between two consecutive cracks remains predominantly constant. Beyond this load, the stress state in the film, which is affected by the difference in lateral contraction of the film and the substrate, may lead to an adhesive failure and possible spallation of the coating. This work aims improving the understanding of the mechanical behavior of the coating after the saturation of inter-crack spacing and before spallation. A set of 3D finite element analyses was conducted to evaluate the influence of the stress state at the coating/substrate interface on the adhesive failure. Results showed non-uniform stress distributions on film-strips between two consecutive cracks, even when cracks were distributed uniformly. This non-uniformity led to distinct patterns of stress distribution that are function of the mechanical properties of the system components.

4:10pm **F5-1-9 Annealing Induced Structural Evolution and Optical Properties of Block Copolymer Templated Nanostructured Tungsten Oxide Films**, ***C.L. Wu***, National Cheng Kung University, Taiwan, Republic of China, *C.K. Lin*, Taipei Medical University, Taiwan, Republic of China, *C.K. Wang*, National Cheng Kung University, Taiwan, Republic of China, *S.C. Wang*, Southern Taiwan University of Science and Technology, Taiwan, Republic of China, *J.L. Huang (jlh888@mail.ncku.edu.tw)*, National Cheng Kung University, Taiwan, Republic of China

The effect of microstructure on the optical and electrochemical properties of nanostructured tungsten oxide films has been evaluated as a function of annealing temperature. The films using block copolymer as the template were prepared from the peroxotungstic acid (PTA) by spin-coating onto the substrate and post-annealed at 200-500 ^{o}C to form the tungsten oxide films with nanostructure. The microstructure of the films were measured by the X-ray diffraction, Raman spectroscopy and transmission electron microscopy. The films annealed at temperatures below 300 ^{o}C are characterized by amorphous or nanocrystalline structures with the pore size less than 20 nm. The evaluated annealing temperature caused the monoclinic crystalline structure and larger pores. The cyclic voltammetry measurements were performed in the $LiClO_4$-propylene carbonate electrolyte. The results showed that the exchange charges are maximized for films annealed at 200-300 ^{o}C and decrease with the increasing of annealing temperature. The electrochromic properties of the nanostructured tungsten oxide films were evaluated simultaneously by potentiostat and UV-Vis spectroscopy. The films annealed at 300 ^{o}C exhibit the high transmission modulation ($\Delta T \sim 60$ %) at $\lambda = 633$ nm and good reversibility for the lithium insertion-extraction process in cycling. As a result, the correlation between the microstructure and electrochemical properties was established, and the electrochromic properties have been demonstrated.

Applications, Manufacturing, and Equipment
Room: California - Session G5-1

Coatings, Pre-Treatment, Post-Treatment, and Duplex Technology

Moderator: T. Takahashi, KCS Europe GmbH, K. Yamamoto, Kobe Steel Ltd.

1:30pm **G5-1-1 Nitriding Duration Reduction with Improving Mechanical Characteristic and Fatigue Behavior, the Beneficial Effect of Prior Severe Shot Peening**, *A. Moridi*, ***S.M. Hassani-Gangaraj***, Politecnico di Milano, Italy, *S. Vezzù*, Associazione Civen, Italy, *M. Guagliano (mario.guagliano@polimi.it)*, Politecnico di Milano, Italy

Majority of failures in engineering materials such as fatigue fracture, fretting fatigue, wear and corrosion, are very sensitive to the structure and properties of the material surface, and in most cases failures originate from the exterior layers of the work piece. Therefore, it would be considerably effective to apply some technological process to enhance the material properties on the surface of the part.

Gas nitriding is a case hardening process whereby nitrogen is introduced into the surface of a solid ferrous alloy by holding the metal at a suitable temperature (below Ac1, for ferritic steel) in contact with nitrogenous gas, usually ammonia. Temperature and time are two important nitriding processing parameters. The possibility of nitriding duration reduction by performing prior sever plastic deformation can be of a great interest both in technological and economical points of view.

In this study shot peening is applied with particularly severe parameters to generate ultra-fine grains on the surface of a low alloy steel. Three different batches of specimens are prepared. The first is the as-received specimens. Nitriding is performed for the second series. The last series is exposed to severe shot opening and then nitriding at reduced time. The treated specimens are characterized by optical and SEM micro-structural observation, micro hardness, surface roughness and XRD measurement of residual stress. The fatigue limit of treated specimens was experimentally determined and compared with the as-received specimens. Based on the result of this study, a critical discussion on the possibility of nitriding duration reduction by performing prior severe plastic deformation is presented.

1:50pm **G5-1-2 Growth Kinetics and Mechanical Properties of Boride Layers Formed at the Surface of ASTM F-75 Biomedical Alloy**, ***I. Campos-Silva*** *(icampos@ipn.mx)*, *D. Bravo-Bárcenas*, *A. Meneses-Amador*, Instituto Politecnico Nacional, Mexico, *H. Cimenoglu*, Istanbul Technical University, Turkey, *U. Figueroa-López*, ITESM-CEM, Mexico

Cobalt-based alloys have been widely used in implant components due to their corrosion resistance and wear properties. Two types of cobalt-based alloys are the most common implant materials (the cast and wrought alloys denoted as ASTM F-75 and F-1537, respectively). Once implanted and exposed to the aggressive body environment, CoCrMo alloys tend to corrode over time, releasing Co, Cr and Mo ions into body fluids by electrochemical corrosion or chemical dissolution. Over time the level of metal ions may become clinically significant. In addition, the mechanical properties at the surface of the cobalt-based alloy can be affected by the presence of wear, corrosion fatigue and fretting corrosion.

One alternative to increase the chemical and mechanical properties at the surface of the cobalt alloys is the boriding process. A combination of high corrosion resistance, wear resistance, and high hardness is the basis for the application of boride layers in CoCrMo alloy.

In this study, new data about the growth kinetics and mechanical properties of cobalt boride layers formed at the surface of the ASTM F-75 biomedical alloy have been estimated. The formation of CoB/Co_2B layers was carried out by the powder-pack boriding process at temperatures of 1223-1273 K with different exposure times for each temperature.

A diffusion model evaluated the evolution of the boride layers at the surface of the biomedical alloy, where the boron diffusion coefficients were estimated as a function of the boron concentration limits in each layer, the boride incubation time and the parabolic growth constants. In addition, an expression to estimate the cobalt boride layer thickness was developed, and the calculated results were compared with the experimental data obtained for the CoCrMo borided alloy exposed to 1323 K with 6,8 and 10 h of treatment. The estimation of the theoretical values of the CoB and Co_2B layer thicknesses showed good agreement with the experimental data over the range of exposure times.

Finally, the mechanical characterization of cobalt boride layers was evaluated by Berkovich nanoindentation technique using a constant indentation load of 50 mN. The indentations were performed along the depth of boride layers for the set of experimental conditions of the boriding process. The results showed that the ratio between the hardness and the Young´s modulus could be used to explain the wear behavior of the boride layers. Furthermore, the hardness dissipation parameter (HDP) of the CoB/Co_2B layers was evaluated, whose values above 0.5, denoted the ability of the surface to dissipate a significant part of the energy of mechanical deformation under adhesive wear conditions.

2:10pm **G5-1-3 Combining Thermal Spraying and PVD Technologies: a New Aproach of Duplex Surface Engineering for Ti Alloys**, *F. Casadei (f.casadei@c-s-m.it)*, ***M. Tului***, Centro Sviluppo Materiali SpA, Italy **INVITED**

There is a rapid growth in demand for improved surface performance in many priority industrial sectors. There have also been rapid developments in methods of surface engineering and in tribological understanding. There is accordingly an exciting opportunity for cost effective industrial exploitation of materials with desirable properties. Among these materials, titanium and its alloys occupy an important place: they are very promising candidates for an increasing number of industrial applications, provided some weak points are solved, as tribological performances.

The system studied in a first program of research introduced a strong character of originality in the context. Beside the multilayer coatings and the duplex processes, a new class of systems process /product seems to be able to show with success on scientific/technical panorama, thanks to preliminary results that are quite encouraging. Such class of systems consist in the combination in succession of thick coatings obtained by means of thermal-spraying and of thin films deposited through PVD. If in a preliminary work it has been developed a specific combination (Reactive Plasma Spray-PVD), this does not exhaust the potentialities of such typologies of approach; in principle it would be possible combining all the technological variants of thermal-spraying (Plasma-Spray, Arc-Spray, HVOF, PTA) and of the PVD (arc, sputtering, EB), for the planning and the realization of surface systems, with graded mechanical characteristics.

In this context, first experiments combining HVOF and Arc-PVD, were carried out relating piston pins for sport automotive. The objective is the realization of a multilayered coating resistant to the concentrated loads, with a surface roughness very low.

The Surface Engineering, especially in the field of Aerospace, at present is characterized by important efforts in terms of R&D. These works can be considered a original approach to these applications where the conventional coatings/treatments show their limits.

2:50pm **G5-1-5 Corrosion Testing by Potentiodynamic Polarization and EIS in Borided Steels**, ***I. Mejía-Caballero***, Instituto Politecnico Nacional, Mexico, *H. Herrera-Hernández*, Universidad Autónoma Metropolitana- Azcapotzalco, Mexico, *J. Martínez-Trinidad*, Instituto Politecnico Nacional, Mexico, *M. Palomar-Pardavé*, *M. Romero-Romo*, UAM-A, Mexico, *I. Campos-Silva (icampos@ipn.mx)*, Instituto Politecnico Nacional, Mexico

Boriding considerably enhances the corrosion-erosion resistance of ferrous materials in non-oxidising dilute acids and alkali media. Different attempts to estimate the corrosion resistance of borided steels were performed using alternative techniques instead of immersion corrosion testing. One of the principal tests used is the electrochemical test or one of its variants, according to the procedure method.

In this study, the corrosion resistance of boride layers formed in the AISI 1018 and AISI 304 steels was evaluated by the potentiodynamic polarization and EIS techniques. The boriding of the steel samples was carried out by the powder-pack method at a temperature of 1223 K with 6 h of exposure. Structural examinations at the surface of the borided steels revealed the presence of the Fe_2B layer (AISI 1018 borided steel) with a layer thickness of 164 μm, and a FeB/Fe_2B layer with a total layer thickness of 55 μm in the AISI 304 borided steel.

The potentiodynamic polarization and EIS measurements over the borided as well as non-borided steels were evaluated in a corrosive solution of 0.1 M HCl. All the experiments were performed at open circuit potential (Ecorr) in a electrochemical cell with three-electrodes: a working electrode (the test specimen) attached to an acrylic cylinder leaving an exposed area of 1 cm^2, the reference and counter electrodes were of Ag/AgCl, and AISI 316 L steel, respectively. The anodic polarization curves were obtained using an AUTOLAB PGSTAT 100 equipment from – 350 mV to 1200 mV at a scan rate of 10 mV/s. Moreover, the EIS data were collected with an IM6 ZAHNER equipment, in which the borided and non-borided samples were exposed for more than 40 days in the HCl solution. The frequency range was from 8 MHz to 1 mHz under excitation of a sinusoidal AC signal of 10 mV amplitude for a required time of exposure. After the electrochemical tests, the samples were analyzed by SEM to identify the corrosion mechanisms at the surface of the borided and non-borided steels.

The results from the Tafel plots showed high corrosion resistance of the steels exposed to the boriding process. In addition, the presence of the FeB/Fe_2B layer at the surface of the AISI 304 borided steel, the chemical composition of the steel, and the low porosity in the boride layer, have a beneficial effect in the values of the corrosion resistance in comparison with those estimated in the AISI 1018 borided steel.

Finally, the EIS data were modelled using an appropriate equivalent electric circuit to establish the electrochemical properties and corrosion behavior of the borided and non-borided steels as a function of the exposed days in the corrosive solution.

3:10pm **G5-1-6 Improved Adhesion of Diamond Coatings on Cemented Carbide Tools by Surface Reconstruction via MPCVD**, ***M. Mee*** *(manuel.mee@iwm.fraunhofer.de)*, *S. Meier*, Fraunhofer IWM, Germany

The possibility of synthesizing diamond by means of CVD was established almost thirty years ago. Due to their outstanding characteristics, diamond coatings enable a wide range of applications. Especially the high hardness and the associated suitability for wear protection make diamond as an interesting coating element for cemented carbide tools. Cobalt, which acts as a binder for the tungsten carbide grains, proves to be extremely incompatible with diamond synthesis. Since the beginning, considerable approaches have been developed to control the detrimental effects of cobalt. Meanwhile, a number of approaches with some good results have been established. Nevertheless, all these approaches are accompanied by a compromise, which has a significant effect on the adhesion of the diamond coating. By means of a newly developed MPCVD treatment it is now possible to significantly increase layer adhesion to meet the most stringent of demands .

The aim of this approach is the reconstruction of the surface after cobalt etching, with coincidental recovery of its hardness via substitution of cobalt with graphite, which has an extremely low thermal expansion coefficient and at the same time, acts as a diffusion barrier. In addition, the reconstruction helps to increase adhesion and can be controlled. Subsequently a process for low temperature diamond synthesis restrains the back diffusion of cobalt. Infrared spectroscopy allows a continuous process monitoring.

3:30pm **G5-1-7 Improvement in the Tribological Characteristics of Si-DLC Coating by Laser Surface Texturing at Elevated Temperatures**, ***A. Amanov*** *(amanov@rs.tus.ac.jp)*, *S. Sasaki*, Tokyo University of Science, Japan

This paper presents and discusses the tribological behavior of untextured and textured silicon diamond-like carbon (Si-DLC) coatings in the temperature range of room temperature to 200 0C. Dimples were produced using a laser surface texturing (LST) technique on a Si-DLC coating deposited onto a bearing steel substrate using a chemical vapor deposition (CVD) system to achieve good tribological behavior. The friction and wear behavior of untextured and textured Si-DLC coatings was investigated by conducting friction tests against an alumina (Al2O3) ball. The results showed that the textured Si-DLC coating led to a lower friction coefficient and wear compared to that of the untextured Si-DLC coating throughout the temperature range tested, which may be attributed to the storage of wear debris and microstructural alteration.

Topical Symposia
Room: Royal Palm 1-3 - Session TS3-1

Energetic Materials and Micro-Structures for Nanomanufacturing

Moderator: C. Rebholz, University of Cyprus, D. Adams, Sandia National Laboratories

1:30pm **TS3-1-1 Hermetic and Room-Temperature Wafer-Level-Packaging Based on Nanoscale Energetic Systems**, ***J. Braeuer*** *(Joerg.Braeuer@enas.fraunhofer.de)*, *J. Besser*, Fraunhofer ENAS, Germany, *E. Tomoscheit*, Chemnitz University of Technology, Germany, *M. Wiemer*, *T. Gessner*, Fraunhofer ENAS, Germany **INVITED**

Reactive bonding is a new wafer bonding technique and is becoming an attractive approach for MEMS (Micro-Electro-Mechanical-Systems) encapsulation and packaging due to several advantages: very short bonding time, high bond strength, and internal heating, thus, lower process temperatures compared to traditional bonding techniques, such as glass-frit or anodic bonding [1]. Reactive bonding is based on self-sustaining exothermic reactions in nano scale energetic systems. Such systems typically consist of several alternating layers of two different thin layers. With the application of an initial energy pulse, the system starts to rapidly form intermetallic phases. By choosing material combinations with high negative enthalpy of formation this reaction can be running exothermic and self-propagating [2]. Currently, exothermic and self-propagating reactions are used in Ni/Al foils (NanoFoils©) for different joining applications on the macro scale [3]. Nevertheless, for wafer bonding this method is not similarly applicable due to handling as well as foil patterning limitations [4].

In this study, so called reactive and nano scale multilayer systems (RMS) will be used for room-temperature and hermetic bonding. The bonding approach focuses on the direct deposition and process flow integration of thin Pd/Al-RMS with total thicknesses smaller than 2.5 μm. In addition to that, the used integrated RMS enable the integration into typically used process steps for MEMS device fabrication, such as lithography and waferbonding.

The integrated Pd/Al-RMS were deposited by using alternating DC magnetron sputtering from high purity Al- and Pd-targets. It will be shown that high reaction velocities ranging up to 75 m/s in patterned (minimum lateral dimensions are 20 μm) reactive systems can be achieved. In addition to that, the feasibility for hermetic wafer bonding for up to 150 mm Si-Si as well as glass-Si wafer bonding at room-temperature is presented. Furthermore, it will be shown that high shear strengths (up to 340 MPa) as well as high-temperature stable (up to 400 °C) and reliable (up to 1000 temperature shock cycles at -40°C/+130°C) bond interfaces can be achieved.

[1] P. Ramm et al., in Handbook of Wafer Bonding, Wiley-VCH, Weinheim (2012).

[2] A.B. Mann, et al., Journal of Applied Physics 82 (1997) 1178-1188.

[3] J. Wang, et al., Applied Physics Letters, Vol. 83, (2003), pp. 3987-3989.

[4] B. Boettge et al., Journal of Micromechanics and Microengineering, 20 (2010) pp 064018 1-8.

2:10pm **TS3-1-3 Self-Sustained Deflagration Reactions in Sputter-deposited Al_xPt_y Multilayers**, ***D. Adams*** *(dpadams@sandia.gov)*, *R. Reeves*, *M. Rodriguez*, *E. Jones*, *Jr.*, Sandia National Laboratories, US

Reactive multilayers grown by vapor deposition techniques have recently attracted interest for emerging applications including soldering and brazing.

For these applications, a metal-metal multilayer is typically designed to have a composition that corresponds to the peak enthalpy for a given material system as this maximizes heat output. With the focus on a single composition, it is not surprising that little work has explored the full range of composition that gives rise to self-sustained, high temperature formation reactions for a given reactive metal pair. With this presentation, the reactive Al/Pt system is described. The net composition of Al/Pt multilayers has been systematically varied over a large range from $Al_{0.2}Pt_{0.8}$ to $Al_{0.8}Pt_{0.2}$ and reactivity is evaluated. For multilayers having a total thickness of 1.6 microns, self-sustained, high temperature reactions occur when the net multilayer composition is in the range of $Al_{0.33}Pt_{0.67}$ to $Al_{0.75}Pt_{0.25}$. Equiatomic Al/Pt multilayers have the maximum velocity of all films investigated in this study, consistent with the maximum heat of formation determined by calorimetry. Multilayers having a net composition of $Al_{0.2}Pt_{0.8}$, $Al_{0.25}Pt_{0.75}$ and $Al_{0.8}$ Pt $_{0.2}$ did not react when stimulated at a point. In addition, phase formation is described. Multilayers reacted in air formed intermetallic compounds, and no oxides were detected by x-ray diffraction. With one exception (rhombohedral $Al_{0.5}Pt_{0.5}$), phase formation was consistent with published equilibrium phase diagrams. * Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the United States Department of Energy's National Nuclear Security Administration under Contract DE-AC04-94AL85000.

2:30pm **TS3-1-4 Visualizing Mass Transport in theSself-propagating Formation of B2-RuAl from PVD Multilayers**, ***C. Pauly*** *(c.pauly@mx.uni-saarland.de), H. Aboulfadl,* Saarland University, Germany, *K. Woll,* Johns Hopkins University, US, *F. Mücklich,* Saarland University, Germany

Self-propagating reactions of two or more elements are a commonly known means to produce ceramic or intermetallic compounds. The nature of self-propagating reactions requires finely dispersed reactants, e.g. in form of powders or PVD-multilayers. During the past decades, substantial research has been conducted on a number of metallic systems. Recently, it has been shown that the Ru-Al system is also capable of self-propagating reactions leading to a direct formation of the intermetallic B2-RuAl phase. This phase shows a favorable combination of properties not commonly encountered in intermetallic compounds. While having a high melting point and good oxidation resistance, RuAl has been reported to exhibit room-temperature ductility.

The self-propagation reactions in these kinds of systems are generally studied regarding ignition criteria, reaction speed and propagation of the combustion front. However, little is experimentally known about the mass transport on atomic scale during the reaction. To analyze the atomic redistribution, we incorporated a thin layer of a third element into Ru-Al multilayer stacks. The elemental distribution is measured after reaction by means of atom probe tomography (APT). This technique combines mass resolution in the ppm-range with near-atomic spatial resolution on a length scale of up to several hundred nanometers and can therefore provide valuable information to support the understanding of transport mechanisms during self-propagating reactions.

2:50pm **TS3-1-5 Ti/Al Multilayer Coating Releasing Heat During Slow Thermal Annealing**, ***P. Stupka****, J. Musil (musil@kfy.zcu.cz), S. Proksova, R. Cerstvy, P. Zeman,* University of West Bohemia, Czech Republic

The paper reports on sputtered Ti/Al multilayer coatings composed of many Al and Ti bilayers with a bilayer period Λ ranging from 2 to 172 nm. The effect of Λ on a temperature T_{hr} at which the heat is released during an exothermic reaction between Al and Ti initiated by thermal annealing is investigated in detail. It was found that (i) the temperature T_{hr} decreases from ~600 to 390 °C with Λ decreasing from 2000 to 17 nm, (ii) T_{hr} of multilayer coatings with $\Lambda \leq 12$ nm ranges from ~500 to ~600 °C, (iii) the multilayer coatings with $\Lambda \leq 12$ nm exhibit higher value T_{hr} compared with that of the multilayer coatings with $\Lambda \approx 20$ and (iv) the multilayer coating with $\Lambda = 2$ nm exhibit a diffusive microstructure. Obtained results suggest that the multilayer coatings with Λ ranging from ~17 to ~21 nm are optimal for the heat release at the lowest value of temperature T_{hr}. The evolution of mechanical properties of the Ti/Al multilayer coating with decreasing bilayer period Λ is also given.

Key words: Ti/Al multilayer, TiAl alloy single layer, Heat release, Mechanical properties, Magnetron sputtering

3:10pm **TS3-1-6 Fabrication and Characterization of Microstructured Thermites Derived from Electrophoretic Deposition**, *A.E. Gash (gash2@llnl.gov),* ***K.T. Sullivan****, J.W. Kuntz,* Lawrence Livermore National Laboratory, US **INVITED**

Here we report the use electrophoretic deposition (EPD) as a means to prepare energetic thin films of well-mixed copper (II) oxide/ aluminum (CuO/Al) binary particulate composites. Films were deposited from liquid suspensions of particles onto patterned electrodes. Suspensions were prepared with various particle sizes spanning from nanometer- to micron-sized. The resulting films were examined using electron microscopy and profilometry and their combustion characteristics were analyzed with high-speed videos. The results show that films prepared by EPD display an enhancement in their combustion velocities as the total film thickness increases. Films have been deposited onto patterned electrodes, with very fine feature sizes, which were used for mechanistic investigations of the ignition and combustion. These investigations have lead to a better understanding of the factors that influence the energy release properties of these films. Recent results suggest that films with features large enough to allow gas trapping and pressure unloading, and those with micro-structures which enable more directed transport of hot gases and particles in the desired propagation direction can be used to tailor the reactivity of the composites. These films are also particularly useful for developing thermites for micro-energetic applications.

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

LLNL-ABS-597572

3:50pm **TS3-1-8 Effect of Surface Functionalization of Fuels on Nanocomposite Thermites**, ***K. Kappagantula*** *(keerti.kappagantula@ttu.edu), C. Farley, M. Panotya,* Texas Tech University, US, *J. Horn,* Naval Research Laboratory, US

Combustion analysis of three different thermites consisting of aluminum (Al) particles with and without surface functionalization, combined with molybdenum trioxide (MoO_3) was performed to study the effect of surface functionalization on flame propagation velocity (FPV). Two types of Al particles had self assembled monolayers (SAMs) of perfluoro tetradecanoic (PFTD) and perfluoro sebacic (PFS) acids around the alumina shell respectively; the other one did not. Flame propagation studies of Al with PFTD/MoO_3 are 86% higher than Al/MoO_3 whereas the thermite comprising of Al with PFS/MoO_3 are almost half of Al/MoO_3. Thermal equilibrium studies were performed using a DSC/TGA to determine activation energy (E_a) of the thermites. Results showed an inverse relationship between FPV and E_a. Fluorine content in the acids and their structural differences contribute to difference in FPV. This study shows that the flame propagation velocity of a thermite is dependent of the nature of surface functionalization of the fuel particles.

4:10pm **TS3-1-9 Exothermic Reactions in Spark Ignitable Green Compacts of Continuously Ball-milled Al/Ni Powders**, *A. Hadjiafxenti,* University of Cyprus, Cyprus, *I. Gunduz,* Northeastern University, US, *C. Doumanidis,* ***C. Rebholz*** *(claus.rebholz@yahoo.com),* University of Cyprus, Cyprus

Spark ignition and self-propagating reactions in green compacts of continuously low-energy ball-milled aluminum and nickel powders at the NiAl composition were investigated. The microstructure of the as-milled powders showed uniform mechanical mixing and refinement of alternating Al and Ni layers with increasing milling time. XRD analysis of the as-milled powders confirmed nanoscale grain formation and solid-state diffusion of Al into Ni-rich solid solution for milling times beyond 6 h. Interrupted Differential Scanning Calorimetry (DSC) in combination with X-Ray Diffraction (XRD) analysis revealed that the milled powders have an identical phase formation sequence to those of nanoscale magnetron sputtered multilayer foils. Green compacts of powders milled for 11 and 12 h could be ignited using a low-energy spark from a battery, similar to sputtered foils, and they form metallurgically bonded compacts upon completion of the self-propagating reactions. The thermal front velocity measured using a high-speed optical camera was approximately 0.3 m/s. Infrared camera measurements show that the temperatures reach 1911 K, indicating near adiabatic reactions. Post-reaction X-Ray Diffraction (XRD) analysis of green compacts show near identical conversion to the NiAl phase.

This work focused on ball-milled Ni/Al powders and their characterization, but also showed similarities between ball-milled powder pellets and sputtered foils. Ball-milling could have the potential for an economical processing route for generating powders that can be shaped into useful geometries (such as rolled into thin sheets) for thermal manufacturing applications, similar to sputtered nanostructured foils currently used for bonding applications.

4:30pm **TS3-1-10 Optimization and Functionalization of Anodized Titania Nanotubes for Redox Supercapacitor**, ***Z. Endut*** *(rg253c@yahoo.com), M. Hamdi, W.J. Basirun,* University of Malaya, Malaysia

In this paper, the optimization of electrochemical capacitance of anodized titania nanotubes in KOH electrolyte was done using response surface

methodology. The nanotubes were functionalized with nickel oxide (NiO) nanoparticles using electrophoretic deposition (EPD) for redox-type supercapacitor. Effect of anodization parameter of titania nanotubes on discharge time was studied using Box-Behnken design and their structural, surface morphology and oxidation states were characterized. A study by Box-Behnken design shows that the effect of ammonium fluoride concentration is more significant to improve discharge time and specific capacitance. Optimized amount of fluoride concentration and anodization time resulted in longer nanotubes with high aspect ratio, thus higher discharge time and specific capacitance were obtained. Anodization of Ti foil for 97.78 min using voltage of 39.11 V and 0.42 wt % ammonium flouride concentration will obtain maximum discharge time of 43.69 s and specific capacitance of 145.6 uF cm-2. After functionalization of TNT with nickel oxide using EPD process, the electrochemical capacitance was improved from 0.42 mF cm-2 to 4.65 mF cm-2 measured in 1 M KOH. This enhancement comes from fast surface redox reaction at TNT-NiO electrode. This functionalized TNT-NiO is suitable for redox-type supercapacitor application.

Thursday Afternoon Poster Sessions

Coatings for Use at High Temperature
Room: Grand Hall - Session AP

Symposium A Poster Session
Moderator: A Bolcavage, Rolls Royce, B. Hazel, Pratt and Whitney

AP1 Thermal Stability of Ir – Re Coatings Annealed in Oxygen Containing Atmospheres, *Lin*, National Tsing Hua University, Taiwan, Republic of China, ***Y.I. Chen*** *(yichen@mail.ntou.edu.tw)*, National Taiwan Ocean University, Taiwan, Republic of China, *H.Y. Tsai*, National Tsing Hua University, Taiwan, Republic of China, *K.C. Liu*, National Taiwan Ocean University, Taiwan, Republic of China, *Y.H. Chen*, Young Optics Inc.

Ir–Re coatings were widely applied as protective coatings on glass molding dies. Because of the glass molding process in mass production was performed in an oxygen containing atmosphere at high temperature, the protective coatings need to endure cyclic annealing treatments. Less attention has been paid to the oxidation and thermal stability of the Ir–Re coatings. In this study, Ir–Re coatings were prepared by co-sputtering. The constant-temperature annealing treatments were conducted at 600 °C under atmospheres of 10 ppm O_2–N_2, a glass molding atmosphere, and 1 % O_2–Ar, an accelerating oxidation atmosphere, respectively. The thermal cyclic test was performed between 200 and 600 °C under a 10 ppm O_2–N_2 atmosphere. The variations in crystalline structure, nanohardness, surface roughness, residual stress and chemical composition profiles in depth after various annealing times were investigated.

AP2 Steam Oxidation of Al Slurry Coatings Deposited on Super304H, TP347H and TP347HFG, ***M. Seraffon*** *(maud.seraffon@npl.co.uk)*, *A.T. Fry*, National Physical Laboratory, UK

Commercial, regulatory and social pressures have led the energy industry to improve power plant efficiency by increasing the operating temperatures and pressures of combustion plant, moving from conventional plant, with operating steam temperatures and pressures of 540 °C and 180 bar, to advance ultra-supercritical plant with steam temperatures >700 °C and pressures > 300 bar. Such an increase in operating conditions would increase the plant efficiency from 42% to an estimated 55%. These increased operating conditions place current materials in extremely aggressive environmental conditions. Current ferritic-martensitic steels do not possess the high temperature capability, with a temperature limit of ~620 °C. There is a need therefore to move towards using more austenitic alloys. Experience of austenitic materials in the US has shown that some alloys are susceptible to early spallation under steam oxidation conditions leading to rapid breakaway oxidation. One method to prevent this is the use of high temperature protective coatings. Aluminide coatings have been developed for use on ferritic steels with encouraging results. These coatings combine good high temperature oxidation resistance through the growth of an Al_2O_3 scale and, in the case of Al slurry, the possibility to apply the coating on an industrial scale at moderate cost. However, there is little information and understanding of the behaviour of the same coatings on austenitic alloys. The purpose therefore of the work reported here was to examine and generate the necessary data on the microstructural evolution of Al slurry coated austenitic alloys subjected to oxidising atmosphere of 100% flowing steam at 700 and 750 °C for times up to 5000 hours at atmospheric pressure. The coating prevented breakaway oxidation on samples exposed at 700 °C and delayed the onset of breakaway until 3000 hours at 750 °C showing the protective potential of the coating. Measurement of the Aluminium diffusion showed that it diffused outwardly to form a protective Al_2O_3 layer and inwardly into the substrate to form an Aluminium diffusion zone and precipitates of AlN and Ni-Al. Despite differences in Al diffusion behaviour between the three austenitic alloys, indicating an influence of initial composition and grain size, the time at which breakaway oxidation occurred was identical, suggesting that the Al slurry coating provided the same level of protection on the three alloys.

This paper presents the steam oxidation results for the three coated alloys comparing the oxidation behaviour between the three and also referencing back to the performance of the uncoated alloys.

AP5 Structure of Pd-Zr and Pt-Zr Modified Aluminide Coatings Deposited by CVD Method on Nickel Superalloys, ***M. Pytel*** *(mpytel@prz.edu.pl)*, Rzeszów University of Technology, Poland, *R. Filip*, *M. Goral*, Rzeszow University of Technology, Poland, *J. Sieniawski*, Rzeszów University of Technology, Poland

In the article the structure of newly developed modified aluminide coating will be characterized. The coatings were obtained by Pt and Pt electroplating and CVD low-activity aluminizing process. The Pt and Pd electroplated samples were modified by Zr doping during CVD-low activity aluminizing as well. Coatings were deposited using BPX Pro 325S semi-industrial CVD system on Research and Development Laboratory for Aerospace Materials at Rzeszow University of Technology. In the paper the process parameters were described and the results of microstructural analysis as well. The microstructure analysis was conducted using Hitachi S-3400 scanning electron microscope equipped by EDS analyzer (Thermo). The XRD and GDOES analysis were also made. The results showed that thickness of coatings was in range 40-70 mm. The obtained coatings were single-phase type (Ni,Pt/Pd)Al. The newly produced coatings will be a new type of bond coat for thermal barrier coatings with ceramic layer deposited by EB-PVD coating.

AP6 TBCs Deposited using New EB-PVD Smart Coater System, ***A. Nowotnik*** *(nowotnik@prz.edu.pl)*, Rzeszow University of Technology, Poland, *M. Goral*, *J. Sieniawski*, *M. Pytel*, Rzeszów University of Technology, Poland

In the article the characterization of new type of EB-PVD device will be described. Especially the comparison with actually used industrial EB-PVD systems will be conducted. The current status of electron beam physical vapor deposition in ceramic coating development will be analyzed. The Smart Coater device is a new solution developed by ALD Vacuum Technology in cooperation with Research and Development Laboratory for Aerospace Materials in Rzeszow University of Technology. The newly developed system is smaller and cheaper in comparison with other EB-PVD system. The microstructural and phase analysis of developed TBCs will be presented. The CMSX-4 nickel superalloy was used as a base material. The platinum and palladium aluminide coatings were used as a standard type of bond coats. The newly developed Zr - modified aluminide coatings deposited by CVD method were used as well. The combination of CVD and EB-PVD using newly developed devices enables to cost reduction in TBCs production and increase of turbine blades lifetime.

AP8 Influence of Deposition Parameters on Structure of Diffusion Aluminide Coatings Obtained by CVD Method on Rene 108 DS Superalloy, ***L. Swadzba*** *(lucjan.swadzba@polsl.pl)*, *B. Witala*, Silesian University of Technology, Poland, *R. Swadzba*, Institute for Ferrous Metallurgy, Poland, *M. Hetmanczyk*, *G. Moskal*, *B. Mendala*, Silesian University of Technology, Poland, *L. Komendera*, AVIO Poland sp. z o.o., Poland

Chemical vapor deposition (CVD) method plays meaningful role in deposition of aluminide coatings on nickel based superalloys. Owing to this method it is possible to deposit aluminide coatings in cooling channels which is difficult using other methods. In this paper result of development and properties of high-temperature coating deposited on Rene 108 DS superalloy will be presented. Result of diffusion aluminizing using CVD apparatus built in Silesian University of Technology will be presented. An influence of technological parameters such as: temperature, pressure in retort, chemical composition of reactant gases on microstructure, thickness and phase composition of aluminide coatings will be described. Further processes were conducted using additional source granules consisting of Ni, Al, Cr and were modified by reactive elements. Aluminide coatings were investigated by light microscopy, scanning electron microscopy (SEM), electron probe microanalysis (EPMA) and X-ray diffraction analysis (XRD).

AP9 Research on High Temperature Property of Plasma Sprayed Lanthanum Cerium Oxide Thermal Barrier Coatings, *R. Wang (wsx161@163.com)*, ***T. Wu***, *W. Wang*, Beijing Aeronautical Technology Research Center, China

With the development of aircraft gas turbine, requirement novel ceramic top coating material to improve temperature capability of thermal barrier coatings. In this paper, lanthanum cerium oxide (LCO) spray powder and plasma sprayed coatings high temperature properties was investigated. LCO spray powder keep phase stability at 1500℃. And the powder composition was not changed during thermal treatment. However, the content of Ce element in plasma sprayed coats decreased during thermal treatment at 1500℃. Spray power and exposure temperature has evident influence on

plasma sprayed coats high temperature phase stability. Phase stability of plasma sprayed coat can be improved by reducing spray power.

AP10 Calcium-Magnesium Aluminosilicate (CMAS) Reactions and Degradation Mechanisms of Advanced Environmental Barrier Coatings, *N. Ahlborg*, The Ohio State University, US, ***D. Zhu*** *(Dongming.Zhu@nasa.gov)*, NASA Glenn Research Center, US

Environmental barrier coatings (EBCs) are used to protect future Si-based ceramic matrix composite (CMC) turbine engine hot-section components from oxidation and corrosion and extend component lifetimes. Future high efficiency engines require significantly higher operating temperatures and reduced component cooling, leading to accelerated infiltration and reactions of ingested calcium-magnesium aluminosilicates (CMAS) sand and ash within the engine hot section components. This study primarily focuses on the reactions and degradation mechanisms between CMAS and several advanced EBC material systems, including rare earth (RE)-silicates Yb_2SiO_5, $Y_2Si_2O_7$, and RE-oxide doped HfO_2 and ZrO_2 at 1500ºC. The microstructure and phase characteristics of CMAS-EBC specimens were examined using Scanning Electron Microscopy (SEM) and X-ray Diffraction (XRD). Results showed that the CMAS dissolved RE-silicates to form crystalline, highly non-stoichiometric apatite phases. Cross-section images show that the CMAS deeply penetrated into the EBC grain boundaries and formed extensive grain boundary low-melting eutectic phases, causing grain boundary recession with increasing testing time in the silicate materials. The preliminary results also showed that CMAS reactions also formed low melting grain boundary phases in the higher concentration RE-oxide doped HfO_2 systems. The effect of the test temperature on CMAS reactions of the EBC materials will also be discussed.The faster diffusion exhibited by apatite and RE-doped oxide phases and the formation of extensive grain boundary low-melting phases may limit the CMAS resistance of some of the environmental barrier coatings at high temperatures.

AP11 An Experimental Method for Determining the Mode II Interfacial Toughness of Thermal Barrier Coatings, ***S.J. Lockyer-Bratton***, *J.A. El-Awady, K.J. Hemker (hemker@jhu.edu)*, Johns Hopkins University, US

Experimentally measured interfacial fracture toughness is a critical parameter in determining the lifetime of thermal barrier coating (TBC) systems. Currently no reliable test method has been created to evaluate this property under pure Mode II conditions, which are most representative of critical TBC delamination upon turbine engine cool down. A newly developed compression edge delamination test sample has been employed to measure the strain energy release rate, G, associated with delamination between the bond coat and top coat under a nearly pure Mode II loading condition. The material systems tested consist of an electron beam physical vapor deposited (EBPVD) 7% yttria-stabilized zirconia (YSZ) top coat on either a 1) Pt-modified aluminide diffusion bond coat on a René N5 substrate or a 2) low pressure plasma spray (LPPS) NiCoCrAlY bond coat on a PW1484 substrate. Sample design as well as a unique sample fixture designed for use during the bond coat and top coat application processes are discussed. A detailed finite element model is used to evaluate the experimental results and show the effects of material layer properties and crack face friction on *G*.

AP12 Isothermal Oxidation of a Single Crystal N5 Superalloy in the Range of 1050°C to 1150°C, ***R. Swadzba*** *(rswadzba@gmail.com)*, Institute for Ferrous Metallurgy, Poland, *B. Witala*, *L. Swadzba*, Silesian University of Technology, *L. Komendera*, AVIO Polska

The paper concerns behavior of Rene N5 2nd generation single crystal Ni superalloy during isothermal oxidation in dry oxygen at 1050°C, 1100°C and 1150°C for 100h. The oxidation tests were performed using Mettler Toledo apparatus for isothermal oxidation tests with high accuracy mass control. The mass change curves of the samples oxidized at 1050°C, 1100°C and 1150°C are presented along with corresponding microstructures. High resolution CTEM and S/TEM techniques were applied for a detailed characterization of oxide scales formed after 100h of oxidation at 1050°C, 1100°C and 1150°C for a direct comparison of the phase composition and chemistry of the oxides and the interfaces between them. High resolution S/TEM EDS elemental mappings were performed in order to study segregation of elements to grain boundaries of the alumina scales. The samples for S/TEM analysis were prepared using FIB (Focused Ion Beam).

AP13 Boron Distribution in High Temperature Silicide Coatings for Niobium Alloys: An Analytical Problem Which can be Solved using a Coupled WDS-EDS System, *S. Mathieu (sandrine.mathieu@scmem.uhp-nancy.fr), L. Portebois*, ***N. Chaia***, Université de Lorraine, France

Progresses in the field of gas-turbine engine for aircraft are controlled by the availability of structural materials able to withstand higher-temperature hostile environments (very significant flow conditions containing aggressive elements such as water vapor, at more than 1150°C). The efficiency of intermetallic silicides $Ti_3X_3CrSi_6$ (M_7Si_6-TiX with X=Fe,Co or Ni) as protective coatings (bond coats) for niobium alloys against oxidation was demonstrated through many works. These compounds are manufactured by halide activated pack-cementation technique. During oxidation tests, these coatings develop a duplex protective chromia /silica oxides scale. These refractory silicides present a ductile brittle temperature transition around 900-1000°C that led sometimes to the formation of cracks throughout the coatings. This behavior is mainly observed when the coated pieces endure rapid change of temperature, e.g, oxidation in cyclic conditions. Therefore boron was added in these coatings by the cementation way in order to increase the fluidity of silica and to obtain self-healing oxides scale.

Whatever the nature of the matrix around, boron is generally difficult to characterize both qualitatively and quantitatively using SEM and its associated analyses techniques (EDS and WDS spectrometry) based on X-ray emission because of the low rate of emission of this light element. In the present case, the complex chemical composition of the substrate (Nb, Ti, Hf, Fe, Cr, Si) renders still more difficult the characterization of boron because of the spectral interference which exists between the Nb (M_z) and B (K_α) X-ray. To separate both contributions, those of boron and niobium, a coupled WDS-EDS system was employed. Elaboration of boron containing standards was also required.

The present paper aimed at presenting the optimization of the analytical conditions that allowed the location of boron in the coating both post-manufacturing and post-oxidation tests.

AP14 Evaluation of EBPVD Top Coat Modulus Using Micro-beam Bending Techniques, ***B. Zhang*** *(binwei.zhang5@gmail.com), K.J. Hemker*, Johns Hopkins University, US

Layered thermal barrier coatings are widely used to protect underlying superalloy components from high temperature oxidation. Commercial systems are typically composed of a yittra-stabilized zirconia (YSZ) top coat, a thin thermally grown oxide (TGO), and an intermetallic bond coat on top of the superalloy substrate. Interfacial delamination between the top coat and the bond coat are often observed after cyclic thermal exposure, due in part to the stresses that arise from the mismatch of thermal expansion coefficients of the materials. To evaluate the thermally induced residual stress and predict resulting interfacial failure, the Young's modulus of the top coat is of primary interest. In this study, micro-beam bending techniques for both attached and free-standing YSZ coatings has been developed to assess the as-deposited top coat modulus as a function of substrate geometry. A tension/compression asymmetrical behavior of top coat was observed, and finite element analysis was carried out to quantify the modulus values.

Hard Coatings and Vapor Deposition Technology
Room: Grand Hall - Session BP

Syposium B Poster Session

Moderator: A. Anders, Lawrence Berkeley National Laboratory, US, C. Rebholz, University of Cyprus, J. Vetter, Sulzer Metaplas

BP1 High Temperature Wettability of Ion Implanted Multicomponent CrAlSiN by Molten Glass, *YY Chang (yinyu@mail2000.com.tw)*, ***H.M. Lai***, National Formosa University, Taiwan, Republic of China, *H.Y. Kao*, MingDao University, Taiwan, Republic of China

Metal plasma ion implantation has being successfully developed for improving wear, corrosion, and physical properties of engineering materials. In this study, the multicomponent CrAlSiN coating was deposited on tungsten carbide substrates by using a cathodic-arc deposition system with lateral rotating arc cathodes. Mo, V and C ions were co-implanted into the multicomponent CrAlSiN film using a metal-plasma ion implantation apparatus. The accelerating voltage of metal ions was set at 40 kV with implantation doses of 1~2 x 10^{17} ions/cm^2. The microstructure of the implanted 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. X-ray diffractometry was performed for phase identification using a PANalytical X'pert Pro diffractometer with a high resolution ψ goniometer and Cu radiation in both glancing angle and high-angle configurations. Mechanical properties, such as the hardness and elastic modulus, were measured by means of nanoindention. The wettability of the implanted CrAlSiN by molten glass at temperatures at 500°C in controlled air was measured by using an improved sessile drop method. The Mo, V and carbon ion implanted CrAlSiN had a lower oxidation rate and a higher contact angle than the CrAlSiN coated samples. Therefore, the kinetic oxidation behavior and wettability varied with the surface alloy composition and phase segregation via high temperature oxidation. Results of this study demonstrate the potential of metal plasma ion implantation in improving the wettability behavior of the CrAlSiN film by molten glass.

BP2 Mechanical Properties and Impact Resistance of Multilayered CrAlSiN/TiN Coatings, *Y.Y. Chang (yinyu@nfu.edu.tw)*, National Formosa University, Taiwan, Republic of China, ***Y.Y. Liou***, MingDao University, Taiwan, Republic of China

Transition metal nitrides, such as TiN and CrN, have been used as protective hard coatings due to their excellent tribological properties. In this study, TiN, CrAlSiN and multilayered CrAlSiN/TiN coatings were synthesized by cathodic-arc evaporation with plasma enhanced duct equipment. Titanium and CrAlSialloy cathodes were used for the deposition of CrAlSiN/TiN coatings. During the coating process of multilayered CrAlSiN/TiN, TiN was deposited as an interlayer to enhance better adhesion. The total cathode current of both Ti ($I_{[Ti]}$) and CrAlSi ($I_{[CrAlSi]}$) targets was controlled at 140 A. With different bias voltages and cathode current ratios ($I_{[CrAlSi]}/I_{[Ti]}$) of 0.75, 1.0, and 1.33, the deposited multilayered CrAlSiN/TiN coatings possessed different chemical contents and periodic thicknesses. The nanolayer 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 coatings. 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 multilayered CrAlSiN/TiN 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.

BP3 Mechanical Properties and Physicochemical Characteristics of CrN/Si_3N_4 Multilayers, ***C. Aguzzoli*** *(caguzzol@ucs.br)*, *T. Soares*, Universidade de Caxias do Sul, Brazil, *G. Soares*, Universidade Federal do Rio Grande do Sul, Brazil, *C.A. Figueroa*, Universidade de Caxias do Sul, Brazil, *I. Baumvol*, Universidade de Caxias do Sul, Brazil and Universidade Federal do Rio Grande do Sul, Brazil

We investigated the mechanical and physicochemical properties of CrN/Si_3N_4 multilayered coatings in the period interval 2 to 10 nm, produced by depositing the thin film multilayer structure at substantially higher substrate temperatures than in previously reported works. This resulted in an appreciable increase in hardness at a multilayer period around 4 nm, as well a corresponding increase in the resistance to plastic deformation of the coating for multilayer periods around 4 to 6 nm. The various physicochemical characterization techniques used here revealed that the individual CrN and Si_3N_4 layers were stoichiometric and the interfaces were abrupt, while the Si_3N_4 layers were amorphous and the CrN ones crystalline. Furthermore, Si is mainly bonded to N as Si_3N_4 and maybe some other non-stoichiometric Si-N compound, whereas Cr was bonded as CrN and chromium oxides.

Keywords: Multilayers; Hardness; Si_3N_4/CrN

BP4 Reliability Characteristics of Multi-Step Deposition-Annealed HfO_2 Film under Static and Dynamic Stress, *YL Cheng (yjcheng@ncnu.edu.tw)*, *C.Y. Hsieh*, National Chi-Nan University, Taiwan, Republic of China, ***T.C. Bo***, National Chi Nan University, Taiwan, Republic of China

The physical, electrical and reliability characteristics of the HfO_2 gate stack fabricated by a single-step and a multiple-step deposition-annealing method are compared in this study. After the same high temperature (750°C) annealing, the single-step HfO_2 has transformed into a polycrystalline phase, while the multi-step HfO_2 is found to remain in a nanocrystalline phase, indicating that a multi-step deposition-annealing method could significantly improve the thermal stability of the high-*k* HfO_2 film with respect to the grain formation process. Additionally, the density and composition of the high-*k* HfO_2 film are enhanced by multi-step deposition-annealing process. These changes lead to an improvement in the electrical characteristics, breakdown voltage, and reliability of the multi-step HfO_2 film. The reliability characteristics of multi-step deposition-annealed HfO_2 dielectric under unipolar and bipolar AC stresses were also evaluated. Dielectric breakdown failure time of bipolar AC stress becomes longest in comparison to the other two stresses. Moreover, as the number of deposition-annealing steps increases, a larger lifetime enhancement is detected due to the effective charge de-trapping for multi-step deposition-annealed HfO_2 dielectrics under bipolar stress.

BP5 Wear Properties and Microstructure Characterization of Various Fe-W-C-B-Cr System Clad Layers, ***Y.C. Lin***, *Y.C. Chen (chen735@ntu.edu.tw)*, National Taiwan University, Taiwan, Republic of China

Hard boride and carbide were both synthesized *in situ* as clad layers generated using the GTAW method. In this investigation, Fe, C and Cr-containing SKD61 and SKD11 substrates with tungsten boride (WB) powder were synthesized *in situ* in various phases in the clad layer. According to the results concerning hardness and microstructure, the Fe-W-C-B-Cr system clad layers had a high hardness, caused by precipitation hardening by various precipitates. Additionally, high C and Cr contents (WB-SKD11 specimen) lead to a clad layer with a hard and complex structure. The Fe-W-C-B-Cr system clad layers are quite thick, with a mean thickness of 6 mm. In the scanning electron image, the soft region of the heat-affected zone (HAZ) of the WB-SKD11 specimen had a bainite and retained austenite structure, owing to the high C and Cr contents in the substrate. However, the WB-SKD61 specimen had no soft region; its HAZ displayed the martensite structure. The hardness of the WB-SKD61 specimen gradually decreased as the distance from the clad surface increased. Cryogenic treatment of the WB-SKD11 specimen reduced some of the retained austenite structures and significantly improved the hardness values of the HAZ. During sliding, the hard vein-shaped phase in the WB-SKD11 clad layer provided strong mechanical interlocking. Therefore, the wear performance of the WB-SKD11 clad layer was substantially better than that of the other specimens under all test conditions.

BP6 Effect of Cu Diffusion on Electrical and Reliability Characteristics for Low Dielectric Constant Dielectric, *YM Chang*, National Chiao Tung University, Taiwan, Republic of China, *YL Cheng (yjcheng@ncnu.edu.tw)*, ***K.C. Kao***, National Chi-Nan University, Taiwan, Republic of China, *J.P. Leu*, National Chiao Tung University, Taiwan, Republic of China, *T.C. Bo*, National Chi-Nan University, Taiwan, Republic of China

The interaction between copper interconnect and dense or porous low dielectric constant films under thermal annealing was investigated in this study. The electrical and reliability characteristics were investigated using Cu/Low-k film/Si metal insulator metal capacitors. The experimental results showed that copper diffusion depth increased with the annealing temperature and annealing time in both low-*k* films. Moreover, the copper diffusion rate in the porous low-*k* films is faster and is dominated by the annealing temperature, so that a large increase in the dielectric constant was observed. The lifetimes of porous low-*k* films are shorter than those of dense low-*k* films by about two orders when stressed under the same electric field (4.7 MV/cm). Furthermore, we found that the leakage current increase and the low-*k* dielectric breakdown lifeti me are proportional to the copper diffusion depth for dense or porous low dielectric films. Therefore, the copper diffusion depth ca n be an indication of the fast reliability evaluation for the future low-*k* dielectrics applications.

BP7 Zirconium Modified Aluminide Coatings Obtained by the CVD and the PVD Methods., ***J. Romanowska*** *(jroman@prz.edu.pl)*, *M. Zagula-Yavorska*, *J. Sieniawski*, Rzeszów University of Technology, Poland, *J. Markowski*, Wrocław University of Technology, Poland

The paper presents the comparison of the structures of the zirconium modified aluminide coatings deposited on pure nickel by the CVD and PVD processes.

In the CVD process, zirconium was deposited from the $ZrCl_3$ gas phase at the 1000 ºC. In the PVD process, the zirconium layer 7 μm thick and the aluminum layer 0.5 μm thick or zirconium layer 7 μm thick and the aluminum layer 0.7 μm thick were deposited by the Electron Beam Evaporation method. Deposition velocity was about 1 μm/min. The layers obtained by the Electron Beam Evaporation method were subjected to diffusion heating at 1050 ºC for 2 h in the argon atmosphere. The obtained coatings were examined by the use of an optical microscope (microstructure and coating thickness) a scanning electron microscope (chemical

composition on the cross-section of the modified aluminide coating) and XRD phase analysis. Microstructures and phase compositions coatings obtained by different methods are differ significantly. NiAl(Zr), Ni_3Al and Ni(Al) phases were found in the CVD aluminide coatings, whereas Ni_5Zr and γNi(AlZr) were observed in coatings obtained by the PVD method. The results indicate, that the microstructure of the coating is strongly influenced by the method of manufacturing.

BP8 Phase Stability, Thermal Stability and Oxidation Resistance of Arc evaporated Ti-Al-Ta-N Coatings, ***R. Hollerweger*** *(robert.hollerweger@tuwien.ac.at)*, Christian Doppler Laboratory for Application Oriented Coating Development at Montanuniversitat Leoben and Vienna University of Technology, Austria, *M. Arndt*, *R. Rachbauer*, OC Oerlikon Balzers AG, Liechtenstein, *P. Polcik*, PLANSEE Composite Materials GmbH, Germany, *J. Paulitsch*, *P.H. Mayrhofer*, Vienna University of Technology, Austria

Alloying Ti-Al-N with Ta has proven to enhance the hardness, thermal stability and oxidation resistance of sputter deposited coatings. To meet a balance between all these requirements for protecting tools during drilling and cutting applications, an optimized chemical composition of Ti, Ta and Al within the cubic stability range is necessary. However, only limited information is available on arc-evaporated Ti-Al-Ta-N coatings. Therefore, coating developments with an industrial scaled INNOVA Oerlikon Balzers plant, using powder metallurgical $(Ti_{0.50}Al_{0.50})_{0.95}Ta_{0.05}$, $(Ti_{0.50}Al_{0.50})_{0.90}Ta_{0.10}$, $(Ti_{0.34}Al_{0.66})_{0.95}Ta_{0.05}$ and $(Ti_{0.34}Al_{0.66})_{0.90}Ta_{0.10}$ targets, were carried out and investigated with respect on their phase stability, mechanical properties as well as thermal stability and oxidation resistance. Vacuum annealing treatments exhibit retarded film decomposition by the addition of Ta. Consequently, the formation of the stable wurzite AlN phase is shifted to higher annealing temperatures of ~1200°C, accompanied by the formation of hexagonal Ta_2N. Furthermore, alloying Ta to Ti-Al-N promotes the formation of a dense oxide scale. Therefore, the Ti-Al-Ta-N coating is still intact under a protective oxide, even when treated at 950°C for 20h in ambient air.

BP9 Superhard and Corrosion Protective Coatings of Ta-Si-N and Nb-Si-N, ***G. Ramirez*** *(enggiova@hotmail.com)*, Argonne National Laboratory, US, *S. Rodil*, *S. Muhl*, Universidad Nacional Autónoma de México - Instituto de Investigaciones en Materiales, Mexico, *E. Camps*, *L. Escobar-Alarcon*, Instituto Nacional de Investigaciones Nucleares de Mexico

In this work two different superhard coatings that improve the corrosion resistance were prepared, Nb-N-Si and Ta-N-Si.

The coatings were deposited using a reactive dual magnetron sputtering system, using two targets, one metallic target (Nb or Ta) and a silicon target, in a reactive mixture of gases (argon and nitrogen). Coatings with different concentrations of silicon were grown, which was controlled by varying the RF-power applied on the silicon target.

The microstructural properties, measured using X-ray diffraction, showed the growth of crystalline coatings presenting the FCC phase of the metallic nitrides (NbN or TaN). The composition of the films was measured using x-ray photoelectron spectroscopy (XPS). The hardness was obtained using the nanoindentation technique, finding the maximum values of hardness around to 5% at. of Si in both systems (Ta-N-Si and Nb-N-Si), with values higher of 35 GPa for the Nb-N-Si, and higher of 40 GPa for the Ta-N-Si.

The hardest films of Nb-N-Si and Ta-N-Si were grown on stainless steel substrates and evaluated using two different electrochemical techniques: DC polarization and electrochemical impedance spectroscopy. The films were compared with the substrate and with the NbN and TaN without silicon inclusion. The results showed a good improvement of the corrosion resistance in comparison to both the bare substrate and the metal nitride coating without silicon.

Scratch test was used to measure the adhesion of the coatings to the substrate, and the results showed that the Si inclusion in the TaN system improved the adherence of the coating compared with the TaN. However in the system of the Nb-N-Si there were not significant changes in the substrate-coating adhesion relative to the NbN coatings.

The most important conclusion of this research was that it was possible to design coatings presenting both properties; corrosion resistance and high hardness.

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BP10 Simple Relationships Between Characteristics of Complex Nitrides and Electronegativities and Radii of Constituent Elements, *V. Petrman*, University of West Bohemia, Czech Republic, ***J. Houska*** *(jhouska@kfy.zcu.cz)*, University of West Bohemia - NTIS, Czech Republic

The paper deals with characteristics of ternary (M_1M_2N) and quaternary ($M_1M_2M_3N$) metal nitrides (M = Ti, Zr, Hf, V, Nb or Ta) of various compositions obtained by ab-initio calculations. We focus on comparison of formation energies (E_0), bulk moduli (B), shear moduli (G) and an improvement of B and G over weighted average of B and G of binary metal nitrides (ΔB and ΔG) with electronegativities and atomic radii of the constituent elements.

For elastic moduli of M_1M_2N we find that ΔB (up to 19 GPa), ΔG (up to 20 GPa) and G itself increase with increasing difference between atomic radii of M_1 and M_2. In parallel, higher E_0 leads to higher ΔB (but lower B), and higher $|E_0|$ leads to higher ΔG.

For formation energies of M_1M_2N we find that (i) close atomic radii of M_1 and M_2 are sufficient for close to zero or highly negative E_0, while (ii) close electronegativities of M_1 and M_2 are necessary for highly negative E_0. The solubility of M_1N and M_2N surprisingly increases (formation energy of M_1M_2N decreases) with increasing difference between electronic structures of M_1N and M_2N. The lowest E_0 values were observed for Ta-containing M_1M_2N compositions.

For formation energies of quaternary M_1M_2TaN we show that in agreement with the above statement, E_0 is in all cases lower compared to M_1M_2N (at higher B). The drop in E_0 (improved solubility) resulting from Ta incorporation is more significant for lower atomic radius and higher electronegativity of the other metals M_1 and M_2.

Overall [1], we present trends which allow one to understand and predict which materials form (stable) solid solutions, and which materials exhibit enhanced elastic moduli. There is a special role of tantalum in stabilizing the solid solutions. The phenomena shown can be tested experimentally, and examined for a wider range of materials.

[1] V. Petrman and J. Houska, J.Phys: Condens. Matter, submitted (2012)

BP11 Internal Oxidation of Nanolaminated Nb–Ru Coatings, *Y.I. Chen (yichen@mail.ntou.edu.tw)*, ***H.N. Chu***, National Taiwan Ocean University, Taiwan, Republic of China

Nb–Ru multilayer coatings with various chemical compositions were deposited on silicon wafers by using a direct current magnetron co-sputtering system. By varying the substrate-holder rotation speeds, the Nb–Ru coatings exhibited distinct nanolaminated structures with various periods. The annealing treatments were conducted at 400°C, 500°C, and 600°C under atmospheres of 50-ppm O_2–N_2 and 1% O_2–Ar, respectively. The Nb oxidized preferentially when annealed in oxygen-containing atmospheres. The oxidized Nb–Ru coatings formed a nanolaminated oxide/metal structure, attributed to the internal oxidation behavior. The maintenance of nanolaminated structure for various Nb–Ru coatings after annealing was studied. The variations in crystalline structure, nanohardness, surface roughness and chemical composition of Nb–Ru coatings caused by annealing were widely investigated.

BP12 Phase Stability, Structural and Elastic Properties of Ternary $Cr_{1-x}TM_xN$ alloys: An Ab-initio Study, ***L. Zhou*** *(liangcai.zhou@tuwien.ac.at)*, Vienna University of Technology and Montanuniversität Leoben, Austria, *D. Holec*, Montanuniversität Leoben, Austria, *P.H. Mayrhofer*, Vienna University of Technology, Austria

In order to improve the mechanical properties, wear resistance and high temperature oxidation resistance of CrN coatings, alloying with other group IIIB-VIB transition metal (TM) elements (e.g., Y, Ti, Zr, Hf, V, Nb, Ta, Mo, W) becomes an important concept in the industrial area, and hence attracts also attention of the scientific community. In this paper with present an extensive first principles study of the phase stability, structural and elastic properties of Cr-containing cubic TM nitrides, where Cr substitutes for TM (i.e. $Cr_{1-x}TM_xN$). The calculated equilibrium lattice parameters exhibit a deviation from Vegard's linear interpolation to larger values. An addition of a small amount of TM elements into CrN results in softening of the material as measured by the bulk modulus, while significant increase in bulk modulus is predicted for Ta- and Nb-rich $Cr_{1-x}TM_xN$ alloys (x>0.6). The phase stability is studied as a function of the TM valence electron concentration and thus linked with the electronic structure. Finally, the single crystal elastic constants of $Cr_{0.5}TM_{0.5}N$ are calculated using the stress-strain method. Employing some representative sample textures allows us to discuss the influence of the TM on the polycrystalline elastic behavior of CrN. All these compositional trends are compared with the available experimental data.

BP13 Substrate Bias eEfects on the Wear and Hydrophobic Properties of CrAlN Coatings Prepared by Close Filed Unbalanced Magnetron Sputtering, *Y.S. Yang (yusen@nkfust.edu.tw)*, ***T.P. Cho***, *J.H. Lin*, National Kaohsiung First University of Science and Technology, Taiwan, Republic of China

CrAlN coatings were deposited in Ar/N2 plasma at 30-50% nitrogen flow rate ratios and DC pulsed substrate bias by using the reactive magnetron sputtering process. The hydrophobic and hydrophilic properties were evaluated by using water contact angle (WCA) measurement. Wear-resistant properties were evaluated by using ball-on-disc testers. Microstructure and morphology were observed using X-ray diffraction (XRD) and scanning electron microscopy (SEM). The experimental results show that the hardness and wear resistance increases obviously with increasing substrate bias from 0V to -100V. Due to the formation of (CrAl)2N solid solution phase at -60V substrate bias, the coatings exhibits the hydrophobic behavior with WCA at 104 degree. At high nitrogen flow rate ratios and low substrate bias the surface become hydrophilic with WCA lower than 90 degree.

BP14 Electrolyte-Insulator-Semiconductor (EIS) with Gd_2O_3-based Sensing Membrane for pH-Sensing Applications, ***H. Chen*** *(hchen@ncnu.edu.tw)*, National Chi-Nan University, Taiwan, Republic of China, *C.H. Kao*, Chang Gung University, Taiwan

The electrolyte-insulator-semiconductor (EIS) devices with $Gd_2O_{3\ 5}$ sensing membranes were fabricated on 4-in p-type (1 0 0) Si wafers, which have a resistivity of 5–10 Ω -cm. After standard RCA clean process, samples were dipped into 1% hydrofluoric acid to remove native oxide from the surface. A ~ 25nm Gd_2O_3 film was deposited on Si substrate through reactive sputtering from a Gadolinium target in diluted O_2 Samples were annealed at different temperatures (700℃.800℃.900℃) by rapid thermal annealing (RTA) in O_2 ambient for 30 sec. The back-side contact of the Si wafer was deposited by Al film with 300nm-thick. Then sensing membrane size was defined through photolithographic processing under a photosensitive epoxy (SU8-2005, MicroChem Inc.) that behaves as an antacid polymer. EIS devices were then fabricated on the copper lines of a printed circuit board by using a silver gel to form conductive lines. A hand-made epoxy package was employed to encapsulate the EIS structure and the copper line. The physical properties of the high-k Gd_2O_3 and Gd_2TiO_5 sensing membrane are investigated by Atomic Force Microscopy (AFM). Besides, to evaluate the sensor performance, PH sensitivity, hysteresis, and drift rate were measured to find the most preferable treatment condition.

BP15 Reactive and Non-reactive Sputter Deposition of Metallic, Intermetallic and Ceramic Target Materials to Prepare Al-Cr-N Coatings, ***C. Sabitzer*** *(corinna.sabitzer@tuwien.ac.at)*, Christian Doppler Laboratory for Application Oriented Coating Development at the Institute of Materials Science and Technology, Vienna University of Technology, Austria, *J. Paulitsch*, Vienna University of Technology, Austria, *P. Polcik*, PLANSEE Composite Materials GmbH, Germany, *M. Arndt, R. Rachbauer*, OC Oerlikon Balzers AG, Liechtenstein, *P.H. Mayrhofer*, Vienna University of Technology, Austria

$Al_xCr_{1-x}N$ coatings are highly valued for various industrial applications based on their outstanding mechanical properties and oxidation resistance. Even though deposition parameters like partial pressure, gas mixture or temperature are well investigated and optimized; only little information is available on the influence of the target material itself. Therefore, $Al_xCr_{1-x}N$ coatings were deposited by reactive and non-reactive unbalanced magnetron sputtering using three different powder-metallurgically prepared targets: a metallic Al/Cr target, an intermetallic $AlCr_x$ target and a ceramic AlN/CrN target. XRD analyses indicate for all targets tested a single cubic microstructure. The coatings deposited from the metallic and intermetallic target demonstrate a columnar structure with a pronounced (111) orientation whereas the coating deposited from the ceramic target is fine crystalline with (200) orientation. Furthermore, the hardness is highest for those coatings prepared from the ceramic target material.

BP16 The Young's Modulus of Composite Spacer Contributed on the Stress Effect of N-MOSFET with Contact-etch-stop Layer Stressor, *Y.C. Chiou*, National Chiayi University, Taiwan, Republic of China, *C.C. Lee*, ***T.L. Tzeng***, Chung Yuan Christian University, Taiwan, Republic of China, *C.C. Huang (cchuang@ndl.org.tw)*, National Nano Device Laboratories, Taiwan, Republic of China

Contact-etch-stop layer (CESL) stressor is able to generate higher tensile stress on channel direction (s_{xx}) for enhancing N-MOSFET drive current. To analyze the analytic solution of residual stresses and bending in multi-layer/substrate systems, the Young's modulus of thin film could control this stress level of substrate surface except for the stress and thickness of thin film. In general, two dielectrical layers, LPCVD oxide and SiN, were formed a composite spacer with liner oxide and spacer nitride in succession for most of the device structures. The Young's moduli of LPCVD oxide and nitride were determined to 67-GPa and 375-GPa by using the nanoindenter, respectively . To address the concern topic, the Young's modulus of composite spacer with CESL stressor by using the Sentaurus/TSUPREM4 simulation is to study. The analytic result shows that the channel stress is obviously reduced with decreasing the Young's modulus of spacer materials. Furthermore, if liner oxide is kept at 15-nm, the reduction of spacer SiN width does not increase channel stress obviously, even the CESL stressor is closer to channel. Our experimental data strongly supports the aftermentioned simulation for identifying the role of liner oxide and spacer nitride. When the thickness of liner oxide is reduced from 15-nm to 5-nm, drive current of N-MOSFET is enhanced by 4% and without performance gain for thin remained SiN spacer but with 15-nm liner oxide.

BP17 Thermal Stability and Oxidation Resistance of TiAlN/TaAlN Multilayer Coatings, *C.M. Koller*, Christian Doppler Laboratory for Application Oriented Coating Development at Montanuniversitat Leoben and Vienna University of Technology, Austria, *R. Hollerweger*, Vienna University of Technology, Austria, *R. Rachbauer*, OC Oerlikon Balzers AG, Liechtenstein, *P. Polcik*, PLANSEE Composite Materials GmbH, Germany, ***J. Paulitsch*** *(joerg.paulitsch@tuwien.ac.at)*, Vienna University of Technology and Montanuniversität Leoben, Austria, *P.H. Mayrhofer*, Vienna University of Technology, Austria

Mechanical properties, thermal stability and oxidation resistance of $Ti_{1-x}Al_xN$ coatings are well investigated and recent studies indicated that these properties can considerably be improved by alloying elements such as Cr, Ta or Y to form quaternary nitrides. However within this study we want to focus on an architectural approach by depositing multilayer arrangements of TiAlN and TaAlN. Further on, combined processing of reactive arc-evaporated $Ti_{1-x}Al_x$ targets with either arced (arc) or sputtered (rsd) $Ta_{1-y}Al_y$ targets are carried out opening the possibility to deposit coatings with variable chemical and structural modulations.

Our investigations show that the $TiAlN_{arc}/TaAlN_{arc}$ multilayers exhibit enhanced thermal phase stability with peak hardness values of ~ 35 GPa up to T_a=1200 °C, whereas the $TiAlN_{arc}/TaAlN_{rsd}$ multilayers exhibit hardness values of ~35 GPa up to T_a=800 °C which decrease to ~32 GPa when T_a=1100 °C. However, oxidation investigations clearly demonstrate the advantage of this hybrid arc/rsd process as the $TiAlN_{arc}/TaAlN_{rsd}$ nitride coatings still remain intact after oxidising in air at 850 °C for 20 h, whereas the $TiAlN_{arc}/TaAlN_{arc}$ multilayer coatings are completely oxidised.

BP18 Investigation of Corrosion Properties in TiAlN/TiCrN Multilayer Coatings Deposited by CFUBMS, ***E. Demirci*** *(eedemirci@atauni.edu.tr)*, Atatürk University, Turkey, *O. Baran*, Erzincan University, Turkey, *Y. Totik, I. Efeoglu, T. Morteza*, Atatürk University, Turkey

Advanced tribological properties, high temperature oxidation resistance, excellent corrosion performance of Ti alloy coatings (such as TiN, TiAlN and TiAlN/CrN) make them an important candidate to be utilized in many applications such as tool coatings. In actual working environments one of the main degradation causes of thin films is corrosion; therefore its evaluation processes have high importance. In the present study, TiAlN/TiCrN multilayer coatings were deposited by closed field unbalanced magnetron sputtering from two Cr, one Al and one Ti targets. The structural properties of coatings have been analyzed by electron microscopy (SEM), X-Ray diffraction (XRD) and energy dispersive spectrometry (EDS). Additionally, corrosion properties of these coating were investigated by using polarization test unit.

Keywords: TiAlN/TiCrN; Corrosion; Multilayer Coating; Sputtering

BP19 Simulation of Neutral Gas Dynamics for PVD DC-MSIP and HPPMS Processes, *K. Bobzin*, ***N. Bagcivan***, *S. Theiss, R.H. Brugnara, M. Schäfer*, Surface Engineering Institute - RWTH Aachen University, Germany, *R. Brinkmann, T. Mussenbrock*, Institute for Theoretical Electrical Engineering - Ruhr University Bochum, Germany, *J. Trieschmann (trieschmann@iot.rwth-aachen.de)*, Surface Engineering Institute - RWTH Aachen University, Germany

PVD processes such as DC Magnetron Sputtering Ion Plating (DC-MSIP) and High Power Pulse Magnetron Sputtering (HPPMS) are commonly used to produce hard protective coatings for corrosion and wear resistance applications. A uniform layer of coating material is an essential requirement for an effective protection of the coated parts. It is therefore important to understand the gas dynamic processes inside the reactor chamber to optimize the quality of the coatings. In particular, the dynamics of the process gas as well as of the film forming particles sputtered from the target material are of interest. In complex industrial scale coating units the spatial distribution of particles can only be predicted using numerical models. Depending on the geometry of the reactor chamber and the process pressure, different computational models can be used. The flow regime and in consequence the appropriate numerical model is determined by the

Knudsen number (Kn) equal to the mean free path over the typical length scale. For Kn < 0.01, continuum models such as computational fluid dynamics (CFD) models allow for a precise description of the gas flow. In contrast, in pressure regimes with Kn > 2 only kinetic models provide an accurate description, e.g. the Direct Simulation Monte-Carlo (DSMC) method. Generalized limits for the validity of the different models in the transition regime 0.01 < Kn < 2 cannot be found.

In this work we investigate an industrial scale hybrid magnetron sputtering coating unit operated at pressures around $5 * 10^2$ mPa. Due to the low pressure, the magnetron discharge operates in the already mentioned transition regime. In consequence, both CFD as well as DSMC simulations may provide an appropriate physical description. For our analysis we employ the commercially available FLUENT software V14 and the freely available OpenFOAM simulation package. Results obtained using the CFD and the DSMC approach are compared to investigate the applicability of the different models. The CFD simulations reveal all the principle flow characteristics at relatively low computational costs. The computationally costly DSMC method, however, provides a more detailed picture of the flow dynamics inside the reactor chamber, in particular in regions where Kn ≈ 1. The kinetic approach provides a more precise description especially at small features of the geometry. In addition, the DSMC routines provided with OpenFOAM can easily be extended with respect to a kinetic description of the coating forming particles sputtered from the target materials. Resulting, this allows for an analysis of the coating formation on the substrates.

BP20 Oxidation Resistance and Mechanical Properties of Ta – Si – N Coatings, *Y.I. Chen (yichen@mail.ntou.edu.tw),* ***K.Y. Lin***, National Taiwan Ocean University, Taiwan, Republic of China

Ta–Si–N coatings were prepared by reactive direct current magnetron co-sputtering on silicon substrates. By varying the sputtering powers, Ta–Si–N coatings exhibited various chemical compositions and crystalline characteristics. The low Si-content Ta–Si–N coatings revealed a face centered cubic phase, whereas the high Si-content coatings revealed an amorphous phase in the as-deposited states. To explore the oxidation resistance and mechanical properties of the Ta–Si–N coatings, the annealing treatments were conducted in a 1%O_2-99%Ar atmosphere at 600 °C for 4–100 h. The material characteristics of the annealed Ta–Si–N coatings were examined by Auger electron spectroscopy, transmission electron microscopy, atomic force microscopy, and a nanoindentation tester. The Si oxidized preferentially in the Ta–Si–N coatings. The in-diffusion of oxygen during annealing was restricted by the formation of a SiO_x surface scale. Because of its resistance to oxidation and low surface roughness of 2–3 nm, Ta–Si–N coatings were proposed as a protective coating for die material utilized at high temperature in low oxygen containing atmospheres.

BP21 Structural and Optical Properties of Brominated Plasma Polymers, *M. Appolinario, A. Neto*, UNESP, Brazil, *W. Schreiner*, UFPR, Brazil, *N. Cruz, E. Rangel,* ***S. Durrant*** *(steve@sorocaba.unesp.br)*, UNESP, Brazil

Brominated amorphous hydrogenated carbon films were produced by the plasma polymerization of bromoform-acetylene mixtures. There is little extant literature on this type of film. Varying the proportion of bromoform in the mixture allowed the production of non-brominated to highly brominated films (up to about 43 at% Br); thus the main parameter of interest was the degree of bromination, R_B. The films were characterized by Fourier Transform Infrared Spectroscopy (FTIR) and X-ray Photo-electron Spectroscopy (XPS). Ultraviolet-visible Near-Infrared Spectroscopy was employed to allow calculation of the optical properties, such as the refractive index, n, absorption coefficient, α(E), where E is the photon energy, and the optical gap, E_g, as a function of R_B. Semi-empirical modeling of E_g as a function of R_B was applied. In addition, nano-indentation studies revealed the hardness, modulus and stiffness of the films.

BP22 First Principles Study of Alloying Trends in Ti—Al—N and Cr—Al—N Systems, ***D. Holec*** *(david.holec@unileoben.ac.at)*, Christian Doppler Laboratory for Application Oriented Coating Development at Montanuniversitat Leoben and Vienna University of Technology, Austria, *L. Zhou*, Vienna University of Technology and Montanuniversität Leoben, Austria, *R. Rachbauer*, Montanuniversität Leoben, Austria, *P.H. Mayrhofer*, Vienna University of Technology, Austria

We employ Density Functional Theory modelling to study the effect of early transition metal (TM) elements (Y, Zr, Nb, Hf, and Ta) on the structural and mechanical properties of Ti–Al–TM–N and Cr–Al–TM–N systems.

While Y decreases significantly the maximum solubility of AlN in the cubic phase of the alloy, the other elements have only a negligible effect when their amount is less than ~10at.% on the metallic sublattice. The lattice parameter bows out to larger values as compared with Vegard's linear interpolation, owing to a gradually changing character of the bonds in the alloy with composition. The chemical strengthening is most pronounced for Ta and Nb, although also causing smallest elastic distortions of the lattice due to their atomic radii being comparable with Ti and Al. This is further supported by the analysis of the electronic density of states.

Mixing enthalpy, used as a measure of the driving force for decomposition into the stable constituents, is enhanced by adding Y, Zr and Nb, suggesting that the onset of spinodal decomposition will appear in these cases for lower thermal loads than for Hf and Ta alloyed $Ti_{1-x}Al_xN$.

BP23 Pulsed Laser Deposition of Tetrahedral Amorphous Carbon Layers (ta-C) – Properties in Dependence of Laser Fluence on the Target- Surface, ***K. Guenther*** *(guenthe2@hs-mittweida.de), S. Weißmantel*, University of Applied Sciences Mittweida, Germany

Recently, we developed a novel method for the preparation of several micrometer thick super-hard tetrahedral amorphous carbon (ta-C) films with low internal stress. The method is a combination of excimer laser ablation for film deposition and excimer laser irradiation of as-deposited sub-layers for the reduction of the high stresses.

We will show that the variation of the laser beam spot size on the target surface influences the creation of particulates in the ta-C layers. With this the mechanical properties are affected. For the investigations ta-C layers have been deposited on hard metal substrates using only the nearly perpendicularly from the target surface ablated species. With the SEM, the particulates will be characterized. Nanoindentation was used for the measurement of hardness and the scratch test shows the critical loads.

Furthermore the influence of the repetition rates of the laser beam during the ablation process was analyzed. It was found that mechanical properties are not affected by the change of the repetition rates.

We will show that this variation of the laser beam spot size with the particulates must be taken into account if the mechanical properties of the ta-C layers should be optimized and that the deposition rate can be increased by using higher laser beam repetition rates.

BP24 Tribological Properties of TiN/TaN and TiN/TaN Doped CrY Multilayer Coatings at High Temperature, ***I. Efeoglu***, Atatürk University, Turkey, *O. Baran (obaran@erzincan.edu.tr)*, Erzincan University, Turkey, *E. Demirci, Y. Totik*, Atatürk University, Turkey

In this study, TiN/TaN and TiN/TaN doped CrY multilayer coatings were deposited on M2 substrates using Closed Field Unbalanced Magnetron Sputtering (CFUBMS). The structural properties of coatings were analyzed by using Xray Photoelectron Spectroscopy (XRD), (energy-dispersive spectroscopy) EDS, Scanning Electron Microscopy (SEM). The hardness values of coatings were determined with a microhardness tester. Friction and wear properties of the coatings were determined by using pin-on-disc tribometer at humid air and high temperature.

Key Words: TiN/TaN, CrY, multilayer coatings, CFUBMS

BP25 The Effect of Annealing Temperatures on the Hydrophobic Property of CrAlN Coatings, ***Y.S. Yang*** *(yusen@nkfust.edu.tw), T.P. Cho, J.H. Lin, S.H. Yang*, National Kaohsiung First University of Science and Technology, Taiwan, Republic of China

The CrAlN coatings were deposited in Ar/N2 plasma by using the reactive magnetron sputtering process. The coating parameters were controlled at bias voltage -100 V and N2 flow rate ratio 40 %. The film thickness was controlled to be around 2μm. The CrAlN coatings were annealed for one hour between 600 and 1100℃ at 100℃interval. The hydrophobic and hydrophilic properties were evaluated by using water contact angle (WCA) measurement. The experimental results show that the as-deposited CrAlN coatings and annealing temperatures below 800℃ the surface exhibit hydrophobic property with WCA around 102°. As the annealing temperature increases from 800 to 1100℃, the WCA decrease evidently from 102° to 45° and the surface become more hydrophilic. The XRD results show that when the annealing temperatures were greater than 900 ℃ the Cr-Al-N phases were fully oxidized to become Cr_2O_3 and WCA drops from 78° down to 45°.

BP26 Effect of CO Gas for CVD Ti(C,N,O) Coating Layers on MT-TiCN Ⅰ: CO Gas Effect, ***S. Na*** *(nsw@taegutec.co.kr), J. Kim, E. Lee, D. Kim, S. Song, M. Sharon*, TaeguTec, Republic of Korea, *B. Min*, Yeungnam University, Republic of Korea

CVD deposited TiCNO layer was well known in cutting tool applications as one of buffer layer between the mid-temperature TiC_xN_y and alpha-Al_2O_3. The role of TiCNO layer is strong bonding between mid-temperature TiC_xN_y and alpha-Al_2O_3 layer, and texture control of Al_2O_3. Especially, the shape, composition and texture of TiCNO determine the alpha-Al_2O_3 texture and size.

In this study, $TiCl_4$-CH_4-CO based gas mixture was used for coating of TiCNO on the (422) and (311) based mid-temperature TiC_xN_y, which stands on the cemented carbide substrate. The range of CO gas volume was 0 to 2 % and over 2 μm coating layer was obtained to identify the shape and texture of TiCNO layer. Small amount of CO gas abruptly changed the shape and texture of TiCNO layer and the low Kv EDS mapping data showed incorporation of relatively large amount of oxygen at high temperature. Along with the EDS analysis, SIMS and EPMA analysis was also done for the composition variations of TiCNO with CO variations. Low angle backscattering SEM mode was used to achieve the exact shape of cross section of lenticular TiCNO, pore size and pore distributions. As increasing the CO gas volume, thickness of TiCNO layer goes to double at the same deposition time that compares to 0 % CO gas condition, and thinner and longer lenticular TiCNO was developed. The pore size of lenticular TiCNO reduced and the specific surface area increased at high amount of CO gas. Compare to mid-temperature TiC_xN_y, texture of CO gas involved TiCNO layers showed the strong (111) preferred orientation and portion of (200) and (220) also increased. XRD analysis indicated that low to high amount addition of CO gas brings the lattice contraction of TiCNO layer.

BP27 Effect of CO Gas for CVD Ti(C,N,O) Coating Layers on MT-TICN Ⅱ : Temperature Effect, *S. Na (nsw@taegutec.co.kr), **E. Lee**, J. Kim, D. Kim, S. Song, H. Han,* TaeguTec, Republic of Korea, *J. Lee,* Yeungnam University, Republic of Korea

There are many kinds of buffer layers between the mid-temperature TiC_xN_y and alpha-Al_2O_3 CVD coating on the cemented carbide cutting tool substrate. The role of buffer layer is strong bonding between mid-temperature TiC_xN_y and alpha-Al_2O_3 layer, and texture control of Al2O3. Additionally, buffer layer also requires the adequate physical properties as one of active layer for cutting. So, the size, density, composition and texture formation of buffer layer are important for the total performance of CVD based cutting tool.

This study focused on the temperature effect for one of carbon rich TiCNO base buffer layer formation. (422) and (311) based mid-temperature TiC_xN_y coating on the cemented carbide substrate was selected for substrate of buffer layer. Coating temperature was 1000 ℃, 950 ℃ and 900 ℃, and $TiCl_4$-CH_4-CO based gas mixture was used. Although the coating time was the same for three coating conditions, total coating thickness of three temperature condition was similar. But low angle back scattering SEM image for cross section of the coated buffer layer indicated that total volume of the coating layer was decreased by pores as the temperature decreasing. Shape of buffer layer also decreased with temperature deceasing and more sharp lenticular type buffer layer was obtained at low temperature. Low Kv EDS mapping data showed incorporation of relatively large amount of oxygen at entire temperature range. Along with the EDS analysis, SIMS and EPMA analysis was also done for the composition variations of each TiCNO layers. As the temperature decreasing, (111) preferred orientation was declined but intensity of (200) and (311) peak was increased.

BP28 Wear and Oxidation Behaviors of Ti(C, N, O) Coatings, *J.H. Hsieh (jhhsieh@mail.mcut.edu.tw), **Y.L. Lai**, Y.R. Cho*, Ming Chi University of Technology, Taiwan, Republic of China

It has been known that the life time of Ti-based hard coatings is dependent on the oxidation rate of Ti. Here, Ti(C,N,O) coatings prepared by a unbalance magnetron sputtering were studied and compared using a static oxidation approach as well as a pin-on-disc tribometer. Ti(C,N,O) thin film prepared with different N2/O2 flow rates were deposited on M2 steel substrates. The films properties were analyzed by Raman spectroscopy, SEM and X-ray diffraction. These samples then went through static oxidation and tribological testing. The surface morphology and the thickness of oxidation layer were obtained by using scanning electron microscopy (SEM).

In static oxidation, the formed titanium oxide (TiO2) was found to have mainly anatase structure at temperatures between 500ºC to 600ºC and transform to rutile structure at temperature higher than 600ºC. Through this study, oxidation rate and activation energy of oxidation for each sample were evaluated. It is found the samples exhibited higher activation energy could have higher oxidation resistance. These results are consistent with those obtained from wear testing.

BP29 Improved Performance of Metal-based Dye-sensitized Solar Cells by Introducing a TiN Nanocrystalline Thin Film, ***W.L. Tai**, F-Y. Ouyang (fyouyang@ess.nthu.edu.tw),* National Tsing Hua University, Taiwan, Republic of China

Metals foils have been increasingly used as alternative substrates for the flexible dye-sensitized solar cells (DSSCs) to overcome the limitations arising from the low sintering-temperature tolerance of the plastic substrates. However, the potential problem of metal corrosion in the iodide-based electrolytes threatens to degrade the performance and long-term stability of the metal-based DSSCs. To resolve this dilemma, we have employed unbalanced magnetron sputtering systems to prepare nanocrystalline TiN barriers on the metal substrates as a photo-electrode. The energy conversion efficiency of TiN deposited DSSC reaches about 4.5% under illumination with a light intensity of $100mW^{-2}$. The improved durability of DSSC has also been observed as compared to uncoated metal based DSSC. The mechanism of enhanced efficiency and durability of TiN coated DSSC will be discussed in this talk.

BP30 Super Smooth Nano-Structured Carbon Films with Cross-linked Graphitic Sheets Induced by ECR Ion Irradiation, *X. Fan,* Key Laboratory of Education Ministry for Modern Design and Rotor-Bearing System, School of Mechanical Engineering, Xi'an Jiaotong University, China, *D.F. Diao (dfdiao@mail.xjtu.edu.cn),* School of Mechanical Engineering, Xi'an Jiaotong University; College of Mechatronics and Control Engineering, Shenzhen Univeristy, China, ***L. Yang***, Key Laboratory of Education Ministry for Modern Design and Rotor-Bearing System, School of Mechanical Engineering, Xi'an Jiaotong University, China

Nano-structured carbon films with cross-linked graphitic sheets exhibited good mechanical and electrical properties. When applying the films in the ultra precision system, very smooth surface is needed. We studied that the nanostructure of carbon films was tailored by ion irradiation energy in electron cyclotron resonance (ECR) sputtering, and the surface morphology was smoothed simultaneously. The nanostructure and bonding configuration were characterized by transmission electron microscopy (TEM) observation, Raman and X-ray photoelectron spectroscopy (XPS) spectra analysis. Upon increasing of ion irradiation energy, the graphitic sheets in nanocrystalline graphite were cross-linked with sp^3 bonds. XPS results and the peak density ratio of I_D/I_G from Raman spectra also showed the increase of sp^3 bonds content. The surface morphology of the nano-structured carbon films were tested by atomic force microscopy (AFM). Results indicated thatthe mean surface roughness (Ra) was decreased from 0.2 nm to 0.03 nm when the nanostructure changed from graphite clusters to cross-linked graphitic sheets. Super smooth carbon films correlated with the cross-linked graphitic sheets nanostructure was obtained by ECR ion irradiation.

BP31 Influence of the Bilayer Period on the Structure of AlN and the Mechanical Properties of CrN/AlN Multilayer Coatings, ***P.H. Mayrhofer** (paul.mayrhofer@tuwien.ac.at),* Vienna University of Technology, Austria, *M. Schlögl,* Vienna University of Technology and Montanuniversität Leoben, Austria, *B. Mayer, V Chawla, D. Holec,* Montanuniversität Leoben, Austria

CrN/AlN multilayer coatings exhibit improved mechanical properties and thermal stability, especially when a superlattice structure is formed. To obtain this superlattice structure both layer materials (CrN and AlN) have to exhibit the same crystal structure and a similar lattice parameter. However, a systematic study on the influence of the individual layer thicknesses of CrN and AlN on structural and mechanical properties of CrN/AlN superlattice coatings is still missing. Therefore, CrN/AlN multilayer coatings were prepared by DC reactive magnetron sputtering with AlN layer thicknesses of 1, 2, and 3.3 nm and varying the CrN layer thicknesses from 0.9 to 10 nm. The thereby obtained bilayer period (Λ) and structure of the CrN/AlN coatings was investigated by low-angle and high-angle X-ray diffraction (LAXRD and HAXRD) as well as high-resolution transmission electron microscopy (HRTEM). The hardness as a function of Λ was determined with an ultra-micro-indentation system and the residual stresses were obtained by the substrate-curvature method at room temperature.

The results suggest that the minimum CrN layer thickness, necessary to stabilize the AlN layers in their metastable cubic structure, is in the range of the AlN layer thickness themselves. Hence, for the CrN/AlN coatings composed of 1, 2, and 3.3 nm thin AlN layers the CrN layers need to be at least 1, 2, and ~3 nm, respectively. For thinner CrN layers an X-ray amorphous structure or a multiphase arrangement of cubic, wurtzite-like, and amorphous phases is obtained. Exemplarily, the CrN/AlN superlattice coating composed of 1 nm thin AlN and 1.9 nm thin CrN layers (Λ = 2.9 nm) was investigated by cross-sectional HRTEM. These studies confirmed the superlattice structure–suggested by LAXRD and HAXRD–by the almost perfect hetero-epitaxial relationship between c-CrN and c-AlN. This CrN/AlN superlattice coating, as well as the one composed of 2 nm thin AlN and 3.5 nm thin CrN (Λ = 5.5 nm) exhibit a hardness maximum of ~31 GPa. If the AlN layer thickness is ~3.3 nm the hardness peak is obtained only with ~28.5 GPa for a bilayer period of Λ = 6.3 nm. The resulting hardness-peak as a function of the bilayer period becomes broader with increasing AlN layer thickness. A corresponding dependence on the bilayer period is also obtained for the compressive stresses.

Based on the results it can be concluded that the arrangement of 1 nm thin AlN layers with 1.9 nm thin CrN layers or 2 nm thin AlN layers with 3.5 nm thin CrN layers will result in the formation of a superlattice CrN/AlN

structure having a hardness of ~40 % above that of the layers they are formed.

BP34 Mechanical Properties and Interface Adhesion of Molybdenum Single Layer on Soda-lime Glasses, ***H.H. Sung***, National Chung Hsing University, Taiwan, Republic of China, *Z.C. Chang*, National Chin-Yi University of Technology, Taiwan, Republic of China, *L.Y. Kuo, F.S. Shieu (fsshieu@dragon.nchu.edu.tw)*, National Chung Hsing University, Taiwan, Republic of China

In this study, the Mo thin films were deposited on soda lime glass substrates through varies sputtering current by DC magnetron sputtering system. The structure of Mo films showed (110) preferred orientation. The electrical properties of Mo films indicated well conductive in this study. The mechanical properties of Mo thin films which were measured by nano-indentation, and the adhesion properties of interface between glass substrate and Mo film were investigated by nano-scratch. We were found that interface adhesion energy between Mo film and glass substrate was enhanced from 0.06 to 9.48 J/m^2, as sputtering current was increased. In this study, we were offered quantitative method to analysis adhesion properties, also including verify the feasibility in tribological application.

BP35 Effects of Silicon Content on the Structure and Mechanical Properties of (AlCrTaTiMo)N Coatings by Reactive Magnetron Sputtering, ***D.C. Tsai***, *F.S. Shieu (fsshieu@dragon.nchu.edu.tw)*, National Chung Hsing University, Taiwan, Republic of China

Si-doping (AlCrTaTiMo)N coatings were deposited onto Si substrate by the radio-frequency (RF) magnetron sputtering of a AlCrTaTiMo alloy target under direct current bias in a N_2/Ar atmosphere. The crystal, microstructural, mechanical, and electrical properties at different N_2-to-total (N_2+Ar) flow-rate ratios (R_N) values were investigated. As the silicon content reached 7.43 at%, the nitride remained as a simple NaCl-type face-centered cubic (FCC) structure. The lattice decline occur, implying that the incorporated silicon atoms can dissolve into the (AlCrTaTiMo)N lattice by substitution. The silicon incorporation significantly improved the mechanical properties and oxidation resistance of (AlCrTaTiMo)N coatings, however, deteriorated the electrical properties.

BP36 Effect of In-Situ Crystallization on the Microstructural and Photo-induced Properties of TiO_2 Coatings Prepared by Magnetron Sputtering, ***I. Sayah*** *(ima.sayah@gmail.com)*, *M. Arab Pour Yazdi*, LERMPS-IRTES, France, *F. Schuster*, CEA-Saclay, France, *A. Billard*, Lrc Cea/irtes-Lermps, France

TiO_2 coatings are still widely studied because of numerous potential industrial applications especially in the environmental fields such as water purification technology, due to its chemical stability, low toxicity, corrosion resistance and low cost [1].

In this study, TiO_2 thin films are deposited by reactive magnetron sputtering at high pressure on heated glass slides substrates (from 250 to 550 °C). All of the substrates are covered by 250 nm SiN_x barrier layer to avoid the alkali elements diffusion of glass and degradation of TiO_2 photocatalytic activity [2-3]. X-ray diffraction, scanning electron microscopy, water angle contact measurement and Orange G decomposition upon UV irradiation are used as characterization technics.

Synthesized films were crystallized in anatase phase and their morphology exhibits a porous structure. The study of the photo-induced properties shows an activity maximum at 450 °C.

Finally, microstructural and photocatalytic properties of the TiO_2 coatings in-situ crystallized are compared with those of the films prepared under the same conditions but crystallized ex-situ.

BP37 Thermal Stability of Quaternary TiZrAlN Sputtered Thin Films, ***G. Abadias*** *(gregory.abadias@univ-poitiers.fr)*, Institut P' - Universite de Poitiers, France, *I. Saladukhin, S. Zlotski, V. Uglov*, Belarussian State University, Belarus

The aim of the present work is to study the thermal stability, under vacuum and air annealing, of quaternary transition metal nitride films, namely TiZrAlN, with emphasis on the role of Al content on the structure and phase formation.

$(Ti,Zr)_{1-x}Al_xN$ films with thickness of 300 nm have been deposited onto Si (001) wafers by reactive unbalanced magnetron co-sputtering from individual metallic targets under mixed Ar+N_2 plasma discharges. Ti and Zr targets were operated in dc mode, at fixed power of 300 and 220 W, respectively, while an RF power was applied to the Al target. The working pressure during deposition was fixed at 0.19 Pa. Varying the RF power of the Al target from 20 to 200 W resulted in metallic atomic fraction of aluminum, x, in the films to increase from 0.026 to 0.364, while the Ti:Zr concentration ratio was kept constant to ~1.0. RBS analysis revealed that N content decreased from ~50 at.% for low Al content (x<0.10) to ~30 at.% for x>0.25.

XRD, AFM, SEM and TEM analyses revealed a structural and morphological evolution upon Al incorporation in the TiZrN lattice. Three growth regimes were identified: i) nanocrystalline TiZrAlN solid solutions with cubic structure for x< 0.11, ii) dual-phase nanocomposites consisting of cubic TiZr(Al)N nanograins surrounded by amorphous TiAlN matrix for 0.11 < x < 0.25, and iii) XRD amorphous films for x> 0.25.

Annealing in vacuum (~10^{-4} Pa) at the temperature of 600°C doesn't cause any structural changes of TiZrAlN films. After annealing in vacuum at 950°C, the structure of the films depends essentially on the aluminum content. Cubic TiZrAlN films with x=0 and 0.048 remained stable, while phase decomposition into c-TiN and c-ZrN was revealed for x>0.10.

Annealing under air atmosphere was carried out for temperature intervals ranging from 400 to 950°C using in situ temperature XRD. For low Al content (x<0.13), oxidation started at 500°C. Interestingly, an intermediate oxidized amorphous phase was found in the 600-700°C temperature range, followed by crystallization of the orthorhombic $(ZrTi)O_4$ oxide phase at 780°C. For x>0.25, the reduction of oxide formation can be explained by the passivating role of the Al_2O_3 outer layer. Thus, amorphous TiZrAlN films with high Al content are desirable for a better oxidation resistance.

BP38 The Development and Application on the Process Technique of (Zr_xHf_{1-x})N Thin Film, ***Y.W. Lin*** *(james722@itrc.narl.org.tw)*, Instrument Technology Research Center, National Applied Research Laboratories, Taiwan, Republic of China, *J.H. Huang*, Department of Engineering and System Science National Tsing Hua University, Taiwan, Republic of China, *G.P. Yu*, Institute of Nuclear Engineering and Science National Tsing Hua University, Taiwan, Republic of China

ZrHfN thin film has attractive attention for its superior mechanical properties (hardness, adhesion, friction resistance), corrosion resistance, higher packing factor, chemical stability and warm golden color as similar to TiN, and it was widely applied in industry in the current decades. ZrHfN film will be deposited by reactive magnetron sputtering, based on modification of the previous results of optimum coating conditions (substrate bias, substrate temperature, system pressure, nitrogen flow etc.) for metal nitride thin films to develop a new deposition condition, to investigate the microstructure, corrosion and mechanical properties of different proportion of the Hf-Zr components. Based on the early studies, metal nitride coatings have attracted attention for good mechanical properties, hardness up to 30 GPa. Moreover, the addition of Zr may further improve the thermal stability of the metal nitride coating. In the study, we should have a generalized definition for substitutional solid solution. The addition of Hf into ZrN (or addition of Zr into HfN) forms the substitutional solid solution ZrHfN (or HfZrN). Different ratios of Hf/Zr will form various structure for (Zr_xHf_{1-x})N with interesting properties, and many characteristics, such as nanostructure, hardness, and residual stress remain to be studied further. The thickness of films will be determined by scanning electron microscope (SEM). Hardness of the films can be measured by nano-indenter, and atomic force microscopy (AFM) is applied to measure the surface roughness of thin film. The preferred orientation and lattice parameter of ZrHfN films will be studied by using X-ray diffraction (XRD). The ratio of N/Hf/Zr and composition in ZrHfN thin film will be ascertained by X-ray Photoelectron Spectroscopy (XPS) and Rutherford Backscattering Spectrometer (RBS). Characterizing the structure and properties of single ZrHfN layer coating with the different ratio of Hf-Zr to find out the optimum processing parameters, and further to tailor a variety of surface coating applications is the objective of this project.

BP39 Deposition of TiN Films by High Power Impulse Magnetron Sputtering, ***W. Wu***, *S. Shih, P. Chen, C.L. Chang (jackaljr@mdu.edu.tw), D.Y. Wang*, MingDao University, Taiwan, Republic of China

High power impulse magnetron sputtering (HiPIMS) is a novel technique in physical vapor deposition (PVD) technology. The advantages of HiPIMS include low process temperature, well-adherent coating, better quality of the films, and droplet-free coating process. It provides higher gas dissociation and highly ionized plasma by inputting a high power in short pulses to the target. The target materials are therefore not only sputtered but also ionized during the deposition process. As a result, high power density and plasma density in the order of 10^{17} to 10^{19} m^{-3} can be achieved in HiPIMS process. In this study, TiN thin films exhibiting high hardness and low friction coefficient were deposited using a unipolar mode in HiPIMS. The Ti target used has a purity of 99.99%. Nitrogen was used as the reactive gas to deposit TiN along with Ar gas. The effect of duty cycle on the deposition of TiN film was investigated in this study by varying the duty cycle from 5 to 50%. The cycle time of 100, 500, 1000, 5000, 10000 μs were also studied. Besides, TN thin film was also deposited by conventional dc magnetron sputtering (dcMS) for comparison. During the deposition, target voltage and current were recorded while the ions and neutrons in the plasma were

diagnosed by optical emission spectroscopy, OES (EMICON). Thickness of the obtained TiN films was measured using scanning electron microscopy (SEM, JEOL-JSM 7000F). The surface morphology and surface roughness were investigated by atomic force microscopy (AFM, Veeco-DI 3100). Compositions were analyzed using Auger Electron Spectroscopy (AES, MICROLAB 350). Crystallinity and microstructures were investigated using grazing incidence X-ray diffractometry (GIXRD, PANalytical-X'Pert PRO MRD). The hardness and elastic modulus were investigated using nanoindenter (Nano Hardness Tester, CSM) equipped with a Berkovich 142.3° diamond probe tip at a maximum applying load of 2400 μN. The wear behavior was investigated using a ball-on-disk tribometer (CSM Instruments Inc.).

BP40 Development of Uniform Coating Technique of Tetrahedral Amorphous-Carbon Film by T-shape Filtered-Arc-Deposition with Deflected Plasma beam and Multi-Motion Substrate Holder for Semispherical Object, ***H. Tanoue*** *(tanoue@ee.tut.ac.jp), H. Okuda, Y. Suda, H. Takikawa,* Toyohashi University of Technology, Japan, *M. Kamiya,* Itoh Optical Industrial Co., Ltd., Japan, *M. Taki, Y. Hasegawwa, N. Tsuji,* Onward Ceramic Coating Co., Ltd., Japan

Tetrahedral amorphous-carbon (ta-C) is hydrogen-free and high-density diamond-like carbon (DLC) film. In particular, chemical inertness, since it is able to prevent the adhesion of glass at high temperature and, focused as a protective film of glass lens mold. A Vacuum arc deposition, DLC is able to produce commercially, including ta-C. On the other hand, the vacuum arc plasma has a problem that the cathode emits a plenty of macrodroplets as well as ions and electrons. The macrodroplets deteriorates the film properties; uniformity, surface roughness, friction coefficient, hardness, etc. In order to overcome this droplet problem, the filtered arc method has been developed to remove the droplet from the plasma, as the most powerful method. However, the droplets emitted from the graphite cathode are in solid phase so that the conventional filtered arc system is hard to filter them. The one of authors has been developed the T-shape filtered arc deposition (T-FAD) system, in which the droplets are separated from the plasma at the 90 degree bent position. Though, the ta-C preparation to semi-spherical object was difficult by T-FAD until now. In this study, new preparation technique by T-shaped filtered-arc deposition (T-FAD) system has been developed for ta-C preparing to semi-spherical object.

First, number of droplets was reduced for capable large-aperture lens. A few droplets were attached film that prepared by T-FAD. Droplets were crash the duct wall, it was reflection and exploding, and it was flied to the substrate. Therefore, substrate position was set in the line of sight non-visible from the duct wall by controlling the plasma beam deflection. As a result, it was improved removing droplets performance. Plasma beam was deflected at about 15° upward from the horizontal line of duct exit, number of droplets was one-third.

Second, plasma beam was irradiated on normal axis of the substrate for uniform film thickness. So, we developed a multi-motion substrate holder which is able to move in direction of vertically and rotatory. Ta-C was coated to object simulated semi-spherical object, the film thickness distribution was confirmed. So, α is the angle between the normal axis of object and plasma beam center line. α is 0° (downward of object) and 40° (upward of object). A swing motion pattern in the vertical direction was programmed under the distribution of film thickness. As a result, uniform thickness ta-C film was coated on polished semi-sphere object in this condition, a uniform coating of the semi-sphere object was realized.

BP41 Optical Emission Spectroscopy of Cr-Al-C Arc Ion Plating Plasma, ***T. Takahashi*** *(takahashi@kcs-europe.de), R. Cremer, P. Jaschinski,* KCS Europe GmbH, Germany

A ternary transition metal carbide of Cr_2AlC, also referred to as MAX-phase, is known to exhibit both the properties of metals and ceramics, providing high stiffness, high hardness, high oxidation resistance, thermal-shock resistance, and machinability. Due to the unique mechanical and chemical properties, Cr_2AlC is a promising candidate for protective hard coatings on tools or components operated in severe mechanical and thermal load conditions.

We explore the depositions of phase pure Cr_2AlC by an industrial arc ion plating. The phase and microstructural evolution of the growing films are known to be affected by the plasma properties, and hence the understanding thereof is of significance for the process optimization. This study analyzes the Cr-Al-C arc ion plating plasma using Optical Emission Spectroscopy (OES) towards contributing the Cr_2AlC deposition. In the Cr-Al-C arc ion plating plasma ignited, OES peaks associated with Cr-neutral, Cr-ions, and Al-neutrals were identified whereas those of C were not detected in the present study. The relative intensity of Al to Cr neutral is found to be affected by the Ar gas pressure. Also, the relative intensity of Cr-ions to Cr-neutral decreases with increasing the working Ar gas pressure, which could be explained in terms of the charge-exchange collision processes.

BP42 Growth of Boron Nitride with a High Temperature Chemical Vapor Deposition (HTCVD) Reactor using BCl3 and NH3 as Precursors, *N. Coudurier,* ***R. Boichot*** *(raphael.boichot@phelma.grenoble-inp.fr),* Grenoble INP, France, *E. Blanquet, M. Pons,* CNRS, France

Boron Nitride (BN) with its various properties like high thermal conductivity, high chemical and thermal stability, a wide optical bandgap and a high electrical resistivity is a potential material for optoelectronic, piezoelectric sensors and high power electronics applications. Many different polytypes of BN exist. Previous studies report the difficulty to obtain other phase than the poorly crystallized graphite-like turbostratic phase (t-BN). Cubic BN (c-BN) phase was however obtained with plasma aided CVD processes. Recent attempts to obtain epitaxial layers of hexagonal (h-BN or r-BN) have succeeded with triethyl boron [1] and diborane [2] as boron source and NH3 as nitrogen source. This phase is expected to be the most promising material after diamond for optoelectronic.

Growth of BN at high temperature (1500-1800°C) on various substrates (lab-made AlN templates on c-sapphire and c-sapphire alone) in a cold wall HTCVD reactor has been studied using NH3 and BCl3 as nitrogen and boron sources, and H2 as carrier gas. The experiment set-up consists of a vertical water-cooled quartz reactor with a graphite susceptor covered with AlN and heated by induction. Temperature of the substrate, N/B ratio in the gas phase and reactor pressure influence on the growth layer has been investigated. As-grown BN layers have been characterized by Field Emission Scanning Electron Microscopy (FE-SEM), X-ray diffraction (XRD) and Raman spectroscopy.

The study shows that the t-BN phase is systematically obtained at high growth rates as expected, whatever the temperature in the range investigated. To stabilize the h-BN growth on hetero substrate, a very low partial pressure of BCl3 should be used, leading to very low growth rates.

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BP43 Novel TiAlN Nanostructured CVD Coatings with Superior Oxidation Resistance, ***J. Keckes*** *(jozef.keckes@mu-leoben.at), R. Daniel, V. Terziyska, C. Mitterer,* Montanuniversität Leoben, Austria, *A. Köpf, R. Weißenbacher, R. Pitonak,* Böhlerit GmbH, Kapfenberg, Austria

In this contribution, microstructure and properties of $Ti_{1-x}Al_xN$ coatings with x > 0.9 prepared using moderate temperature chemical vapour deposition are described. The coatings characterization was performed by X-ray diffraction and transmission electron microscopy techniques. The coatings consisting of fcc-$Ti_{1-x}Al_xN$, fcc-TiN and hexagonal AlN phases exhibit a special nanolamellar microstructure and an extraordinary high oxidation resistance up to 1.100 °C (air / 1h), which is considerably higher than it is known for $Ti_{1-x}Al_xN$- and even $Cr_{1-x}Al_xN$ grown by physical vapour deposition techniques.

BP44 Silicon Carbide Interlayers for HFCVD Diamond on Cemented Carbide Cutting Tools, *U. Heckman (Ulrike.heckmann@ist.fraunhofer.de),* Fraunhofer Institute for Surface Engineering and Thin Films, Germany, *A. Hagemann,* Fraunhofer Institute for Surface Engineering and Thin Films IST, Germany, ***J.A. Oyanedel Fuentes***, Institute for Machine Tools and Factory Management (IWF), TU Berlin, Germany, *J. Gäbler, M. Höfer,* Fraunhofer Institute for Surface Engineering and Thin Films IST, Germany, *F. Sammler,* Institute for Machine Tools and Factory Management (IWF), TU Berlin, Germany, *L. Schäfer,* Fraunhofer Institute for Surface Engineering and Thin Films IST, Germany, *E. Uhlmann,* Institute for Machine Tools and Factory Management (IWF), TU Berlin, Germany

The performance and tool lifetime of cemented carbide tools (WC:Co) can be significantly improved by chemical vapor deposited thin film diamond (CVD diamond). As the cobalt binder of the cemented carbides leads to graphitization during diamond deposition, the tools are usually pretreated by chemical etching procedures which remove the cobalt binder from the boundary zone of the tool substrate. This pretreatment may have a detrimental effect on the mechanical integrity of the tool and is highly time-consuming and costly.

A promising method to achieve good adhesion of diamond films on cemented carbides is to deposit a carbide interlayer, such as silicon carbide. This interlayer acts as a diffusion barrier and thereby protects the diamond film against the cobalt binder phase. The interlayer strategy is not only beneficial for the properties of the layer system but also reduces costs and time effort during tool coating. Furthermore, these interlayers enable to deposit diamond on cemented carbides with higher cobalt content than the conventional 6 to 10 wt-%.

Investigations on hot-filament activated chemical vapor deposited (HFCVD) SiC/diamond systems were performed without chemical etching of the cemented carbide tools with Co content of 6-13 wt-%.

Tetramethylsilane (TMS) was used as a precursor gas which delivers both silicon and carbon species. Diamond and silicon carbide were deposited in separate coating processes (ex-situ). An in-situ deposition of both silicon carbide and diamond coating in the same batch will be developed by performing experiments on optimization of the SiC coating and on diamond in-situ nucleation.

The performance of the tools coated with SiC interlayers and CVD diamond was tested in cutting tests as well as in model wear tests. The turning tests on the workpiece material AlSi17Cu4Mg, with regard to the tool life and wear form, were conducted without any coolant. The results of the experiments were compared with conventional CVD diamond tools. Additionally, the wear mechanisms adhesion, abrasion and surface fatigue of the innovative coating systems were investigated in model wear experiments.

BP45 Role of the Si-addition on the Mechanical and Tribological Properties of AlCrN-based Films Deposited by Cathodic Arc Deposition, ***A. Billard*** *(alain.billard@utbm.fr)*, IRTES-LERMPS-UTBM, France, *F. Lomello*, DEN/DANS/DPC/SEARS/LISL CEA, France, *F. Sanchette*, ICT, France, *F. Schuster*, *M. Tabarant*, CEA, France

The study was focused on the development of AlCrN hard layers for high speed machining applications since during the last years, it was proved that commercially available coatings present high abrasion and oxidation resistance over 800°C, thus increasing the tool lifetimes. Recently, the addition of alloying elements such as silicon, tungsten and boron are believed to be suitable for enhancing the oxidation resistance at high temperatures, as reviewed by many authors [1, 2].

In this study nitride-based coatings have been deposited by vacuum cathodic arc deposition (CAD). This technique has been chosen due to its versatility, allowing easily the industrial up-scaling.

The results were discussed taking into account the role played by the stratification and the silicon and oxygen content in AlCrN coatings. It is believed that surface and bulk oxides are sufficiently plastic to sustain abrasive wear at high temperatures without spalling effects [3]. Moreover, they are supposed to increase the wear resistance as they reduce the friction coefficients [4].

Microstructures and morphology of the deposited coatings, before and after tests, have been investigated by means of X-ray diffraction, scanning electron (SEM) and transmission electron (TEM) microscopy observations. However, in order to determine the dispersion of oxides and silicon nitrides inside the microstructure, the glow discharge optical emission spectroscopy (GDOES) was employed.

Finally, samples were subjected to mechanical (nanoindentation) and tribological characterization (up to 800°C) with the aim of correlating the microstructures to the mechanical behaviour.

BP46 Influence of RF and Plasma Parameters on Film Properties for Layer Transfer by an Advanced PECVD Process Control Method, ***T. Grotjahn*** *(tobias.grotjahn@iwm.fraunhofer.de)*, Fraunhofer IWM, Germany, *R. Rothe*, Plasmetrex GmbH, Germany, *S. Meier*, Fraunhofer IWM, Germany

For layer property optimization and transfer of PECVD deposited diamond-like-carbon (DLC) coatings usually the very time consuming "trial-and-error"-method is used. To improve the layer transferability it is necessary to develop a better understanding of the RF-network, the plasma state and the interaction between the plasma and the substrate surface. For this reason several diagnostic methods were used to investigate the influence of RF and plasma parameters on film properties according to the load condition of the chamber at different generator powers and gas fluxes. The matching network was equipped with several additional calibrated RF-sensors. Additionally, the non-invasive diagnostic methods of Nonlinear-Extended-Electron-Dynamics and Optical Emission Spectroscopy were used to monitor the plasma state. Through these techniques the plasma resistivity, the collision rate, the gas temperature and, by means of the actinometrical approach, the electron temperature and particle densities of emitting species may be determined. To obtain a time-resolved overview of all of these parameters a monitoring system, which connects all of these parameters, was developed. In addition, mechanical layer properties such as hardness, young's modulus and tribological behavior were measured. This work investigates the correlations between all of the outlined parameters and properties and illustrates how they are used to design a process control technique which transfers reliably established layer properties directly to different substrate sizes or to another devices.

BP47 Arc evaporated coatings for machining application, ***D. Schlegel***, ESTA, France, *M. Arab Pour Yazdi*, IRTES-LERMPS-UTBM, France, *F. Lomello*, DEN/DANS/DPC/SEARS/LISL CEA, France, *F. Sanchette*, ICT, France, *A. Billard (alain.billard@utbm.fr)*, IRTES-LERMPS-UTBM, France, *F. Schuster*, CEA, France

Arc evaporation is a powerful process for the deposition of very hard nitride coatings due to the high ionization rate of the discharge which allows a tuneable control of the impinging species energy. In particular, this technique is suitable to improve machining efficiency of carbide tools. Both mono- and nano-layer coatings based on Al, Ti and Cr nitrides have already been involved to coat machining tools.

In this paper, we first describe the industrial prototype used for the deposition of nitride single or nanolayer coatings. This device allows the deposition of nano-layer coatings with periods if about 5 to 50 nm by controlling the rotation speed of the triple-rotation substrate holder.

The structural, mechanical and tribological characteristics of different nitride coatings such as (Al,Cr)N, (Al,Ti)N monolayers and TiN-CrN, (Al,Ti)N-TiN, (Al,Cr)N-CrN nano-layers are then presented in relation with the coatings their deposition.

Finally, instrumented machining tests are performed using carbide tools coated with those different coatings to compare their ability to high speed machine several hard materials.

BP48 Structure and Properties of CrN/TiN Multilayer Coatings Deposited by Modulated Pulsed Power and Pulsed dc Magnetron Sputtering, ***Y. Ou***, *J. Lin (jlin@mines.edu)*, Colorado School of Mines, US, *I. Dahan*, Ben Gurion University of the Negev, Israel, *B. Wang*, *J. Moore*, Colorado School of Mines, US, *W. Sproul*, Reactive Sputtering, Inc., US, *M. Lei*, Dalian University of Technology, China

CrN/TiN multilayer coatings with different bilayer periods (l)were synthesized by using the combination of modulated pulsed power magnetron sputtering (MPPMS) and pulsed dc magnetron sputtering (PDCMS) in a close field unbalanced magnetron sputtering system. The structure and properties of the coatings were investigated by means of X-ray diffraction, transmission electron microscopy, nanoindentation and ball-on-disc wear test. The corrosion resistance of the coatings was evaluated by anodic polarization measurement in 3.5 wt% NaCl aqueous solution. The coatings showed face centered cubic nanolayered structure. Although no oriented TiN or CrN layer were prepared as an adhesion layer prior to the coating depositions, the coatings with relatively large l (e.g. 8.9 nm and 13.5 nm) exhibited a dominated (111) texture, while the coatings with relatively small l (e.g. 4.7 nm and 2.2 nm) exhibited a strong (200) peak. With a decrease in the l from 13.5 to 2.2 nm, the hardness and the elastic modulus of the coatings increased and achieved the highest values of 22.8 GPa and 276 GPa at a l of 2.2 nm, respectively. The anodic polarization curves of CrN/TiN multilayer coatings in a 3.5 wt% NaCl aqueous solution showed excellent pitting corrosion resistance with an increase in corrosion potential and a decrease in passive current as compared with untreated AISI 304L substrate.

Key words: CrN/TiN; Modulated pulsed power (MPP); High power pulsed magnetron sputtering (HPPMS); Pulsed dc magnetron sputtering (PMS); Multilayer coatings; Corrosion

BP49 Hardness and Structure Evolution of Annealed Zr-TiAlN Films, ***R. Pilemalm*** *(robpi@ifm.liu.se)*, Linköping University, Sweden

TiAlN has been used as an effective protective coating for cutting tools since the 1980's. Recently and triggered by the demands for improved high temperature protection, research on different alloying concepts have been explored, e.g. Cr-TiAlN and Y-TiAlN. Some of these alloy compositions have shown improved high temperature properties and better cutting performance. Here we build on this concept and explore the Zr-TiAlN system and to systematically investigate how Zr-additions to TiAlN affects thermal stability and hardness. The background for choosing Zr as the alloying element is ab initio calculations of the Gibb's free energy of mixing that points out the possibility to tailor the driving force for spinodal decomposition though Zr-additions.

For this study we have used $Ti_{50}Al_{50}N$ as the reference material and then added Zr resulting in the following compositions: $Ti_{0.44}Al_{0.40}Zr_{0.17}N$, $Ti_{0.25}Al_{0.24}Zr_{0.51}N$, $Ti_{0.09}Al_{0.07}Zr_{0.84}N$, and $Ti_{0.04}Al_{0.04}Zr_{0.92}N$. The coatings were deposited on hard metal (WC-Co) substrates with cathodic arc evaporation. After deposition the coatings were isothermally annealed for two hours at 800°C, 900°C, 1000°C and 1100°C respectively.

X-ray diffractometry shows that $Ti_{0.44}Al_{0.40}Zr_{0.17}N$ decomposes isostructurally into cubic (c)-TiZrN and c-AlN, which is consistent with theoretical predictions. It also shows the unstable nature of this composition resulting in a driving force for spinodal decomposition. As a consequence of the decomposition age hardening occurs at 800°C. In contrast, for high additions of Zr, i.e. $Ti_{0.09}Al_{0.07}Zr_{0.84}N$ and $Ti_{0.04}Al_{0.04}Zr_{0.92}N$, no

decomposition occurs at the investigated temperatures. Instead the alloys remained in their original cubic state after annealing. This result is also in agreement with the theoretical predictions, which indicate a very weak driving force for decomposition for these compositions. Instead the heat treatments resulted in an annihilation of the lattice defects present from the deposition and a significant drop in hardness already after 900°C of annealing.

In summary we conclude that alloying TiAlN with Zr opens new avenues for control of the driving forces for spinodal decomposition such that the high temperature properties can be tuned.

BP50 Synthesis of the CrZrSiN Thin Films and its High Temperature Tribological Properties, *D.J. Kim, J.H. La, S.M. Kim,* ***S.Y. Lee*** *(sylee@kau.ac.kr),* Korea Aerospace University, Republic of Korea

Recently, challenges to meet the ever increasing requirements to cover severe working conditions for thin films, multi-compositional films with more than 3 elements could be one of the excellent solutions. Using segment or mosaic targets to synthesize multi-compositional films could be a simple way to produce these thin films with multi compositions. In this work, three different segment targets were used to synthesize the CrZrSiN coatings with various Si contents on the Si wafer substrate and H13 tool steel using unbalanced magnetron sputtering process. Tribological properties of coatings as a function of the Si content were investigated by ball-on-disk type wear tester at room temperature and 500°C. After wear test, various tribological characteristics such as surface morphology, wear rate and wear debris were examined by atomic force microscopy (AFM), field emission scanning electron microscope (FE-SEM) and Raman Spectroscopy. Our results showed that tribological properties of CrZrSiN films at high temperature were increased significantly, compared with those of CrZrN coatings. Si content in the thin films has strong influence on the improvement of the high temperature tribological performance of the films. At the room temperature, however CrZrSiN films and CrZrN films showed similar tribological performance. Detailed experimental results will be presented.

BP51 Improvement of Wear Resistance of Nitrile Rubber Surfaces by Hydrocarbon Plasma Treatments, *R. dos Santos, E. Santos Jr.,* ***S. Camargo Jr.*** *(camargo@metalmat.ufrj.br),* Federal University of Rio de Janeiro, Rio de Janeiro, RJ, Brazil.

Nitrile rubbers (NRB) are widely employed in engineering as mechanical seals, for instance. However, they usually exhibit high coefficient of friction (COF) when sliding against hard counterparts. Besides to that, the presence of severe wear limits their service lifetime. So, plasma surface treatment may be considered to enhance the NBR tribological performance. In this work the wear behavior of NBR surfaces modified by radio frequency (rf) hydrocarbon plasma treatment is investigated. Surface treatment was carried out using methane (CH_4) and acetylene (C_2H_2) as precursor gases at 0.05 torr working pressure and -50 and -100 V self-bias voltages (bias voltages in excess of -100V damaged the sample surface). The surface morphologies were observed by scanning electron microscopy (SEM) with energy-dispersive X-ray spectroscopy (EDS), while the physicochemical characterizations were carried out by Raman scattering and Fourier transform infrared (FTIR) spectroscopy. The CH_4 plasma did not seem to affect much the NBR surface morphology when compared to the untreated samples, as the elastomer matrix and the particulate phase present in the bare samples are still clearly observed. On the other hand, NBR samples treated in C_2H_2 plasma present completely different surface morphologies and seem to be covered by a film of rough appearance. In this case EDS analysis shows an almost pure carbon surface showing the presence of a thick film. FTIR and Raman spectra of CH_4 plasma treated samples are also very similar to bare NBR, while C_2H_2 treated ones present only a broad Raman peak characteristic of DLC films centered around 1525 cm^{-1}. Wear tests were performed by pin-on-plate technique using a CETR-UMT tribometer. A stainless steel ball (1/4" diameter) was employed as the counter-pin. All tests were carried out at room temperature using to the following parameters: 0.5 N load, 2.0 and 5.0 mm wear radii, 0.05 and 0.20 m/s linear velocities. Wear was basically evaluated in terms of mass (volume) loss. In general, all surface treatments were effective to enhance the wear resistance of NBR samples, regardless the deposition conditions. Further, a noticeable COF reduction of up to about 70% was found in relation to the bare samples, from 0.5 to 0.15. For samples treated with CH_4 plasma, the wear rates were surprisingly decreased of about 70-85%, while in case of C_2H_2 treated samples wear was reduced by up to about 60%. In conclusion, hydrocarbon plasma treatment can be effectively employed on nitrile rubber. The effect of plasma treatment seems to deposit a film with structure similar to DLC carbon, resulting in great improvement of NBR tribological performance.

BP53 Preparation and Characterization of Ti-Al-N Thin Films Deposited by Reactive Crossed Beam Pulsed Laser Deposition, ***L. Escobar-Alarcon*** *(luis.escobar@inin.gob.mx),* Instituto Nacional de Investigaciones Nucleares de Mexico, Mexico, *D. Solis-Casados,* Universidad Autonoma del Estado de Mexico, Mexico, *S. Romero, J. Perez-Alvarez,* Instituto Nacional de Investigaciones Nucleares de Mexico, Mexico, *G. Ramirez,* Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de Mexico, México, *S. Rodil,* Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de Mexico, México, Mexico

Ti-Al-N thin films were deposited on stainless steel substrates using the reactive crossed beam pulsed laser deposition technique. The Al content in the films was varied in a controlled way by changing the ablation conditions on the Al target, particularly the Al^+ mean kinetic energy. The aluminum ion mean kinetic energy was varied from 46 to 423 eV, resulting in Ti-Al-N films with Al contents from 5.4 up to 39.0 at. %, suggesting the aluminum content can be controlled by the Al^+ kinetic energy. The characterization of the mechanical properties showed that the hardness increased from 18.0 to 26.0 GPa as the Al^+ mean kinetic energy was increased. Raman Spectroscopy was used to characterize the microstructure of the deposits, and the obtained results revealed the development of different local microstructures as a function of the Al^+ kinetic energy. The corrosion resistance of deposited films was evaluated using two different electrochemical techniques: DC polarization and electrochemical impedance spectroscopy. The results showed a good improvement of the corrosion resistance in comparison to both the bare substrate and the titanium nitride coating without aluminum. The obtained results reveal that it was possible to design coatings with good corrosion resistance and high hardness.

BP54 Characterization of Diamond-like Carbon Film Synthesized by HIPIMS System for Medical Application, *M.H. Shih,* ***W.C. Chen****, C.L. Chang, D.Y. Wang (jackaljr@mdu.edu.tw),* MingDao University, Taiwan, Republic of China

The diamond-like carbon (DLC) film has been widely used for molds and components protection in automotive and aerospace industries with its high hardness, low friction coefficient, high wear resistance, and chemical inertness. For medical applications such as the protective coating for artificial implants, typical DLC films are suffered by concentrated corrosion at pin holes and associated corrosion cracking which leads to the premature implant failure. In this study, the improved DLC film was synthesized by using the high power impulse magnetron sputtering (HIPIMS) technology to assess the feasibility of producing a pin-hole-free, low internal stress, and chemically stable DLC coating by the characteristic HIPIMS high energy plasma impingement during the coating process. The HIPIMS deposited DLC coatings were characterized for structural integrity and tribological behaviors. Additional in-vitro test, which emulates the actual bio-chemical and mechanical conditions, will be conducted.

Keywords: High Power Impulse Magnetron Sputtering (HIPIMS), wear, DLC, medical

BP55 Design and Fabrication of Bilayer Wire Grid Polarizers (B-WGPs) with Sub-wavelength Metal Gratings, ***J.J. Kim****, T.Y. Kim, W.Y. Kim, B.H. Ku, P. Pazhanisami, C. Hwangbo (hwangbo@inha.ac.kr),* Inha University, Republic of Korea

Wire grid polarizers (WGPs) are very essential optical components because of low cost, compactness, and high polarization efficiency than typical polarizers. Also they are compatible with an integrated circuit fabrication in nano photonics. The WGPs for visible and near infrared wavelength region require fabrications of sub-wavelength metal gratings. Recently, in order to achieve high performance polarizer, bilayer metal WGPs (B-WGPs) have considered as new type of polarizer composed of two sub-wavelength metal gratings separated by a certain distance. In the B-WGP, the s-polarized light is reflected, and the p-polarized light is transmitted. To fabricate WGPs with sub-wavelength gratings, the nanoimprinting lithography is attracting attention. In this study, we have designed and fabricated bilayer wire grid polarizers with sub-wavelength aluminum gratings using ultra-violet (UV) curing nanoimprinting method and physical vapor deposition. An Al metal B-WGPs was fabricated on two type transparent substrates with different size. The substrates with 120 nm period and 100 nm height are applied for visible wavelength region. The substrates with 450 nm period and 150 nm height structure are available for near infrared wavelength applications. We have employed the finite difference time domain (FDTD) method to analyze optical performance of B-WGPs as metal thickness and to calculate the field distribution in the B-WGPs. The experimental results reveal that TM transmittance is above 50 % and also the polarization extinction ratio (PER) between TM and TE wave are respectively up to 100 in visible and above 250 in near infrared region. For high quality B-WGPs, these values are not enough to reach to simulation results above 1000, however, we are improving our skills to increase them more. Thus, it is expected that the B-

WGP with sub-wavelength metal gratings by using nanoimprinting is good candidate as a high performance polarizer for a variety of applications.

BP56 Alumina Coatings for use under High Radiation Conditions, ***F. Majid***, *S. Riaz (saira_cssp@yahoo.com), S. Naseem*, University of the Punjab, Pakistan, *I. Ahmad, G. Husnain*, National Centre of Physics, Pakistan

Alumina (Al_2O_3) is being studied as a radiation resistant coating for various applications. The surface modification and irradiation effects on aluminum alloy 7407 after coating with alumina (Al_2O_3) was carried out using electrochemical and sol–gel method. Alumina coatings, synthesized by a sol–gel route, were deposited on Al7407 substrates by spin coating. Other series of samples were prepared electrochemically by varying DC voltage in the range 1 – 5 volts. Coatings are optimized by controlling various deposition parameters. For comparison purposes RF Magnetron sputtering technique is also used. The various characterization results indicate that relatively smooth coatings can be achieved by simple and scalable techniques such as electrodeposition and sol-gel. Coated substrates were then irradiated with Ni^+, H^+ and Ar^+ ion beams by using Pelletron accelerator at several KeV to a few MeV. The nature and fluency of ions was varied to correlate to different environments. The surface modifications and structure of the coated surfaces before and after ion beam irradiations were characterized by FTIR, XRD, SEM, AFM and XRD, whilst the mechanical properties of modified surfaces were determined using nano-indentation. The results showed that the alumina xerogel films coated on the Al7407 substrates are successfully converted into crystalline alumina ceramic coatings by ion beam irradiations. Electrodeposited alumina films also show recovery and improved crystalline structure after ion beam exposure. Structure of resulting coatings is observed to be strongly depending on the ion beam types and dose conditions. By increasing dose intensity of Ar^+ and Ni^+ ion beams, γ-Al_2O_3 was observed which transformed to α-Al_2O_3 at higher energy. Nano-indentation results reveal that significant improvement in hardness and Young's modulus of the alumina -coated surface at optimized conditions can be achieved even after recovery from irradiations.

BP57 A Detailed Investigation into the Preparation and Properties of ZrO_2- Fe_2O_3 Coatings for Bio-Medical Applications, ***S. Riaz*** *(saira_cssp@yahoo.com), S. Naseem*, University of the Punjab, Pakistan

Tetragonal zirconia (ZrO_2) ceramics find a useful application in human dentures for reconstruction and filling purposes because of their unusual combination of strength, fracture toughness, hardness, and low thermal conductivity. These attractive characteristics are largely associated with the stabilization of tetragonal phase through alloying with aliovalent ions. The high fracture toughness exhibited by many of zirconia ceramics is attributed to the tetragonal to monoclinic phase transformation and its release during crack propagation. However, tetragonal phase of zirconia is not stable at room temperature. A number of ways are being sought, and we are investigating Fe_2O_3 addition in ZrO_2 for stabilization purposes. RF magnetron sputtering and Sol-Gel techniques have been used for preparation of the coatings, whereas XRD, SEM/EDX, AFM and IS techniques are used for characterization purposes. The optimized conditions are shown to lead to a stable tetragonal phase of ZrO_2 at room temperature. In sol-gel synthesis temperature, pH, nature of solvent and synthesis conditions played critical role in the size reduction and stabilization of zirconia at room temperature . ZrO_2 and Fe_2O_3 targets were used to prepare coatings by RF sputtering. Layer by layer growth of ZrO_2 and Fe_2O_3 was optimized for the preparation of stable zirconia coatings. Post annealing was done to investigate the alloys conditions and properties. X-ray diffraction (XRD) results show formation of tetragonal phase at 300^{o}C when sample was heated for 60 minutes. Coatings, prepared by sol gel, at 500^{o}C exhibit crystallite size as low as 11 nm as revealed by XRD results, whereas grain size ~30 nm was observed by scanning electron microscopy (SEM). Vickers Hardness measurements showed ~564 HV hardness of ZrO_2 samples prepared by sol-gel. Thus, sol-gel has proven to be a low cost, reliable and application oriented technique for the preparation of ZrO_2 coatings.

BP58 Preparation and Characterization of CIGAS Thin Films and Their Solar Cells, ***S. Naseem*** *(shahzad_naseem@yahoo.com), S. Riaz*, University of the Punjab, Pakistan

Thin films of copper indium gallium aluminum selenide Cu(In,Ga,Al)Se_2 (CIGAS) are prepared by sequential elemental layer deposition in vacuum at room temperature. The as-deposited films were heated in vacuum for compound formation. These films were concurrently studied for their structural properties by X-ray diffraction (XRD) technique. The XRD analyses include phase transition studies, grain size variation and microstrain measurements with the reaction temperature and time. It is also seen that the compound formation starts at 250^{o}C, with ternary phases appearing at 350^{o}C or above. Whereas, there is another phase shift, at 450^{o}C, with preference to the quaternary and / or pentenary compound. CdS is used as a window layer for the solar cell fabrication, whilst zinc-aluminate has been used as transparent conducting layer. The current-voltage results, at various illumination levels, are used to calculate the internal and external parameters of these solar cells; the internal parameters being obtained by a simple one-diode fitting of the experimental data. A maximum efficiency of around 9% is reported with a poor fill factor of 60%. Analytical calculations have also been performed and the analytical results point out towards loss of fill factor due to high series resistance.

BP59 Effect of Droplet Inclusion in Arc-evaporated Multilayer Coatings on the Anisotropy of Thermal Conductivity, ***M. Böttger*** *(phmb@mat.ethz.ch)*, ETH Zurich, Department of Materials, Switzerland, *A. Gussarov*, ENISE, France, *V. Shklover*, ETH Zurich, Department of Materials, Switzerland, *J. Patscheider*, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland, *M. Sobiech*, OC Oerlikon Balzers AG, Liechtenstein

Thermal conductivity (TC) and its anisotropy is one of the coating properties that can be adjusted by appropriate multilayer structuring and thus has received recently great attention in the context of application of TC-designed hard coatings for machining of difficult-to-cut materials like Ni- and Ti-based superalloys. Cathodic arc evaporation is a standard technology to synthesize multilayer coatings for wear resistant applications. However, arc-evaporated hard coatings typically contain droplets of different sizes which are generated during evaporation of the target material. These droplets may have a big influence on the thermal conductivity in multilayers, especially if they are larger in size than the bilayer thickness In this study it is presented how the inclusion of metallic droplets of different material, size, volume fraction and shape can affect the anisotropy of thermal conductivity in a multilayer coating system.

We use the Maxwell Garnett Approximation (MGA) for the description of isotropic inclusions in an anisotropic matrix. Its applicability is evaluated by comparison with a 2D finite element method (FEM) simulation of a prototypical multilayer coating. The MGA model agrees well with FEM simulation in predicting independence of thermal conductivity anisotropy of droplet material and size, only depending on the volume fraction for spherical droplets. In the case of elliptical droplet shapes the inclusion of such droplets can be beneficial or detrimental regarding TC anisotropy depending on droplet material, excentricity of the droplets and their orientation with respect to the multilayer coating structure.

BP60 Structural, Electrical Conductivity and Mechanical Properties of TiN_x Thin Films, *J. Goupy*, CEA Grenoble, France, ***P. Djemia*** *(djemia@univ-paris13.fr)*, LSPM-CNRS, Université Paris 13, Sorbonne Paris-Cité, France, *S. Pouget*, CEA Grenoble, France, *L. Belliard*, UPMC-Institut des NanoSciences de Paris, France, *G. Abadias*, Institut P' - Universite de Poitiers, France, *J.C. Villégier*, CEA Grenoble, France, *J.L. Sauvageot, C. Pigot*, CEA Saclay, France

For thermal applications, we need to manufacture Titanium Nitride film with as high as possible Critical temperature while minimizing the mechanical constraint. We thus tried different physical conditions during realization and characterized the films obtained. We also studied the influence of the substrate onto these films. We investigated the structural and mechanical properties of titanium nitride thin films TiN_x with $0.385 \leq x \leq 1.13$ deposited in a temperature range [320 K, 400 K], at 800 W, by reactive DC magnetron sputtering deposition from a Ti target in Ar + N_2 plasma discharge. The Ar working pressure was fixed at 0.2 Pa and the nitrogen concentration, x, modified by increasing the N_2 flow from 4.2 to 15 sccm. The Ar flow was set at 60 sccm. The chemical analysis was performed with the Rutherford backscattering (RBS) and nuclear reaction analysis (NRA) techniques. The structural properties of the films were characterized by X-ray Diffraction (XRD) and X-ray reflectivity (XRR), the electrical conductivity by the four-point probe method, whereas the picosecond ultrasonics and Brillouin light scattering techniques were employed to measure their acoustic and elastic properties as function of the nitrogen concentration.

BP61 Tribological and Electrochemical Properties of HVOF Sprayed CrC-40NiCr and WC-40NiCr Coatings, ***P. Olubambi*** *(polubambi@gmail.com), Z.H. Masuku, B. Obadele, T. Rapoo*, Tshwane University of Technology, South Africa

CrC–NiCr coatings have been extensively employed in high temperature applications and automotive industries to improve high temperature corrosion resistance of component surfaces, improve their wear resistances and decrease the friction coefficient between varying sliding parts. With the recent technological advancement in the mining industries and the need to develop improved materials for the varying harsh mine environments, the need to investigate the tribological and corrosion behaviour of these coatings in both dry and wet environments, typical of mine conditions is very imperative. The present study described and compared the corrosion

and tribological properties of HVOF sprayed coatings from two types of CrC-40NiCr feedstock powders and WC-40NiCr powders. Reciprocating sliding wear test was performed using the CETR UMT-2 test system under a load of 25 N and sliding velocity of 0.4 mm/s for 1000 seconds while wet abrasion test using the same wear parameters as well as electrochemical behaviour of the coatings were carried out in synthetic mine water environments. The morphology and microstructures present from the as sprayed, polished cross-section, wear and corroded coatings were examined using FE-SEM while the different phases present where analysed by XRD. The microhardness value was obtained using Vickers microhardness tester at a load of 100g. Hardness value obtained from the WC-NiCr coating is significantly higher than that of CrC-40NiCr. Results obtained from wear analysis showed that WC-NiCr coated steel substrate gave a higher wear depth of 0.93 mm when compared to CrC-NiCr 0.7 mm and this could be attributed to the presence of WC in the coating and also the use of WC ball which is a harder phase carbide than CrC. From the corrosion results, there is no much significant difference in the E_{corr} and I_{corr} observed. However, CrC-NiCr coatings showed more corrosion resistant with a negative shift in I_{corr}.

BP62 TiCrN/NiMnSb Thin Film Heterostructures for Vibration Damping in MEMS, ***N. Choudhary***, *D. Kaur (dkaurfph@iitr.ernet.in)*, Indian Institute of Technology Roorkee, India

The present study explored the in-situ deposition of TiCrN/NiMnSb thin film heterostructures using magnetron sputtering. Room temperature nanoindentation was performed to obtain the mechanical and damping properties of these heterostructures and results were compared with pure NiMnSb films. A significant improvement in the hardness and elastic modulus was observed in TiCrN/NiMnSb films, which is due to the presence of superhard TiCrN thin layer. Creep and Impact test performed using berkovich and spherical indenter revealed better damping in surface modified NiMnSb ferromagnetic shape memory alloy (FSMA) thin films. The improved damping in surface modified FSMA was attributed to the good adhesion and strong combination of TiCrN and NiMnSb damping layers. The novel TiCrN/NiMnSb heterostructure with enhanced mechanical and damping properties would be a potential material for vibraton damping applications in MEMS.

BP63 Characterization of a Cylindrical Planar Hollow Cathode and it's use for the Preparation of Bi Nanoparticles, *S. Muhl*, Universidad Nacional Autónoma de México - Instituto de Investigaciones en Materiales, Mexico, *A. Perez (ekargy@hotmail.com)*, Universidad Nacional Autonoma de Mexico, Mexico, ***A. Tenorio***, Universidad Nacional Autónoma de México - Instituto de Investigaciones en Materiales, Mexico

Hollow cathodes are widely used for a variety of applications from intense light sources to for thin film deposition. The particular characteristics of the hollow cathode are that the geometry reduces the loss of electrons by the oscillative motion them between the sheaths on each side of the cathode, with this resulting in the production of high density plasmas. Sputtered atoms from the cathode normally travel from one wall to the other but can be carried toward the substrate through the use of a high gas Ar flow and this can be used to control the deposition rate. It has also been reported that under high pressure operation, the high density plasma can be used to generate nanoparticles in the gas phase; diameters in the range of 10-50 nm. We have developed a new version of the traditional hollow cathode based on the cylindrical planar design. The geometry is similar to a toroidal electrode which is open at the interior surface. In this way the “hollow” discharge occurs between the upper and lower electrode surfaces and the only way that electrons can leave the discharge is via the upper or lower apertures. We have studied the electrical characteristics of the discharge as a function of the applied electrical power and gas pressure, and we have used the system to deposit thin films as a function of the plasma power and gas flow. This hollow cathode was also successfully used to deposit thin films of nanoparticules of bismuth. By varying the different operating parameters, such as pressure (6.7 – 267 Pa), power (40 -120 W) and gas flow (20 – 120 sccm), it is possible to control the size of the nanoparticles (10 – 150 nm), as well as it is possible to control the deposition rate (0.4 – 4.0 nm/min) and the size particles with the applying of a bias (60 – 240 V) to the substrate.

The size and morphology of the nanoparticles were measured by SEM images. X-ray diffraction and XPS were used to determine the structure and composition of the deposits.

BP64 TheIinfluence of the Inert and Reactive Gas Inlet Temperature and Pressure on the Reactive Sputtering Process Outcomes, ***S. Faddeeva*** *(sfaddeva@itesm.mx)*, *J. Oseguera*, ITESM-CEM, Mexico

The influence of the inert and reactive gas inlet temperature and pressure on the reactive sputtering process outcomes is modeled using the thermodynamic model. The numerical simulation results are compared to the available in literature experimental results and are found to be in reasonable concordance with them.

BP65 Hardness and Elastic Modulus of Hard Coatings at High Temperatures, ***M. Rebelo de Figueiredo*** *(marisa.figueiredo@unileoben.ac.at)*, University of California Berkeley, *M. Tkadletz*, Materials Center Leoben Forschung GmbH, *R. Hollerweger*, Christian Doppler Laboratory for Application Oriented Coating Development at the Institute of Materials Science and Technology, Vienna University of Technology, Austria, *A.J. Harris*, Micro Materials Ltd, UK, *M. Abad*, University of California Berkeley, *P.H. Mayrhofer*, Vienna University of Technology, Austria, *C. Mitterer*, Montanuniversität Leoben, Austria, *P. Hosemann*, University of California Berkeley

Nanoindentation has been established as a standard method to evaluate the mechanical properties of coating materials utilizing the Oliver and Pharr approach for data analysis. The measurements to obtain the hardness and elastic modulus are commonly performed at room temperature. Industrial applications like metal cutting cause friction between the tool and the workpiece leading to temperatures up to 1000°C. Therefore, knowledge on understanding and characterizing mechanical properties of hard coatings at elevated temperatures is of vital importance. Within the present work, nanoindentation measurements up to 700°C were conducted in order to study the evolution of mechanical properties of hard coatings close to operational conditions. The coating systems evaluated represent state-of-the-art materials for cutting applications, i.e. Al2O3, TiAlN, TiCN, TiN as well as newly developed coating materials like TiAlTaN. The substrate materials used were cemented carbides and sapphire. As a general trend it was found that the hardness and the elastic modulus decrease with increasing temperature for all tested coatings. The degradation of the properties was found to be between 30 and 80 % of the room temperature value depending on the coating material. The obtained results are intended to aid future studies on the temperature dependence of structure and properties of hard coatings with the final goal of further improvement of hard coating materials to fulfill the ever increasing demands in metal cutting.

BP66 Electrochemical and Impact Wear Behavior of TiCN, TiSiCN, TiCrSiCN, and TiAlSiCN Coatings, ***D. Shtansky*** *(shtansky@shs.misis.ru)*, *K.A. Kuptsov*, *Ph.V. Kiryukhantsev-Korneev*, *A. Sheveko*, National University of Science and Technology “MISIS”, Russian Federation

This study evaluates the performance of magnetron-deposited Cr- and Al-doped TiSiCN coatings, which were previously reported to have an excellent tribological properties, enhanced thermal stability and high-temperature oxidation resistance. Here, the behavior of these coatings during scratch tests, dynamic impact and electrochemical tests was studied and compared with that of the TiCN and TiSiCN reference coatings. The structure, elemental and phase compositions of coatings were studied by means of X-ray diffraction, scanning electron microscopy, and glow discharge optical emission spectroscopy. The coatings were characterized in terms of their hardness, elastic modulus, elastic recovery, and adhesion strength. To evaluate their electrochemical characteristics, the coatings were tested in 1N H_2SO_4 and 0.9% NaCl solutions. The coatings were also subjected to a range of impact tests, first in air, and then in normal saline (to assess a tribocorrosion effect) and distilled water (to assess a hydrodynamic effect in liquid). Under dynamic impact load, the coatings showed different impact resistance improving along the row TiCN→TiSiCN→TiCrSiCN→TiAlSiCN. In air, the TiSiCN, TiCrSiCN, and TiAlSiCN coatings endured a dynamic impact force as high as 1000 N with a minimum impact wear observed for the TiCrSiCN and TiAlSiCN coatings. The accelerated degradation of the TiCN, TiSiCN, and TiCrSiCN coatings in distilled water and normal saline was attributed to both the NaCl-induced corrosive processes and hydrodynamic effect resulting in accelerated abrasive wear. The TiAlSiCN coating was the only sample to sustain a repetitive impact load of 500 N for 10^5 cycles both in distilled water and normal saline.

BP67 A Study of Thermal Stability, Structural and Mechanical Properties of $Zr_xW_{1-x}N_y$ Coatings Deposited by DC/RF Reactive Magnetron Sputtering, *P. Dubey (dubey.paritosh@gmail.com)*, *R. Chandra*, *A. Vivek*, *D. Singh*, ***V. Dave***, Indian Institute of Technology Roorkee, India

In recent years, great attention has been devoted to the development of a new class of thin films with a special structure and unique properties against thermal stability and wears damage. The high metastability of the amorphous structure is the most striking aspect of ternary nitride alloys and is one of the reasons for their successes as thin-film diffusion barriers in semiconductor metallization technology.

Zirconium tungsten nitride ($Zr_xW_{1-x}N_y$) nanocrystalline films represent a new class of ternary metal nitride coating material. In the present work, films were deposited onto Si substrates using DC/RF reactive magnetron sputtering. The temperature dependence of the structure, morphology, stability and mechanical properties have been studied of the films under two different conditions; (i) Films have been deposited in-situ at various substrate temperatures (room temperature ~ 30^0C to 600^0C). (ii) Ex-situ annealing have been done up to 600^0C in the ambient atmosphere of films deposited at 30^0C. It was found from the first kind of treatment that (i) there is a strong correlation between crystallization and deposition temperature and (ii) the thickness and hardness of the films have dual trend depending on the phases present in the films. (iii) the maximum hardness achieved is ~ 25 GPa of the films deposited at 300^0C, while,the outcome of lateral treatment were (i) No significance of oxide phase formation except the broadening of hump.(ii) The O_2 start to incorporate above 200^0C with increasing tendency up to 600^0C. (iii) The RMS roughness (δ_{rms}) and thickness of the films increases with annealing temperature (iv) The hardness decreases (~11GPa) as the percentage of O_2 increases in the films.

The characterizations of the deposited films have been done using XRD, FE-SEM, EDS, AFM and Nanoindentation techniques.

BP68 The Investigation of the Adhesion, Wear and Friction Properties of TiN/TaN Multilayer Coatings, ***O. Baran*** *(obaran@erzincan.edu.tr),* Erzincan University, Turkey, *E. Demirci, I. Efeoglu, Y. Totik*, Atatürk University, Turkey

TiN and TaN coatings widely used due to excellent mechanical and tribological properties. Specifically, TiN/TaN multilayer coatings have been exhibit superior mechanical and chemical properties, such as hardness, adhesion and wear resistance, when compared to single layer nitride coatings. Therefore, in recent years, multilayer coatings composed of two kinds have been investigated. For this reason, in this study, TiN/TaN multilayer films were deposited on Mo-alloy substrate and Cu-alloy substrate by Closed-Field Unbalanced Magnetron Sputtering (CFUBMS). The structural and mechanical properties of these films were analyzed by using XRD, SEM and microhardness tester, respectively. The adhesion and fatigue properties of the coatings were evaluated via a scratch test in two modes. A sliding-fatigue multimode operation was used that involved multi-pass scratching in the same track at different fractions of the critical load (unidirectional sliding), and a standard mode with progressive loading was also utilized. Adhesion and fatigue properties of TiN/TaN multilayer coatings deposited on different substrates were discussed according to microscopic image examinations of the scratch tracks.

Key Words: TiN, TaN, multilayer films, CFUBMS, adhesion, fatigue

BP69 Rapid Annealing of TaN-(Ag,Cu) Thin Films Deposited on PEEK Polymer Substrate by Pulse Current Heating, *J.H. Hsieh (jhhsieh@mail.mcut.edu.tw),* ***Y.T. Su***, Ming Chi University of Technology, Taiwan, Republic of China

Pulse current annealing (PCA) technique has the advantage of heating up conductive film while maintaining low substrate temperature. In this study, a PCA system was used to anneal TaN–(Cu,Ag) nanocomposite films deposited on polyether ether ketone (PEEK). The emergence of Ag and Cu particle and substrate/film temperature difference was studied as functions of frequency and ON/OFF time ratio.

TaN–(Cu,Ag) nanocomposite films were deposited by reactive co-sputtering with Ag/Cu=6.5/3.5 in atomic %. The total amount of soft metal contents is 7 and 11 at.%. After PCA, the films were characterized using XRD, FESEM, nano-indentation. The tribological properties and antibacterial behaviors were also examined. The results show that the increase of pulse frequency and the reduction of ON/OFF ratio would enlarge substrate-film temperature difference. Therefore the substrate could be protected better. Through the anti-wear and anti-bacteria studies, it was found that the film/substrate system, after PCA, could maintain low frication and low wear rate, and high antibacterial efficiency against E. Coli. All these properties were related to pulse frequency and ON/OFF time ratio.

BP70 Synthesis and Characterization as Hydrocarbon Sensors of Nanostructured ZnO Sputter-deposited Coatings, ***M. Arab Pour Yazdi*** *(mohammad.arab-pour-yazdi@utbm.fr),* IRTES-LERMPS-UTBM, France, *J. Sanchez,* Umr Cnrs 6249, France, *E. Monsifrot,* Sarl Dephis, France, *P. Briois,* IRTES-LERMPS-UTBM, France, *F. Berger,* UMR CNRS 6249 University of franche comte, France, *A. Billard,* IRTES-LERMPS-UTBM, France

Recently, zinc oxide (ZnO) thin films have attracted increasing attention due to their excellent properties and their potential applications in various fields; gas sensors, piezoelectric devices, transparent conductive electrodes …. The performance of ZnO coatings in a number of modern devices and especially as gas sensors is strongly linked to their specific surface that can be tuned by controlling their morphology. ZnO nanostructures such as nanowires/nanorods, nanobelts, and nanodots are the object of intensive studies. Most of nanostructured ZnO materials are synthesized by vapour transport based on vapour–liquid–solid (VLS) growth mechanism using a noble metal as catalyst such as Au and Cu. However, some studies show that Au is not necessary for nanowire growth. Among the different deposition methods, the technique used in this study is the reactive magnetron sputtering.

In this paper, we investigate the feasibility of ZnO coatings with different morphologies (dense, porous, nano-wire and nano-tree) 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. We will the report the performance as dodecane-sensors of ZnO coatings with different morphologies as a function of dodecane concentrations and sensor surface temperature.

BP71 A New Dedicated DLC Coating System for Threading in Titanium, ***M. Morstein*** *(m.morstein@platit.com), P. Dessarzin,* PLATIT AG, Switzerland, *K. Gerschwiler,* RWTH Aachen University, *H. Frank, M. Schiffler,* GFE Schmalkalden e.V., Germany

TiAl6V4 and other titanium alloys are high-performance alloys used for lightweight and high strength applications due to their low density (ρ_{Ti} = 4,51 kg/dm^3) in combination with a high yield strength of about 1'000 MPa. However, titanium alloys are considered as difficult to machine materials due to their high strength, the low Young's modulus, the low thermal conductivity and the high tendency to sticking during the cutting process.

The present work shows how the lifetime and productivity of a coated state-of-the-art thread cutter can be improved. Crucial for the tapping is to ensure a reliable process, since the thread cutting in a component is usually one of the last machining steps conducted, and thus tool failure at this point would lead to the loss of an already highly valuable work piece.

The parameters used to optimize the performance of the reference tool were the cutting edge pre- and post-treatment as well as the coating type. Since first experiments showed that the sticking of titanium on the flank of the thread cutter is the lifetime limiting factor, a tribological experiment was used to evaluate the affinity of various nitrides, oxynitrides and DLC coatings to titanium. Measurements were done at 400°C on coated test plates against a TiAl6V4 pin and the build-up was then quantified using a profilometer. The results identified different behavior for the investigated coating types, which will be discussed and correlated to the cutting performance of the coated tools.

By selecting an appropriate coating as well as using optimized pre- and post-treatment the lifetime of the newly developed thread cutter could be more than doubled compared to the reference tool and further on this new generation tool was capable to work at faster cutting speeds in production.

BP72 Study on the Characteristics of MoN Doping Cu Amorphous Thin Film Fabricated by Pulse Magnetron Sputtering Process, ***C.H. Huang***, *W.S. Hwang (wshwang@mail.ncku.edu.tw),* National Cheng Kung University, Taiwan, Republic of China, *C.W. Chu,* Metal Industries Research & Development Centre, Taiwan, Republic of China, *S.J. Liu, H.Y. Chu,* National Unversity of Tainan, Taiwan, Republic of China

The corrosion resistance of NdFeB magnets is improved by direct MoCu and MoCuN thin film treatment of a sintered NdFeB magnet surface. X-ray diffraction and transmission electron microscopy are used to examine the microstructure of the thin films. The hardness, wettability, and surface roughness of the thin films are investigated using nanoindentation, contact angle measurements, and atomic force microscopy, respectively. The MoCu and MoCuN thin films exhibit a typical amorphous microstructure and a smooth surface with an average roughness of about 2 nm. The results of alternating-current (AC) impedance spectroscopy in 5% NaCl solution show that the AC impedance of the thin films increased with time. The $|Z|_{10mHz}$ values for NiCrAlVN (15000 ohms/cm^2), NiCrAlV (4000 ohms/cm^2), and uncoated NdFeB magnets (550 ohms/cm^2) show an 8-fold increase in the low-frequency impedance due to the amorphous state.

BP73 Thermal Stability and Oxidation Behavior of Reactively Sputtered TaN Coatings, ***F.B. Wu*** *(fbwu@nuu.edu.tw), K.Y. Liu,* National United University, Taiwan, Republic of China

Tantalums nitride, TaN, coatings with various microstructure are fabricated by magnetron sputtering. Through N_2/Ar gas flow ratio control, the TaN coatings are manufactured with amorphous, nanocrystalline, and columnar crystalline features. TaN multilayered coating with alternating stacking of the amorphous and crystallized TaN nanolayers is also deposited for comparison. Thermal stability of various TaN films is examined through vacuum and air annealing at 350 to 550 ° C. All the TaN coatings remain their structural features under vacuum annealing, while significant oxidation

occurs in the crystalline TaN coatings. The oxidation penetration is reduced due to the introduction of alternatively stacking amorphous/crystalline TaN nanolayers. The microstructure evolution and oxidation of various TaN coatings are also investigated under a high temperature glass contact experiment. The oxidation mechanisms for the TaN coatings under various annealing environments are discussed.

BP74 Electrochemical Impedance Spectroscopy Evaluation of Aluminium-Based PVD Coatings Exposed to Salt-Spray Corrosion, ***F. Indeir**, O. Fasuba, A. Matthews, A. Leyland (a.leyland@sheffield.ac.uk)*, University of Sheffield, UK

Evaluation of the corrosion behaviour and the protective properties of Al-based PVD coatings in aqueous solution have been carried out by Salt Spray Testing (SST) and Electrochemical Impedance Spectroscopy (EIS). SST offers many advantages, including the fact that it is a standardised method for conducting exposure to a corrosive environment and evaluating the results. However, SST has been criticised for its lack of reproducibility from one test to another, and for failure to provide a quantitative measure of corrosion degradation. The EIS method is a well-established technique and a powerful tool to determine a quantitative, numerical value for corrosion damage of coatings, and to investigate the electrochemical reactions mechanisms of the corrosion process in a short period of time. Coatings produced by physical vapour deposition (PVD) techniques can increase the lifetime and service quality of the system. Two main objectives are taken into account in this study; firstly, to evaluate the corrosion behaviour of Al-based PVD coatings after SST exposure and in 3.5% NaCl solution at different exposure times, by EIS. Secondly, to obtain a correlation between SST and EIS test results for Al-based PVD coatings. SST experiments were carried out after exposure times of 24, 48,123, 216 and 384hrs for ten test panels of PVD AlCr coatings deposited at 300oC & 400oC. EIS experiments of PVD AlCr coatings deposited at 300oC & 400oC have been carried out after open circuit potential (OCP) stabilisation, as a function of the immersion time for 24, 48,123, 216 and 384hrs in 3.5wt% NaCl solution. EIS data was obtained using an electrochemical cell instrument and then the experiments is complemented by scanning electron microscopy (SEM), Energy Dispersive X-ray (EDX) composition analysis and phase analysis by X-Ray Diffraction (XRD).

BP75 Comparison Between Single Phase Ti and Cr-nitrides Thin Films Deposited by Different Processing Routes, ***F. Lomello** (fernando.lomello@cea.fr), DEN/DANS/DPC/SEARS/LISL CEA Saclay, France, *M. Arab Pour Yazdi*, IRTES-LERMPS, France, *D. Schlegel*, ESTA, France, *A. Billard*, IRTES-LERMPS-UTBM, France, *F. Sanchette*, LRC CEA-ICD LASMIS, Nogent International Center for CVD Innovation (Nicci), France, *F. Schuster*, CEA Cross-Cutting Programme on Advanced Materials, France, *M. Tabarant*, DEN/DANS/DPC/SEARS/LISL CEA Saclay, France

Titanium and chromium nitrides were deposited by means of two high energetic deposition techniques such as cathodic arc deposition and high-power impulse magnetron sputtering (HIPIMS) [1,2].

The aim was to establish a correlation between these techniques and the resulting morphological-mechanical properties. Firstly, a physicochemical characterization was conducted employing X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), glow discharge optical emission spectroscopy (GDOES) techniques.

Subsequently, the mechanical-tribological characterization allows the comparison of the different chemical-morphological properties. The resulting properties were strongly depending on the processing routes and their specific parameters. For instance, the differences in terms of surface roughness affected the final tribological properties.

The built-up of material at the edge of the wear tracks found after ball-on-disc tests is in good agreement with higher droplets' density. Indeed, the better surface state (no droplets) in the case of HIPIMS leads to the reduction of the coefficient of friction (COF). It is well known that macroparticles emission creates defects (droplets) in non-filtered cathodic-arc evaporation processes. These droplets act as cutting edges, thus increasing the COF as reported by several studies [3].

Taking into account that until now, HIPIMS has few industrial applications, a final aspect concerning the industrial up-scaling feasibility was investigated. To accomplish this aim, several aspects such as the deposition rates and the measured final properties were considered. Finally, the machining performances on the developed coatings were measured, in order to justify the advantages of HIPIMS if compared with the cathodic-arc process.

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BP76 Improving the Corrosion Resistance of Electroplated Chromium Coatings on AISI H13 Steel by Gaseous Nitriding in Vacuum, ***H. Cifuentes**, J.J. Olaya (jolayaf@unal.edu.co)*, Universidad Nacional de Colombia Bogotá, Colombia

The development of chromium nitrides of type Cr_xN from the surface and subsurface modification of electrolytic chromium coatings applied to ferrous substrates (AISI H13) can improve the corrosion resistance of the metallurgical system. This document shows the results of this process through the realization of a duplex treatment that combines the application of a chromium hard coating $Cr_{(VI)}$ on a steel AISI H13 with a thermochemical treatment of gaseous vacuum nitriding . The electrolytic coating thickness was 15 µm, and N_2 was used as precursor gas with a flow of 100 ml/min at a pressure of 1.2 kPa. The existing phases were determined by means of X-ray diffraction, and the corrosion resistance was evaluated by potentiodynamic polarization and electrochemical impedance spectroscopy techniques in a three electrode electrochemical cell. The characterization by XRD could determine the presence of chromium nitrides of type Cr_2N, with an important texturing in the plane (300) associated with the partial pressure of N_2 and the thermodynamic behavior, which favors the preferential orientation of this phase in the orientation exhibited. The corrosion resistance results of potentiodynamic polarization showed a significant decrease in the corrosion current density compared to those exhibited by samples electrolytically chromed with steel AISI H13 without nitriding . The EIS results showed a significant increase of the load transfer resistance and an increase in the impedance values for low frequencies up to 3 orders, from 10^4 Ohm/cm^2 to 10^7 Ohm/cm^2. These results, coupled with the sealing of characteristic microcracks of the electrolytic chrome coating, could improve the corrosion resistance because of the existence of the Cr_2N phas.

BP77 Enhancement of Mechanical and Tribological Properties in NiTi Shape Memory Alloy Thin Films by Using Graded AlN/Al Multilayer Coating, *N. Kaur*, ***D. Kaur** (dkaurfph@iitr.ernet.in)*, Indian Institute of Technology Roorkee, India

Shape memory alloy (NiTi) thin films coupled with graded AlN/Al multilayers produce an intelligent material having improved mechanical and tribological properties. In the present study $[AlN/Al]_n$/NiTi/Si heterostructures have been deposited on Si substrate using magnetron sputtering technique. AlN/Al multilayers were grown on NiTi/Si in a graded pattern with bilayer period n=1, 4, 8 & 12 and the effect of bilayer period on different properties of heterostructure was evaluated. The heterostructures were characterized in terms of structural, electrical, morphological, mechanical and tribological properties by X-ray diffraction (XRD), four probe resistivity method, atomic force microscopy, field emission scanning electron microscopy, nanoindentation, and scratch tests. The bilayer period of AlN and Al had great influence on the hardness and the toughness properties of the heterostructure. This enhancement in hardness and toughness of the heterostructure could be attributed to the different mechanisms for layer formation with nanometric thickness such as the Hall–Petch effect and the number of interfaces that act as obstacles for the crack deflection and dissipation of crack energy.

Keywords : NiTi, Magnetron Sputtering, Shape memory, Nanoindentation

BP78 Property Evaluation in Humid Environments of Silicon-doped DLC Films Deposited by Plasma Immersion Assisted Deposition, ***C. Liu**, J. Cooper, H. Li, M. Audronis, A. Matthews, A. Leyland (a.leyland@sheffield.ac.uk)*, University of Sheffield, UK

Plasma immersion assisted deposition (PIAD) is an effective deposition technology for synthesising high quality carbon thin films. A graded layer structure which can mitigate delamination and improve adhesion can be achieved by this combined implantation and deposition technique. Hydrogen containing diamond like carbon (a-C:H) films exhibit an ultra-low sliding coefficient of friction (CoF) in dry or inert (e.g. vacuum) environments; however, the CoF of a-C:H changes dramatically with increasing humidity. Silicon-doped a-C:H (Si-DLC) films can show better humidity adaptability compared with a-C:H films. In this study, diamond-like carbon films with different silicon doping contents were deposited by PIAD with different experimental parameters. Nano-indentation and impact testing were used to investigated the mechanical properties e.g. hardness, elastic modulus and adhesion of Si-DLC coatings. Pin-on-disc wear tests were applied in an environmental chamber with humidity control, to examine the friction and wear properties at different RH% values. The chemical compositions are also examined by Energy Dispersive X-ray (EDX) analysis and Raman Spectroscopy.

BP79 First-principles Calculations on the Thermodynamic and Mechanical Properties of Ti-Al-(Zr, Hf)-N Wear-resistant Coating Systems, *A. Wang*, National Center for Quality Supervision and Inspection of Building Decoration Materials, China, ***W. Wang***, *Y. Du (yongducalphad@gmail.com)*, *L. Chen*, State Key Laboratory of Powder Metallurgy, Central South University, P.R. China

Based on the first-principles calculations, the properties of TiAl(Zr, Hf)N system have been systematically investigated and the calculated results are compared with the available experimental data. The predicted structural, phonon, electronic, and thermodynamic properties of cubic binary nitrides MN (M= Ti, Al, Zr and Hf) can give an accurate prediction for the high temperature thermodynamic properties, especially for the thermodynamic data which are difficult to determine by experiments. The temperature dependence of elastic constants are computed for the first time by first-principles quasiharmonic approach and efficient stress-strain method and is beneficial to the determination of residual stress of coatings. The effects of both lattice vibration and pressure on the thermal decomposition of TiAlN, ZrAlN and TiZrN have been first considered in the present work. It is found that the pressure increasing make the temperature of predicted binodal and spinodal curves increase, while the vibration contribution significantly decreases the temperatures. In addition, the study indicates that the improved age hardening of cubic Ti-Al-N coatings by adding Zr is because of the enlarged composition range of binodal and spinodal curves. Finally, the quaternary SQS models have been developed in the present work to describe the disordered solid solution, based on which the mechanical properties of Ti-Al-Zr-N and Ti-Al-Hf-N coatings are calculated. Additionally, the effect of addition of Zr and Hf on the spinodal decomposition is studied. It is concluded that Zr and Hf are effective in influencing the age-hardening as they promotes the coating spinodal decomposition. Present work allows the combination of theoretical predication and experiment research, which provide the theoretical guidance and useful information for the further research of coatings system.

BP80 Interfacial Structure of Ti2AlN Thin Film Deposited on MgO(111): Experimental and Computational Study, ***H. Jin*** *(jinhm@ihpc.a-star.edu.sg)*, Institute of High Performance Computing, Singapore

Single-crystalline Ti2AlN thin films have been grown on MgO(111) substrates at 750oC using DC magnetron sputtering from a Ti2Al alloy target in a mixed N2/Ar plasma. X-ray diffraction and atomic force microscopy confirm epitaxial layered growth of Ti2AlN {0002} on MgO(111). ab initio calculations were carried out to study the interfacial structure between Ti2AlN and oxygen/magnesium terminated MgO polar surfaces. It was found that the adhesion energies of Ti2AlN (0001) with O terminated MgO(111) are stronger than that with Mg terminated MgO(111) surfaces. In particular, strong charge transfers and ortital hybridizations between Ti2AlN and O terminated MgO(111) were observed. In addition, the stacking sequence of N-Ti-Al-Ti/O–Mg exhibited the largest adhesion energy among all, suggesting this interfacial structure might be the most stable structure of Ti2AlN thin film growth.

BP81 Study of the Mechanical Properties of PVD Metallic Nanocomposite Cr(N)-based Coatings with Combined Additions of Silver and Copper, ***X. Liu***, *M. Audronis, A. Yerokhin, A. Matthews, A. Leyland (a.leyland@sheffield.ac.uk)*, University of Sheffield, UK

Hard and superhard nanocomposite coatings have been intensively investigated in recent years. However, consideration of the hardness to elastic modulus ratio (H/E) has been shown to have greater merit than high hardness alone, in optimising coating mechanical properties and durability. In this study, we aim to obtain high H/E ratio coatings by controlling the nanocomposite structure of metallic nitrogen-containing PVD chromium coatings, rather than trying to obtain hard (ceramic) nitrid-containing structures. Solid lubricant (and antibacterial) ingredients – in this case both silver and copper (each of which generate different coating morphological effects) – were added to the coatings, to attempt to improve friction and wear properties, as well as to provide improved multifunctional behaviour. Coatings were deposited using a dual-target unbalanced magnetron sputtering system. Nano-indentation, sliding wear and impact wear tests were used to evaluate mechanical properties such as hardness, elastic modulus, coefficient of friction and wear resistance. X-ray diffraction, scanning electron microscopy and Energy Dispersive X-ray analyses were used to analyse the effects of the chemical composition (Cr-Ag-Cu-N), distribution of these elements (and resulting coating nanostructure) on the functional properties.

BP82 Improving the Corrosion and Tribological Performance of Magnesium Alloys by Using Duplex Surface Treatments, ***L. Liu***, *M. Audronis, A. Yerokhin, A. Matthews, A. Leyland (a.leyland@sheffield.ac.uk)*, University of Sheffield, UK

Magnesium is a promising engineering material with a high strength-to-weight ratio which enables lighter products to be achieved. Moreover, the excellent castability and weldability of magnesium alloys contribute to this material's suitability for prospective markets in the construction, automotive, aerospace and communications industries. However, several undesirable properties of magnesium alloys have prevented their widespread adoption; these include insufficient resistance to creep and poor corrosion and wear resistance.Depositing protective coatings onto magnesium alloy parts is an effective strategy to improve the corrosion and wear performance. In this work, duplex surface treatments incorporating novel PVD techniques are used to explore the wider application of magnesium alloys. To improve the durability of low-strength Mg-alloy products in tribological applications, a relatively soft and compliant, amorphous interface layer (rather than the hard – and brittle – AlMg intermetallic compound-containing layers so far explored in the literature), containing B, N, Zr, Ti or Cr elements (as well as Al), is deposited by plasma-assisted PVD. The introduction of an amorphous and/or nanocrystalline interface, with an elastic modulus closer to that of the underlying Mg-alloy substrate, accommodates substrate strain more effectively. In addition, on top of the interface layer, ceramic coatings such as TiN, CrN (or plasma electrolytic oxidation post-treatments) can be deposited to increase the hardness and corrosion resistance of the surface. Compared to hard coatings deposited directly onto Mg-alloy substrates, this design philosophy improves the matching of coating/substrate interfacial mechanical properties, such that coating toughness is enhanced by accommodation of the deformation energy without fracture. Overall, we show that such duplex layered treatments have potential to provide improved wear and corrosion protection to Mg-alloys.

Fundamentals and Technology of Multifunctional Thin Films: Towards Optoelectronic Device Applications
Room: Grand Hall - Session CP

Syposium C Poster Session

Moderator: E. Schubert, University of Nebraska-Lincoln, M. Cremona, Pontificia Universidade Católica do Rio de Janeiro

CP1 Electrical and Optical Properties of AZO/Ag Bilayer Prepared by Transfer Printing Method, ***M.S. Kim***, *D.H. Lee, Y.H. Cha, B.H.O. O, S.G. Lee, S.G. Park (sgpark@inha.ac.kr)*, Inha University, Republic of Korea

Recently, transfer printing has been widely used to form metal electrodes on various plastic substrates. This process can be applied to flexible display or organic solar cell application. Only a few metals such as Au, Ag and Cu have been employed in these applications because these metals have the property of 'glues' and 'releases' with substrate materials. The surface energy difference and cross-linking between metal and organic materials are key factors. Pure metals have better electrical properties but less optical transparency than transparent conducting oxides (TCO) and thus new structures such as TCO/Metal bilayer or TCO/Metal/TCO tri-layer have been studied. In this work, we have demonstrated that a structure of TCO/metal bilayer can be prepared successfully by a transfer printing method. A bilayer of Al-doped ZnO(AZO) and silver films sequentially deposited on poly(dimethyl siloxane) (PDMS) mold by RF magnetron sputtering is transferred onto polyester film(Obducat UV sheet) at 120^{o}C. Anti-sticking layer (METAX fz-610, Kanto kasei) are coated on PDMS mold pattern. The AZO layer thicker than 8 nm cannot be transferred because of film cracking, and Ag layer thinner than 5 nm is not enough for an adhesion layer. I-V characteristics of line patterns of AZO/Ag bilayer lines were measured. It is found that the transferred bilayer line has higher electrical resistance due to poor uniformity of METAX films formed by spin-coating and that optical transmittance of the bilayer is decreased as thickness of AZO layer is increase at the fixed thickness of Ag layer. As AZO becomes thicker surface roughness becomes larger and causes more scattering of the incident light.

CP2 Characterization of Hysteresis Phenomena in Indium Zinc Oxide Thin Film Transistors with Double-channel Layers via Capacitance-voltage Measurement, ***W. Kim***, *S.H. Lee, J.S. Park (jinsp@hanyang.ac.kr)*, Hanyang University, Republic of Korea

Lately, zinc oxide (ZnO)-based semiconductors have been investigated as active channels of transparent thin-film transistors (TFTs) for organic light-

emitting diodes and transparent displays because of their excellent electrical and optical properties at room temperature. Most of the researches have mainly been focused on improving the device performances of the TFTs. However, the electrical instability such as the threshold voltage shift due to the hysteresis phenomenon in the current-voltage characteristics of oxide-TFTs may need to be considered for practical applications. It is known that the electrical hysteresis may occur through several processes, such as electron injection and trapping within the gate insulator or deep state creation for the explicit case of a metal vacancy or electron trapping within the oxide channel layer. However, the exact mechanism responsible for the hysteresis is not clear yet.

In this study, we have investigated the hysteresis in the oxide-TFT which uses amorphous indium zinc oxide (IZO) as the active channel. The IZO-based TFTs were fabricated with a bottom-gate structure. The IZO channel layers were deposited on thermally oxidized Si substrates (gate) via RF sputtering. Some of the IZO-TFTs had double channels which were formed by two-step deposition procedures. Here, the 1st-IZO layer was deposited at relatively low oxygen contents in the O_2/Ar gas mixture. Then, the 2nd-IZO layer was deposited at the higher oxygen contents without stopping the vacuum. The source/drain electrodes were also deposited with IZO films using the same RF sputtering system under a pure Ar environment. The forward and reverse voltage-sweep transfer characteristics of the fabricated IZO-TFTs were measured. The threshold voltage shift (ΔV_{th}) caused by the hysteresis was increased with the thickness and oxygen content of the IZO layer. The charge trapping mechanism responsible for the ΔV_{th} was examined by constructing the small-signal equivalent circuits for the single- and double-channel structures of IZO-TFTs and also measuring their capacitance-voltage (C-V) characteristics in the frequency range of 1 kHz – 10 MHz. From the C-V measurement, the interface trap density (D_{it}) and channel trap density (D_{ch}) were estimated in terms of the oxygen contents used for deposition of IZO-channel layers. The results indicate that more metal vacancies and oxide interstitials can be created for the IZO-channel layers with the greater incorporation of oxygen and the larger thickness. It is also noted that the channel trapping is dominant at the higher oxygen contents, but the interfacial trapping becomes a majority trap at the lower oxygen contents.

CP3 Effects of RF Power and Oxygen Gas on the Characteristics of Thin Film Transistors with Co-sputtered Silicon Zinc Oxide Channel Layers, ***S.H. Lee***, *W. Kim*, Hanyang University, Republic of Korea, *H.S. Uhm*, Samsung Display, Republic of Korea, *J.S. Park (jinsp@hanyang.ac.kr)*, Hanyang University, Republic of Korea

Zinc oxide (ZnO)-based semiconductors as active channel layers for thin film transistors (TFTs) recently have attracted much attention due to their excellent characteristics such as higher mobility than amorphous silicon, the ability to perform room-temperature deposition, and high transparency. However, most of the successful ZnO-based TFTs incorporate indium (In), e.g. indium zinc oxide (IZO), indium zinc tin oxide (IZTO), and indium gallium zinc oxide (IGZO), which is relatively rare on Earth. This makes those technologies easily subject to a material shortage. Recently, some researchers have reported experimental results which demonstrate new oxide semiconductors free of In, such as aluminum zinc tin oxide (AZTO), magnesium zinc oxide (MZO), and titanium oxide (TiO_x), as another alternative channel layers for oxide TFTs. Also, it has been known that the group IV elements (such as Si, Ge, Ti, Zr, Hf) may act as effective donors in the ZnO lattice because they may be substitutionally placed on the Zn sites and then enhance the carrier concentration and conductivity.

In this study, we suggest a novel transparent oxide TFT which has a silicon zinc oxide (SZO) channel layer. The SZO-based TFTs with a bottom-gate structure were fabricated by the following procedures. An n-type Si (100) wafer with a low resistivity (below 0.002 Ωcm) was used as a gate electrode, and a gate insulating layer was formed by thermally oxidizing the Si substrate. Then, the SZO channel layers were deposited via a co-sputtering method using two separated targets of ZnO (99.999 % of purity, 4 inch of diameter) and boron (B)-doped Si (99.999 % of purity, 0.1 Ωcm of resistivity), by varying the applied RF powers and the flow rates of oxygen gas. Finally, aluminum (Al) films were deposited via DC magnetron sputtering, followed by a lift-off process to form the source-drain electrodes. The various methods, such as four-point probe, X-ray diffraction (XRD), UV/visible spectrophotometer, secondary ion-mass spectrometry (SIMS), and x-ray photoelectron spectroscopy (XPS), were used to investigate the effects of the rf power and oxygen gas on the electrical, structural, and optical properties of the deposited SZO films. The output and transfer current-voltage characteristics of the fabricated SZO-TFTs were measured using a semiconductor parameter analyzer (4200-SCS, Keithley). The role of Si incorporation in determining the device characteristics of the SZO-TFTs was extensively examined. In addition, the relationship between the material properties of the SZO films and the device characteristics of the SZO-TFTs was discussed in detail.

CP6 Effect of Thickness on the Structure and Optical Properties of Yttrium-Doped Hafnium Oxide Nanocrystalline Thin Films, ***C. Ramana*** *(rvchintalapalle@utep.edu), A. Ortega, M. Noor-A-Alam, A. Kongu*, University of Texas at El Paso, US

Hafnium oxide (HfO_2) is a high temperature refractory material with excellent physical, electronic and chemical properties. The outstanding chemical stability, electrical and mechanical properties, high dielectric constant (high-*k*), and wide band gap of HfO_2 makes it suitable for several industrial applications in the field of electronics, magneto-electronics, structural ceramics, and optoelectronics. HfO_2 has been identified as one of the most promising dielectric to replace SiO_2 in nano-electronics. Hafnium oxide exhibits various polymorphs; monoclinic, tetragonal, and cubic. Doping a small amount of yttrium stabilizes the HfO_2 cubic phase. The high temperature cubic HfO_2 phase stabilized by Y-doping has been shown to exhibit increased dielectric constant compared to that in monoclinic phase. In the present work, yttrium-doped hafnium oxide (YDH) films were produced by sputter deposition on quartz and sapphire substrates at 400 °C by varying the deposition time in a wide range. YDH films with a thickness range ~20-1000 nm were produced by sputter-deposition. The grown YDH films were analyzed using X-ray diffraction, scanning electron microscopy (SEM) and optical spectrophotometry to understand the effect of film thickness on the microstructure and optical properties of YDH films. The XRD and SEM results indicate that the phase evolution and grain size were dependent on the film thickness. The cubic phase of YDH is seen for films with a thickness ≥60 nm. An increase in band gap from 5.2 to 5.5 eV is observed with film thickness. A correlation between growth conditions, thicknesses, and optical properties of the YDH is discussed.

CP7 Impact of Mechanical Strain on Hot Carrier Degradation for Partially Depleted Silicon-On-Insulator n-channel Metal-Oxide-Semiconductor-Field-Effect-Transistors, ***W.H. Lo***, *T.C. Chang (tcchang@mail.phys.nsysu.edu.tw), J.Y. Tsai*, National Sun Yat-Sen University, Taiwan, Republic of China

This work studies impact of mechanical strain on hot carrier (HC) degradation for partially depleted silicon-on-insulator (SOI) n-channel metal-oxide-semiconductor-field-effect-transistors (MOSFETs). In general, conventional floating body (FB) effect can aggravate HC effect for SOI FB-type MOSFETs. For ultra-thin gate oxide, gate-induced-floating-body-effect (GIFBE) becomes a candidate to influence device performance under HC stress. By measurement of body current (I_B), we can examine the body charging behavior and clarify mechanism. Additionally, it can be found that the maximum of I_B (I_{Bmax}) shows two stage trends under application of V_D. While V_D<1V, I_{Bmax} decreases as V_D increases, since GIFBE is diminished by expansion of depletion region. Beyond V_D=-1V, I_{Bmax} increases with V_D due to impact ionization. Therefore, aggravated HC degradation for FB device is attributed to conventional FB effect instead of GIFBE, even for ultra-thin gate oxide low power devices. Furthermore, we study the influence of mechanical strain on HC stress for SOI MOSFETs. It can be seen that performance of grounder body (GB) device with strain shows more significant degradation than that without strain during stress. This is because band gap narrowing enhances impact ionization. However, FB device shows invariant under HC stress before and after strain, since FB effect could make a competition between enhancement of impact ionization rate and electric field of depletion region lowing.

Keywords: Hot Carrier Stress, GIFBE, PD SOI, n-MOSFETs, Strain

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CP8 Abnormal Threshold Voltage Shift under Hot Carrier Stress in $Ti_{1-x}N_x/HfO_2$ p-channel MOSFETs, ***J.Y. Tsai***, *T.C. Chang (tcchang@mail.phys.nsysu.edu.tw), W.H. Lo*, National Sun Yat-Sen University, Taiwan, Republic of China

This work investigates the channel hot carrier (CHC) effect in HfO2/Ti1-xNx p-channel metal oxide semiconductor field-effect transistors (p-MOSFETs). We found that the degradation of device is dominated by electron trapping since threshold voltage (Vth) shows a positive shift (Vth lowering) with an invariant of sub-threshold swing (S.S), resulting in an instability on device. It can be seen that Vth under saturation region shows insignificant degradation after CHC stress. This is because depletion region due to drain voltage (VD) covers trapping area to screen the influence of electrons. However, Vth under linear region has unusual shift under CHC stress. In general, electron trapping for p-MOSFETs locates at drain side rather than near center of channel, thus trapping behavior does not vary Vth of channel. According to that, electron trapping induced drain-induced barrier lowering (DIBL) is proposed to explain the abnormal behavior of Vth for linear region. Additionally, the influence of different concentration of nitrogen for HfO2/Ti1-xNx p-MOSFETs on CHCS also investigates in this work. Since nitrogen-induced pre-Nit during process degrade channel

mobility, the device with more nitrogen shows slighter impact ionization, leading an insignificant charge trapping-induced DIBL behavior.

CP9 Electrical Enhancement of Nitrogen Doped Amorphous In-Ga-Zn-O Thin Film Transistors by Microwave Annealing, *C.S. Fuh, P.T. Liu (ptliu@mail.nctu.edu.tw), S.M. Sze, S.W. Huang, M.J. Liu,* ***C.H. Chang***, National Chiao Tung University, Taiwan, Republic of China

We investigated on the physical characteristics and electrical performance of nitrogen doped amorphous In-Ga-Zn-O thin film transistor (IGZO:N TFT) without any channel passivation layer. By using microwave annealing technology instead of thermal furnace annealing, the electrical characteristics of a-IGZO:N (N_2 = 2sccm) thin film transistor could improve obviously from normally off to a transfer characteristic with a carrier mobility of 4.97 cm^2/Vs, threshold voltage of 3.98 V and subthreshold swing of 0.39 V/decade. This TFT performance with microwave annealing of 300s is well competitive with its counterpart with furnace annealing at 450℃ for 1 hr. The a-IGZO:N TFT performance especially in mobility could further improve by increasing the microwave annealing time from 100s to 600s. Besides, we also discussed the nitrogen containment in a-IGZO with different flow rate of nitrogen gas mixed with argon gas during thin film deposition by DC sputtering system. With the nitrogen flow rate increased from 0 to 2sccm, the mobility of device is enhanced significantly from 2.06 to 4.97 cm^2/Vs and the threshold voltage is lowered from 8.83 to 3.89 V. The effective carrier concentration in a conductive oxide semiconductor might be increased due to the doping of nitrogen with low electronegativity.

CP10 Chemical Bath Deposited Zn-Cd-S Buffer Layer for Cu(In,Ga)Se_2 Solar Cells, ***Y.C. Lin***, National Chung Hsing University, Taiwan, Republic of China, *Z.C. Chang*, National Chin Yi University of Technology, Taiwan, Republic of China, *F.S. Shieu (fsshieu@dragon.nchu.edu.tw)*, National Chung Hsing University, Taiwan, Republic of China

Fabrication of Zn-Cd-S films by Chemical bath deposited (CBD) has been studied for use as buffer layers in Cu(In,Ga)Se_2 (CIGS)-based solar celldevices.The Zn-Cd-S films were grown using zinc sulfate, thiourea , cadmium acetate and ammonia water in the temperature 70℃.The process gives good control of thickness and [Cd]/([Cd]+[Zn]) content of the films.

The prepared films were characterized by scanning electron microscopy, X-ray photoelectron spectroscopy and UV–vis spectroscopy.The band gap increased from 2.4 to 3.8eV with increasing [Cd]/([Cd]+[Zn]) from 0 to 1. The Zn-Cd-S buffer layer of efficiency enhance and it was shared better the lattice matched with CIGS.

CP11 Investigation on Amorphous InGaZnO Based Resistive Switching Memory with Low-power, High-speed, High Reliability and Good Flexibility, ***Y.S. Fan***, *C.H. Hsu, P.T. Liu (ptliu@mail.nctu.edu.tw)*, National Chiao Tung University, Taiwan, Republic of China

Recently, nonvolatile memory (NVM) has been widely used in electronic devices. Nowadays, the prevailing NVM is Flash memory. However, it is generally believed that the conventional Flash memory will approach its scaling limit within about a decade. The resistive random access memory (RRAM) is emerging as one of the potential candidates for future memory replacement because of its high storage density, low power consumption as well as simple structure.

The purpose of this work is to develop a reliable a-InGaZnO based resistive switching memory. We investigate the resistive switching characteristics of TiN/Ti/IGZO/Pt structure and TiN/IGZO/Pt structure. The device with TiN/Ti/IGZO/Pt structure exhibits stable bipolar resistive switching. The impact of inserting a Ti interlayer is studied by material analyses. The device shows excellent resistive switching properties. For example, the DC sweep endurance can achieve over 1,000 times; and the pulse induced switching cycles can reach at least 10,000 times. In addition, we demonstrate the possibility of MLC IV operation for the device. By controlling the compliance current, multi-level operation can be achieved. Besides, the pulse induced switching is also performing on the MLC operation by adjusting the pulse amplitude. Furthermore, the impact of different sputtering ambient, the temperature instability, and the conduction mechanisms are also investigated. According to our experiment s, we propose a model to explain the resistive switching phenomenon observed in our devices.

Finally, because the whole fabricating process of the RRAM device is under room temperature, it holds the potential for flexible electronics applications. The TiN/Ti/IGZO/Pt RRAM device is fabricated on flexible stainless steel to test its flexibility and mechanical endurance.

CP12 Effect of Sn-layer Addition to Precursors on Characteristics of $Cu_2ZnSn(S,Se)_4$ Thin Film Solar Cell Absorber, ***K. Sammi***, *K. Woo Kyoung (wkim@ynu.ac.kr), O. Misol, L. Soobin, J. Soyoung*, Yeungnam University, Republic of Korea

Kesterite $Cu_2ZnSn(S,Se)_4$ (CZTS(e)) compound semiconductor is characterized by direct band gap energy and high absorption coefficient ($\alpha \sim 10^4$ cm^{-1}), which are suitable for photovoltaic applications. In addition, rare-earth material such as Ga and In within high-performance Cu(InGa)Se_2 solar cell absorber are replaced by Zn and Sn which are naturally abundant and thus relatively inexpensive. Band gap energies of CZTS(e) semiconductors vary in the range of 0.95~1.5 eV, depending on the relative contents of S and Se. Several vacuum and non-vacuum synthesis methods have been explored to form the kesterite compound. CZTS solar cells with 0.66% efficiency using vacuum-based process were first reported in 1997 by Katagiri et al. Recently, IBM reported considerable conversion efficiency of 8.4% for CZTS cells fabricated by thermal evaporation of elemental Cu, Zn, Sn and S in a vacuum system. The record efficiency of 10.1% (AM1.5) achieved for kesterite photovoltaic absorber of CZTS(e) was also reported by IBM, using hydrazine-based solution process. However, their process may be difficult to be commercialized due to toxicity of hydrazine solvent. In our study, 3-step sputter/selenization/sulfurization process was employed. Precursors were prepared on Mo-coated glass substrate by sequential and/or simultaneous sputtering of Cu, Zn and Sn metal targets. Two kinds of precursor structures, Mo/Zn/(Cu+Sn) and Mo/Sn/Zn/(Cu+Sn), were employed to evaluate the effect of addition of Sn layer to Mo/Zn interface. Selenization and sulfurization of precursors were performed using Se vapor and H_2S gas in a rapid thermal process system, with the reaction temperatures of 380 ℃ for selenization and 480-600 ℃ for sulfurization. The results demonstrated that the insertion of Sn layer into the interface of Mo/Zn mitigated the overall Sn loss and delamination of CZTS(e) films. Further details of sulfurization temperature effect on the resulting CZTS(e) thin films will be discussed.

CP13 Rapid Sulfurization of CuGaIn/Se Precursors, ***L. Soobin***, Yeungnam University, Republic of Korea, *C. Hyun-il, S. Changgil, A. Donggi, K. Byoungdong*, Samsung SDI, Republic of Korea, *K. Woo Kyoung (wkim@ynu.ac.kr)*, Yeungnam University, Republic of Korea

Cu(InGa)Se_2 (CIGSe)-based chalcopyrite thin film has been employed as a desirable light absorber for thin film solar cell, recently yielding 20.3% cell efficiency (2010, ZSW). Typically, either the selenization of CuGaIn metal precursor selenization or elemental co-evaporation is used to fabricate CIGSe layers. Especially, selenization using the rapid thermal processing (RTP) of Se-coated CuGaIn precursors followed by sufurization by H_2S was successfully scaled up by Avancis company, reporting a conversion efficiency of 13.9% at 65 x 165 cm^2 module. It is assumed that the partial substitution of Se with S is intended to improve Ga depth uniformity within absorber and increase band gap energy at the surface of absorber layer.

In this contribution, the sulfurization process of CuGaIn/Se precursors by H_2S was investigated with a particular emphasis on the phase evolution and compositional depth profile. The CuGaIn metal precursors were prepared by either sequential or simultaneous sputtering of CuGa and element In target, followed by thermal evaporation of Se. The reactive selenization and sulfurization of precursors were carried out in a tube-type rapid thermal process system at the temperatures of 450-570 ℃ and 570-600 ℃, respectively. In-situ phase evolution during sulfurization was observed by high-temperature X-ray diffraction scan. Compositional depth profile was measured by transmission electron microscope and secondary ion mass spectrometer. Morphology during sulfurization was analyzed by scanning electron microscopy of samples obtained by intentional quenching during reactive annealing. It was found that replacing Se of CIGSe structure by S would affect the formation of $MoSe_2$ and Ga incorporation. Also, the degree of S dosing would be affected by the degree of selenization at the first stage, which is controlled by selenization conditions such as the thickness of Se layer, reaction time and temperature.

CP14 Electrical and Optical Properties of Magnesium Doped Delafossite Structure $CuCr_{1-x}Mg_xO_2$ Reactively co Sputter Deposited Coatings, ***P. Briois*** *(pascal.briois@utbm.fr), M. Arab Pour Yazdi*, IRTES-LERMPS-UTBM, France, *J.F. PIERSON*, Institut Jean Lamour, France, *A. Billard*, IRTES-LERMPS-UTBM, France

Transparent conducting oxides (TCOs) are materials with rather high electronic conductivity and low optical absorption of the visible light which can be used in many applications in transparent electronics, e.g. light emitting diodes, photovoltaics, smart windows or flat panel displays.

The p-type TCOs mainly consist in spinel and delafossite materials with AB_2O_4 and ABO_2 stoichiometry, respectively. Very few papers deal with the deposition of delafossite structure coatings which however are of strong importance for the development of new transparent devices which are not

feasible with n-type materials alone, e.g. transparent diodes, transistors or heterojunctions.

In this paper, we investigate the feasibility of magnesium doped p-type delafossite structure $CuCr_{1-x}Mg_xO_2$ coatings by co sputtering of metallic targets in argon-oxygen reactive gas mixtures.

After a short description of the experimental device were the substrates are positioned on a rotating substrate holder, the coatings are performed in so called compound sputtering mode by fixing the discharge current of the Cr target and by modifying that of the Cu or Ag one. Hence, the chemical, structural, microstructural and morphological features of the coatings are investigated via scanning electronic energy dispersive X-ray spectroscopy, X-ray diffraction and scanning electron microscopy on thick films. Complementary structural data are assessed by Fourier transmission infrared spectroscopy and Raman spectrometry. The optical properties of the films are assessed by optical transmission spectrophotometry and their electrical conductivity is determined by using four point probe method.

Finally, the influence of annealing performed in air at different temperatures is investigated owing to the structural, optical and electrical properties of $CuCr_{1-x}Mg_xO_2$ coatings.

CP15 High Power Impulse Magnetron Sputtering of Transparent Conducting Oxides, ***L.C. Chang*** *(lcchang@mail.mcut.edu.tw), C.K. Chang, S.C. Wang*, Ming Chi University of Technology, Taiwan, Republic of China

High power impulse magnetron sputtering (HIPIMS) has been used in order to study the deposition of transparent conducting oxides. We summarize the studies carried out on aluminium-doped zinc oxide - AZO using reactive sputtering. For the deposition of AZO reactive HIPIMS for metallic targets has been used. In this study, a plastics was used as a flexible substrate. A feedback control loop has been implemented in order to stabilize the discharge at any given setpoint on the hysteresis curve. The hysteresis was also found to have a rather untypical form. Reactive HIPIMS was found to be a promising tool for obtaining high quality films of low total thickness.

CP16 Synthesis of Silver Nanowire by Polyol Method for Transparent Conductive Film Application, ***J.J. Huang*** *(jjhuang@mdu.edu.tw)*, MingDao University, Taiwan, Republic of China, *J.Y. Lin*, National Yunlin University of Science and Technology, Taiwan, Republic of China, *C.N. Chen*, Asia University, *Y.L. Hsueh*, National Yunlin University of Science and Technology, Taiwan, Republic of China, *M.W. Tsai*, MingDao University, Taiwan, Republic of China

In the study, we used the polyol method to synthesize silver nanowire, and the use of silver nitrate ($AgNO_3$) as the precursor for seeds. The experimental results show that the different synthesis temperature, Poly(N-vinylpyrrolidone) (PVP) molecular weight, the concentration of reactants and the addition rate of silver nitrate will affect the growth characteristics of silver nanowires. Field-emission scanning electron microscopy, UV-vis spectrophotometer and x-ray diffractometer have been employed to characterize the silver nanowires. When the synthesis temperature is higher than 180℃, the nucleation rate is too fast. Therefore, the particles are homogeneous nucleation and the formation of silver particles. When increasing the concentration of PVP, the diameter of the silver nanowires will be widened to cause a smaller aspect ratio. This study successfully prepared silver nanowires with a diameter of 120 nm and a length of 20 μm. Finally, the transmittance and sheet resistance were measured by UV-vis spectrophotometer and four-point probe I-V test, respectively. The solution-type silver nanowire thin film shows high transmittance, low sheet resistance and can be used for transparent conductive film application.

CP17 Performance Improvement of Hybrid Solar Cells with Thermally Evaporated Cuprous Oxide as a Hole Transport Layer, ***Y. Yu*** *(yyyu@mail.mcut.edu.tw), Y. Wang, M. Hsu*, Ming Chi University of Technology, Taiwan, Republic of China

In this study, a polymer solar cell with a thermally evaporated cuprous oxide (Cu2O) as the hole transport layer between the active layer and the top anode was fabricated. The Cu2O thin film can module the Schottky barrier and form an ohmic contact at the organic/metal interface, which make it a great holes transport layer. The device performance obtained from different Cu2O thicknesses and different annealing temperature and time are investigated. The results show that the cell stability increases with Cu2O as the hole transport layer compared to the control cell without Cu2O.

CP18 Nanocomposite Anti Bacterial Sputter Deposited Coatings, ***E. Monsifrot***, Dephis, France, *F. Sanchette*, ICT, France, *A. Billard (alain.billard@utbm.fr)*, IRTES-LERMPS-UTBM, France, *F. Schuster*, CEA, France

Anti bacterial surfaces are of increasing importance for various applications. Among the coatings able to ensure antibacterial activity, both crystallized titanium dioxide that allows photocatalytic destruction of bacteria under UV irradiation and noble metals such as Cu or Ag introduced into a ceramic matrix are known as suitable alternatives.

Association of titanium dioxide with a noble metal in a nanocomposite coating is an alternative susceptible to allow both effects. Among the technologies able to produce nanocomposite TiO_2-Cu(Ag) coatings, reactive co sputtering is known as a powerful technique.

In this paper, after a short description of the industrial vessel used for the deposition of TiO_2-Cu(Ag) nanocomposite coatings using plasma emission monitoring, we investigate the effect of emission setpoint of the titanium target and discharge current dissipated on the noble metal target on the structure of as-deposited TiO_2-noble metal coating.

Finally, anti bacterial tests are performed using two model bacteria, i.e. *escherichia coli* and *staphylococcus aureus*, to give tendancies owing to the nanocomposite structure on the anti bacterial activity.

CP19 Organic Thin-film Transistors with Polymer–nanoparticle Hybrid Dielectrics Layer, ***Y. Yu*** *(yyyu@mail.mcut.edu.tw), M. Chen*, Ming Chi University of Technology, Taiwan, Republic of China

In this study, a high-performance organic thin-film transistors (OTFTs) with a nanocomposite dielectric and semiconducting layer has been demonstrated. The dielectric and semiconducting layer is prepared from the polyimide/barium titanate (PI/BaTiO3) nanocomposite and pentacene, respectively. It was found that the OTFTs with the PI/BaTiO3 nanocomposite dielectric layer have higher field-induced current than that of conventional devices because the dielectric constant of the gate insulator is increased. In addition, the dielectric constant of PI/BaTiO3 is tunable by controlling the solid content of BaTiO3 in nanocomposite. The results shows the present PI/BaTiO3 has a great potential as the dielectric layer for the preparation of high-performance OTFTs.

CP20 Investigation of Sputtered GAZO Films for CIGS Photovoltaics, ***C.-H. Huang*** *(chuang@mail.ndhu.edu.tw)*, National Dong Hwa University, Taiwan, Republic of China, *H.-L. Cheng*, Natioanl Dong Hwa University, Taiwan, Republic of China

With the conversion efficiency of over 20% and the potential of low-cost production, $Cu(In,Ga)Se_2$ (CIGS) solar cells have drawn much attention in recent decades. Aluminum doped zinc oxide (AZO) films have been extensively used as the window layers for the high-efficiency thin-film CIGS solar cells. Due to the high reactivity of aluminum with oxygen resulting in oxidation of aluminum, the long-term stability of CIGS solar cells with the AZO films as the window layers is deteriorated when the CIGS solar modules are under the environments of high temperature and humidity. In contrast to aluminum, gallium is less reactive and more resistant to oxidation. In order to fulfill the requirements of both performance and stability for the transparent electrodes in the photovoltaic applications, the aluminum and gallium codoped zinc oxide (GAZO) thin films were investigated. Most deposition techniques for the preparation of GAZO films require the elevated substrate temperature during the deposition to achieve the better properties of as-deposited films. However, the deposition temperature for the front contacts must be lower than 200°C, otherwise the junction properties of CIGS solar cells will be ruined. The GAZO films were deposited on the glass substrates by magnetron sputtering technique using a single ceramic target. Deposited at the substrate temperature below 200°C, the electrical and optical properties of GAZO films employed as the window layers for $Cu(In,Ga)Se_2$ (CIGS) solar cells were optimized. The deposition parameters including working pressure and working power were varied to investigate their effects on the microstructral, electrical, and optical properties of GAZO films. The crystalline structure of films was studied using X-ray diffraction (XRD), and the surface morphology and cross-sectional view were observed by field-emission scanning electron microscope (FE-SEM). The carrier concentration, mobility, and resistivity of as-deposited films were measured by a Hall measurement system. The optical transmittance was measured with an UV/VIS spectrophotometer. In addition, the band gap energies of GAZO films were determined from the optical properties. The impacts of sputtering parameters on the structural, electrical, and optical properties of GAZO thin films was thoroughly studied through the detailed characterization of as-deposited films. Under the given deposition conditions, the GAZO films of 400 nm in thickness possessed a low sheet resistance below 10Ω/□ and high optical transmittance of over 85% in the visible region.

CP21 Investigation of Green and Yellow Luminescence from Alpha and Beta Zinc Silicate Thin Films Doped with Manganese, ***Y.K. Cho***, *J.H. Kim (joohan@cbnu.ac.kr)*, Chungbuk National University, Republic of Korea

The green and yellow luminescence from alpha and beta zinc silicate (Zn_2SiO_4) thin films doped with manganese were investigated. The Mn-

doped Zn_2SiO_4 films were prepared by radio frequency magnetron sputtering in an argon/oxygen gas mixture. X-ray diffraction (XRD) patterns revealed that the as-prepared Zn_2SiO_4:Mn films were of amorphous structure. The amorphous Zn_2SiO_4:Mn films were crystallized by post-deposition annealing in an air atmosphere at temperatures ranging between 800 and 1200 °C for 1 h. It was found that the Zn_2SiO_4:Mn films annealed at 800 °C possessed a mixture of alpha and beta phases. The obtained photoluminescence (PL) spectrum consisted of two emission bands centered at 525 nm in the green range and 574 nm in the yellow range. The green luminescence originates from the Mn^{2+} ions in alpha phase of zinc silicate (α-Zn_2SiO_4), while the yellow luminescence comes from the Mn^{2+} ions in β-Zn_2SiO_4. However, the films annealed at and above 900 °C exhibited only the alpha phase and the crystallinity was improved with increasing annealing temperature up to 1200 °C. The PL spectra showed only the green emission band with a peak maximum around 523 nm. The PL emission intensity was enhanced as the annealing temperature was increased, resulting from improved crystallinity of the α-Zn_2SiO_4:Mn films. The broad PL excitation band was observed ranging from 220 to 300 nm with a maximum at around 243 nm.

CP22 Effect of the Thin Ga_2O_3 Layer in n^+-ZnO/n-Ga_2O_3/p-Cu_2O Heterojunction Solar Cells, ***Y. Nishi*** *(y_nishi@neptune.kanazawa-it.ac.jp), T. Miyata, T. Minami*, Kanazawa Institute of Technology, Japan

Recently, we reported that Al-doped ZnO (AZO)/non-doped $Zn_{1-X}Mg_XO$/Cu_2O heterojunction solar cells with conversion efficiencies over 4% were fabricated with a Mg content (Mg/Zn+Mg atomic ratio : X) in the range of 0 to 0.09 using Cu_2O sheets that had been prepared by a thermal oxidization of copper sheets. This paper describes heterojunction solar cells with high efficiencies, over 5%, that were fabricated by inserting n-Ga_2O_3 instead of n-$Zn_{1-X}Mg_XO$, producing n^+-AZO/n-Ga_2O_3/p-Cu_2O. The Cu_2O sheets, with electrical properties such as resistivity on the order of 10^3 Ωcm, hole concentration on the order of 10^{13} cm^{-3} and Hall mobility above 100 cm^2/Vs, were prepared by a thermal oxidization of copper sheets under appropriate conditions. Non-doped Ga_2O_3 thin films were prepared on non-intentionally heated Cu_2O sheets by a pulsed laser deposition (PLD) using an ArF excimer laser in a camber where O_2 gas was being introduced at partial pressures in the range from 0 (vacuum) to 3 Pa. The photovoltaic properties of the fabricated Cu_2O-based solar cells were evaluated under AM1.5G solar illumination (100 mW/cm^2) at 25°C. It was found that the obtainable photovoltaic properties such as conversion efficiency (η), open circuit voltage (V_{OC}), short-circuit current density (J_{SC}) and fill factor (FF) in the AZO/Ga_2O_3/Cu_2O heterojunction solar cells were strongly dependent on the thickness as well as the deposition conditions of the Ga_2O_3 films. The external quantum efficiency (EQE) obtained in AZO/Ga_2O_3/Cu_2O heterojunction solar cells was found to be greater at wavelengths below approximately 400 nm than that obtained in AZO/$Zn_{1-X}Mg_XO$/Cu_2O at equivalent wavelengths. In addition, the obtainable photovoltaic properties in AZO/Ga_2O_3/Cu_2O heterojunction solar cells improved considerably as the O_2 partial pressure was increased during the PLD, reaching maximum values at approximately 1.7 Pa, and then decreased as the pressure was increased further. All the maximum values for V_{OC}, J_{SC}, η and FF obtained in AZO/Ga_2O_3/Cu_2O heterojunction solar cells were higher than those obtained in AZO/$Zn_{1-X}Mg_XO$/Cu_2O heterojunction solar cells. An efficiency over 5% was obtained in an AZO/Ga_2O_3/Cu_2O heterojunction solar cell fabricated using a Ga_2O_3 thin-film layer prepared with a thickness of 50 nm under an O_2 partial pressure of 1.7 Pa. It can be concluded that a thin Ga_2O_3 film can serve as an excellent n-type semiconductor layer in Cu_2O-based heterojunction solar cells.

CP23 Influence of Crystallographical Properties on Obtainable Texture-etched Surface Structure in Transparent Conducting Impurity-doped ZnO Thin Films, ***T. Miyata*** *(tmiyata@neptune.kanazawa-it.ac.jp), J. Nomoto, T. Fujita, T. Minami*, Kanazawa Institute of Technology, Japan

For impurity-doped ZnO thin films to be suitable for transparent electrode applications in Si-based thin-film solar cells, they must attain a significant scattering of incident visible and near-infrared light by the textured surface structure formed on the films. This paper describes the relationship between the crystallographical properties and the obtainable texture-etched surface structure in transparent conducting impurity-doped ZnO thin films. Al-, Ga-, or B-doped ZnO (AZO, GZO, or BZO) thin films were prepared with a thickness of 1-2 μm on OA-10 glass substrates at 200°C by pulsed laser deposition using an ArF excimer laser and/or magnetron sputtering deposition (MSD). AZO, GZO, and BZO thin films were prepared by PLD. AZO and GZO thin films were also prepared by direct current (dc) MSD (dc-MSD) and radio frequency power superimposing dc-MSD (rf+dc-MSD). To obtain the light scattering characteristics suitable for applications in thin-film solar cells, we carried out surface texturing of the samples by wet-chemical etching in a 0.5% HCl solution. We also performed surface morphology observations and optical property measurements that included angular resolved scattering (ARS) and haze values on surface-textured impurity-doped ZnO thin films. For the crystallographical property evaluation, out-of-plane or in-plane XRD and X-ray locking curve measurements were carried out for the impurity-doped ZnO thin films. For example, for AZO thin films prepared by rf+DC-MS, the following characteristics were found to be considerably dependent on the crystallographical properties of the films: the etching rate, the surface texture structure formed by wet-chemical etching, and such resulting light scattering properties as the ARS data and the haze values. Note that the ARS intensity at scattering angles from 40 to 80 degrees and haze values at longer wavelengths significantly increased as the c-axis orientation of the AZO films improved, as evidenced from the full width at half maximum (0002) of the locking curve of the AZO films, regardless of the deposition methods. In addition, the AZO films exhibited lower ARS intensity and haze values, as evidenced from the observations of (100), (101), (110), (200), and (201) diffraction peaks in the in-plane XRD patterns. In contrast, the AZO films exhibited higher ARS intensity and haze values, as evidenced from the observations of only (100), (110), and (200) diffraction peaks. These results suggest that the influence of the crystallographical property on the obtainable texture-etched surface of the AZO films described above can be mainly attributed to such crystallinity improvement as orientation and crystallite size.

CP24 Co-Sputtering and RTA Process for Preparation of CIGS Thin Films Using Gallium, Indium and Copper Diselenide Alloy Targets, ***E. Bleza***, *S. Oh, G. Cho, N. Kim (nhkim@chosun.ac.kr)*, Chosun University, Korea

Thin-film solar cells with copper-indium-gallium-diselenide (CIGS) absorber offer the high-efficiency of performance, which are considered as the most promising photovoltaic devices in the new and renewable energy industry with the efficiency up to 20%. The CIGS thin films are generally manufactured by the selenization process in selenium-containing gas after sputtering method or the three-stage process in evaporation method with four sources of copper, indium, gallium, and selenium pure elements. However, the above mentioned methods have some critical problems for mass-production including process complexity with costly equipment. A novel non-selenization method was proposed and demonstrated to prepare CIGS thin film sputtered by using gallium, indium and copper diselenide alloy targets with multilevel stacked structure and rapid thermal annealing (RTA) process in our previous study. In this study, the magnetron co-sputtering method was performed with three sputtering guns for using gallium, indium and copper diselenide alloy targets followed by RTA treatment. The powers in each sputtering gun were varied for adjusting the stoichiometry in CIGS thin films. The crystal structure of the RTA-treated CIGS thin films was analyzed by using X-ray diffraction (XRD) and Raman scattering. A secondary ion mass spectroscopy (SIMS) depth profile was employed to examine the chemical states of the RTA-treated CIGS thin films. The optical properties and electrical characteristics of the RTA-treated CIGS thin films were analyzed by using UV-visible spectrophotometer and a Hall Effect measurement system. Acknowledgement: This research was financially supported by the Ministry of Education, Science Technology (MEST) and National Research Foundation of Korea(NRF) through the Human Resource Training Project for Regional Innovation.

CP25 Analysis of Coatings in Matrix of Conformation Fasteners in Stainless Steel Austenitic, *W. Mattes*, ***J. Paiva Junior*** *(josemario@sc.senai.br)*, Centro Univesitário Catolica de Santa Catarina, Brazil

This work was to study to test the application of three coatings, deposited in arrays conformation, for the manufacture of fastening elements in austenitic stainless steels 302 HQ. One of the problems that occur during the forming process is the adhesion of conformal material (stainless steel 302HQ), forming the arrays were coated with TiN, TiAlN and TiAlSiN. Forming Matrices were machined by a polishing process, to reduce the roughness. To analyze the behavior of the coatings were used the following tests: integrity analysis tools through superficial roughness; tests microstructures characterization by scanning electron microscope (SEM); assay adhesion of the coating, embossing tests; Metallographic analysis: the substrate tool Steel AISI D6, the lines of deformation of a screw formed by the first matrix tested in a tool sectioned regions of: substrate layer of the coating. It was determined that the matrices must have a roughness pattern to avoid wear and improve the process. In the forming process is crucial that no flaws, a variable that must be controlled is the alignment between the tool and blank.

CP26 Influence of Rapid Thermal Annealing Treatment on Transparent Conducting Impurity-Doped ZnO Thin Films for Thin-Film Solar Cell Applications, ***J. Nomoto***, *T. Miyata (tmiyata@neptune.kanazawa-it.ac.jp)*, *T. Minami*, Kanazawa Institute of Technology, Japan

This paper describes an investigation of the influence of a rapid thermal annealing (RTA) treatment on various properties of transparent conducting impurity-doped ZnO thin films prepared by magnetron sputtering depositions that was conducted in an effort to develop thin-film transparent electrodes suitable for thin-film solar cell applications. Impurity-doped ZnO thin films such as Al- or Ga-doped ZnO (AZO or GZO) were deposited with a thickness of 2 μm on OA-10 glass substrates at a temperature of 200 ^{o}C. The Hall mobilities in both the AZO and GZO films doped with impurity contents up to approximately 1.5 at.% always decreased after heat treatment with RTA at 500^{o}C for 5 min in air, which is in contrast to the slight increase of the Hall mobilities exhibited in films doped with an impurity content above approximately 1.5 at.%. In addition, the heat treatment with RTA was found to improve the crystallinity in these films, as evidenced from X-ray diffraction analyses. The heat treatment with RTA always decreased the carrier concentration in both the AZO and GZO films, irrespective of the doped impurity content, whereas the resulting carrier concentration in as-deposited AZO and GZO thin films increased as the impurity content doped into the films was increased. In addition, the etch pit size developed in AZO and GZO films that were surface textured by wet-chemical etching in 0.2 mol./l HCl at 25^{o}C tended to increase as the content of impurity doped in the films was increased up to approximately 2.5 at.%; however, the etch pit size obtained in GZO films decreased as this content was increased further. It should be noted that the heat treatment with RTA resulted in considerably enhanced etch pit size in these films, irrespective of the kind and content of doped impurity. As a result, in the films that were wet-chemically etched after being heat treated with RTA, the transmittance and the haze value in the near infrared range of 800-1200nm both increased as the size of the etch pits increased. The improvement of optical properties described above is attributed to the decrease of carrier concentration as well as the increase in etch pit size that result from the RTA treatment improving the crystallinity. In addition, it should be noted that the improvement in the transmittance and the haze value obtained in texture-etched impurity-doped ZnO thin films doped with an appropriately lower impurity content as well as heat treated with RTA is sufficient to enable the use of the surface textured AZO and GZO films described above for thin-film transparent electrode applications in thin-film solar cells. This work was supported by the NEDO.

CP29 Hole Trapping-induced Anomalous Gate Current Hump after Dynamic Negative Bias Stress in p-MOSFETs with HfO_2 and $Hf_xZr_{1-x}O_2$/Metal Gate Stacks, ***S.H. Ho***, National Chiao Tung University, Taiwan, Republic of China, *T.C. Chang (tcchang@mail.phys.nsysu.edu.tw)*, National Sun Yat-Sen University, Taiwan, Republic of China, *T.Y. Tseng*, National Chiao Tung University, Taiwan, Republic of China

This letter investigates an anomalous hump in gate current after dynamic negative bias stress (NBS) in HfO_2 and $Hf_xZr_{1-x}O_2$/metal gate p-channel metal-oxide-semiconductor field-effect transistors which is found to be a result of hole trapping in high-k bulk. Measuring gate current under initial for body floating and source/drain floating conditions isolates hole current flowing from the source and drain. The fitting of the gate current-gate voltage characteristic curve demonstrates that the Frenkel-Poole mechanism dominates the conduction. Next, fitting the gate current after dynamic NBS confirms Frenkel-Poole, tunneling, then a second Frenkel-Poole mechanism region. These phenomena can be attributed to hole trapping in high-k bulk and the electric field following $E_{high\text{-}k}\,\varepsilon_{high\text{-}k} = Q + E_{sio2}\varepsilon_{sio2}$. To further understand gate current, Zr-undoped and 8% ~ 10% Zr-doped in high-k bulk devices were used for comparison. All the results conform to the hump generation condition $J_{Tunneling} << J_{Frenkel\text{-}Poole}$.

CP30 Temperature Dependent Instability of Drain Bias Stress in Amorphous Indium-Gallium-Zinc-Oxide Thin Film Transistors, ***G.W. Chang*** *(b922030049@gmail.com)*, National Chiao Tung University, Taiwan, Republic of China, *T.C. Chang*, National Sun Yat-Sen University, Taiwan, Republic of China, *Y.H. Tai*, National Chiao Tung University, Taiwan, Republic of China, *Y.E. Syu*, National Sun Yat-Sen University, Taiwan, Republic of China

This paper investigates the behavior of drain bias stress at high temperature for amorphous Indium-Gallium-Zinc-Oxide thin film transistors (a-IGZO TFTs). The abnormal electrical characteristics exhibit a two-stage degradation behavior during drain bias stress, and are explained by the energy band diagrams . The thermal-excited non-uniform hole trapping in the drain region induces drain side barrier lowering and causes an apparent hump phenomenon in the subthreshold swing. This phenomenon only appears at high temperature, above 400K, and is experimentally verified. This work also employs capacitance-voltage measurement to confirm the proposed mechanism. Moreover, we applied a technology computer-aided design (TCAD) simulation system to further clarify the mechanism of degradation behaviors.

CP31 Temperature Dependence on Positive Gate Bias Instability in HfO_2/TiN p-MOSFETs, ***H.M. Chen***, National Chiao Tung University, Taiwan, Republic of China, *T.C. Chang (tcchang@mail.phys.nsysu.edu.tw)*, National Sun Yat-Sen University, Taiwan, Republic of China, *Y.H. Tai*, National Chiao Tung University, Taiwan, Republic of China, *W.H. Lo*, National Sun Yat-Sen University, Taiwan, Republic of China

This work studies positive gate bias temperature instability (PBTI) in high-k/metal gate p-channel MOSFETs. We found that device with different nitrite (N) concentration of metal gate shows contrary trend of V_{th} shift under high temperature during stress. Accordingly, off-state gate leakage (OSGL) is measured to analyze the conduction mechanism of carrier during PBTI. For device with less N, PBTI-induced V_{th} shift is attributed to Poole-Frankle mechanism under high temperature, since V_{th} shift and OSGL decrease as temperature increases. This is because carriers could conduct toward gate electrode likely instead of being trapped in high-k bulk, resulting in insignificant V_{th} shift as high temperature. However, for device with more N, the mechanism of V_{th} shift under high temperature is associated with thermal emission, since V_{th} shift and OSGL show a contrary tendency with temperature. According to that, it indicates that trapping carriers in high-k layer could be supplied by thermal emission continuously.

CP32 Investigation of Random Telegraph Signal in PD SOI nMOSFETs between Moderate and Strong Inversion Region, ***C.E. Chen***, National Chiao Tung University, Taiwan, Republic of China, *T.C. Chang (tcchang@mail.phys.nsysu.edu.tw)*, *B. You*, National Sun Yat-Sen University, Taiwan, Republic of China, *T.Y. Tseng*, National Chiao Tung University, Taiwan, Republic of China

This paper investigates the random telegraph signal (RTS) with partially depleted silicon-on-insulator n-channel metal-oxide-semiconductor field effect transistors (PD SOI nMOSFETs). It was found that the relative amplitude of drain current RTS (ΔID/ID) with different gate voltages reveal a steep decrease in moderate inversion and a temperate decrease in strong inversion. According to drain current RTS (ID-RTS) at different temperatures, the active energies of capture cross section could extract by Shockley-Read-Hall (SRH) model at different gate voltages. These active energies correspond to non-radiative multiphonon (NMP) barrier heights and then provide a fundamental physical model of oxide traps for ID-RTS from moderate to strong inversion region.

CP33 Self Current Compliance Bipolar Resistance Switching Characteristics for Nonvolatile Memory Application, ***H.C. Tseng*** *(burglar1202@gmail.com)*, National Sun Yat-Sen University, Taiwan, Republic of China

This study investigates the self current compliance bipolar resistance switching behaviors of resistive random access memory with ITO/SiO_x:Gd/TiN and Pt/SiO_x:Gd/TiN devices. Generally, because the set process of filament-type resistance switching has to accompany a current compliance, the transistor is a common element to achieve the function of current compliance (1T-1R structure). However, the 1T-1R structure suffers from certain physical limitations from its continual scaling down limit. Hence, a self-formation current compliance structure should be developed. ITO/SiOx:Gd/TiN structure can exhibit a self current compliance property due to an interface formation between ITO/bulk, which can form a self-build series resistor to achieve the current compliance. Moreover, the electroforming process with a higher current compliance can compose a better self-formation current compliance property, one which can reduce the operation current and voltage. Additionally, the Pt/SiO_x:Gd/TiN device exhibits an interface-type bipolar resistive switching, one which has not only a size effect, but also a but also a lower operating current. The resistance transitions are due to the variation in conductance of the switching layer, which also shows a self current compliance phenomenon. Finally, compared with 1T-1R structure, the self-formation current compliance can reduce the cost of the fabrication process.

CP35 Study of the Surface Chemical Composition and Evaluation of Corrosion Resistance of $Bi_XTi_YO_Z$ Thin Films Deposited by RF Magnetron Sputtering, ***J. Alfonso*** *(jealfonsoo@unal.edu.co)*, *J.J. Olaya*, *M. Pinzón*, National University of Colombia, Colombia, *J.F. Marco*, CSIC

Bismuth Titanate Oxide ($Bi_xTi_yO_z$) compounds have been the subject of many studies due to their ferroelectric, piezoelectric and optical properties, which make them interesting material s for the fabrication of optical devices, ferroelectric memories and lead-free piezoelectric sensors and actuators. However, there have been few studies on the corrosion resistance of these materials . Therefore, the main aim of this work is to report on our preliminary data on the corrosion resistance of $Bi_xTi_yO_z$ thin films and to

correlate the observed results with their chemical surface compositionand crystallinity

The BixTiyOz thin films were deposited by RF magnetron sputtering onto stainless steel and titanium alloy (Ti6Al4V) substrates. The structural properties were studied by x-ray diffraction (XRD); the surface chemical composition was determined by x-ray photoelectron spectroscopy (XPS) and the corrosion resistance was evaluated by potentiodynamic polarization Tafel tests.

The XRD preliminary results i ndicate that the films are amorphous or poorly crystalline in nature . The XPS analysis show that the uppermost part of the deposited film s is mainly composed by bismuth oxide (Bi_2O_3) and titanium oxide (TiO_2) and the corrosion tests show that the current density is lower by two orders of magnitude than that shown by the uncovered substrates.

CP36 Light Extraction Enhancement by Metallic Photonic Crystal Nanostructures Embeded in Gallium Nitride Diodes, ***G.M. Wu*** *(wu@mail.cgu.edu.tw)*, Chang Gung MemoUniversity, Taiwan

Higher energy efficient light-emitting diodes (LED) have been highly demanded as green energy alternative in the market place. The gallium nitride LED provides blue light source, and is emerging with solid-state lighting technology. In this report, metallic photonic crystal nanostructures have been embedded in gallium nitride diodes to increase the light extraction efficiency of LED devices. We employed finite-difference time0domain (FDTD) method to simulate the metallic photonic crystal nanostructures with the relevant parameters, such as periodicity arrangement, filling factor, location, space structure and dielectric constant. Not only photonic crystal structures can increase the efficiency for light extraction by optical confinement effects, but also surface plasmon would localize the electromagnetic field enhancement phenomenon that increases the efficiency. The metallic photonic crystals have been embedded on the LED surface, inside the transparent conducting layer, and inside the p-GaN layer. The results showed that the extraction efficiency of the embedded LED could significanly increase by about 8% to 12%.

CP37 Effects of Intermediate GAZO Layer Thickness on the Properties of GAZO/Ag/GAZO/Ag/GAZO Film, *Y.S. Jung, H.W. Choi,* ***K.H. Kim*** *(khkim@gachon.ac.kr)*, Gachon University, Republic of Korea

The Ga-Al doped ZnO (GAZO)/Ag/GAZO/Ag/GAZO transparent conductive multilayer film were prepared by facing targets sputtering (FTS) methods at room temperature. The multilayer thin films consisted of Ag metal thin film layers and transparent conductive GAZO thin films layers. The fabricated GAZO/Ag/GAZO/Ag/GAZO multilayer thin films have a low sheet resistance and a high transmittance in the visible range. As a results, sheet resistance and average transmittance in visible range of the GAZO/Ag/GAZO/Ag/GAZO multilayer thin film with optimal layer thicknesses (50/12/75/12/50 nm) exhibits 2.7 Ω/sq and 82% and the figure of merit of exhibits 4.9x10-2 Ω-1 (T: 0.82 and Rsh:2.7Ω/sq) keywords: GAZO/Ag/GAZO/Ag/GAZO, Multilayer thin film, Facing Targets Sputtering

Coatings for Biomedical and Healthcare Applications
Room: Grand Hall - Session DP

Syposium D Poster Session

Moderator: J. Piascik, RTI International, R. Hauert, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland

DP1 Albumin Adsorption on Zirconium Oxide Thin Films: the Influence of Atomic Ordering, ***P. Silva-Bermudez*** *(suriel21@yahoo.com)*, Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de Mexico, México, Mexico, *S. Rodil*, Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de Mexico, México

Whenever a foreign material comes in contact with a biological media a complex cascade of events is triggered. After the adsorption of water molecules and hydrated ions, the adsorption of proteins from the biological media onto the material surface occurs. This leads to the formation of an adsorbed protein layer that directs the next coming cell – material interactions. Consequently, the protein adsorption studies constitute an excellent model to study the interaction between biological media and foreign materials and to gain a deeper understanding of the influence of the material physicochemical properties in this interaction.

In the last years, the influence of the physicochemical properties of foreign materials on the biological response has been widely studied and some surface properties such as the hydrophobicity and roughness are well known to affect the materials-biological media interaction. However, the influence of the atomic ordering has been less explored. In the present study, zirconium oxide, a widely known biocompatible material was chosen as the model material to study the influence of surface atomic ordering on protein adsorption; Fibrinogen (Fbg) was chosen as the model protein. Quasi-amorphous (q-a) and polycrystalline (p-c) zirconium oxide thin films were deposited on Si(100) substrates by Reactive Magnetron Sputtering. The atomic ordering, wettability, surface energy, roughness, optical properties and chemical composition of the films were characterized. The films were immersed in BSA solution and the protein adsorption was studied in-situ using dynamic and spectroscopic ellipsometry.

The results showed that the film roughness, as well as the water contact angle, increased with the atomic ordering of the film. A slightly higher Fbg adsorption rate was observed on the p-c ZrO_2 film compared to the adsorption rate observed for the quasi-amorphous film. The differences observed in the Fbg adsorption on the two films might be related to the changes in the films roughness/wettability induced by the changes in the surface atomic ordering.

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DP2 Hydroxyapatite Growth Behavior and Osteocompatible Performance of Biomedical Polymer Coated with Titanium Dioxide Interlayer, *M.H. Chi,* Feng Chia University, Taiwan, Republic of China, *H.K. Tsou*, Feng Chia University, Taiwan; Taichung Veterans General Hospital, Taiwan, Republic of China, ***C.J. Chung*** *(cjchung@ctust.edu.tw)*, Central Taiwan University of Science and Technology, Taiwan, Republic of China, *J.L. He*, Feng Chia University, Taiwan, Republic of China

A widely utilized spinal implant materials, polyetheretherketone (PEEK), with its bio-inert and hydrophobic surface was suggested to proceed surface modifications for seeking better biocompatible performance. On the other hand, hydroxyapatite (HAp) exhibits excellent osteoconductive property, has been also regarded as a promising candidate for biomedical applications. The present study employed an arc ion plating (AIP) technique to respectively deposit rutile-rich titanium dioxide (R-TiO_2) and anatase-rich titanium dioxide (A-TiO_2) interlayers onto PEEK substrates, which were then immersed in simulated body fluid (SBF) for studying HAp layer growth. The microstructure observation and osteocompatible tests are carried out to evaluate the effects of HAp growth and osteoblast adhesion ability on adoption of TiO_2 interlayer.

Experimental results showed that HAp growth can be effectively enhanced by adoption of TiO_2 interlayer in SBF environment, with the crystallinity and film thickness of grown HAp layer proportional to immersion time. It was also worth to note that the R-TiO_2/PEEK specimen exhibit superior ability to induce HAp formation, due most likely to negatively charged – OH^- groups on R-TiO_2 coating surface at early stage. Furthermore, the osteocompatibility of bare PEEK substrate and interlayered specimen in terms of cell adhesion significantly correlated positively with the extent of HAp layer formation.

Keywords: polyetheretherketone (PEEK); hydroxyapatite (HAp); titanium dioxide (TiO_2); osteocompatibility.

DP3 Deposition, Characterization and In Vivo Performance of Parylene Coating on General-purposed Silicone for Biocompatible Surface Modification, *C.M. Chou,* Taichung Veterans General Hospital; National Yang-Ming University, *C.J. Shiao,* Feng-Chia University, Taiwan, Republic of China, *C.J. Chung (cjchung@ctust.edu.tw),* Central Taiwan University of Science and Technology, Taiwan, Republic of China, ***J.L. He***, Feng Chia University, Taiwan, Republic of China

In this study, a thorough investigation of parylene coatings was performed, including their microstructures, mechanical properties, surface properties and biocompatibility tests. The structure of parylene coatings identified by X-ray diffractometer (XRD) was disclosed its crystallinicity, which was consistent with the cross-sectional morphology shown in field emission scanning electron microscope (FESEM) images. In regard to the mechanical properties, parylene coatings exhibited a very low film hardness value but good film adhesion, as evaluated by a pencil hardness graded at 6B and the cross-cut test of the film adhesion graded at 5B, respectively. The water contact angle of parylene coatings in our study was measured at 86.1°. The relative hydrophobicity contributed to their effective barrier properties, which was related to the residual amount of aromatic rings shown in infrared spectrometry (IR). The surface chemistry of parylene films analyzed by X-ray photoelectron spectroscopy (XPS) showed a large O1s peak and C-O bonding at 286.1 eV because the thin parylene films react with atmospheric oxygen in addition to C-C binding at 285.1 eV. A cell culture on the parylene deposited specimen exhibited a higher cell count than the reference control (Medical grade silicone sheet) group. Platelet adhesion on parylene-coated silicone presented blood compatibility

equivalent to or even better than that on medical grade silicone. In the animal study, parylene coatings exhibit similar subcutaneous inflammatory change in comparison with the reference control group. The results of both *in vitro* and *in vivo* testes demonstrated relatively good biocompatibility of parylene coatings.***Keywords****:* parylene; *in vitro*; *in vivo*; biocompatibility

DP4 The Biological Characteristics of MG-63 Human Osteosarcoma Cell Line and Human Gingival Fibroblast Cells on Tantalum Doped Carbon Films, *M.T. Tsai*, Hungkuang University, Taiwan, Republic of China, *Y.Y. Chang (yinyu@nfu.edu.tw)*, National Formosa University, Taiwan, Republic of China, ***YC Chen***, MingDao University, Taiwan, Republic of China, *J.T. Hsu*, *H.L. Huang*, China Medical University, Taiwan, Republic of China

Biomaterials are widely used in repair, replacement, or augmentation of diseased or damaged parts of the musculoskeletal system such as bones, joints and teeth. Metal-doped carbon films are gaining interest as an attractive surface modification for medical device materials. Because of their amorphous nature, amorphous carbon films are capable of embedding metallic elements, which can improve their functionality. Tantalum is considered a biocompatible metal with high corrosion resistance and biocompatability. In this study, biocompatible Tantalum (Ta)-doped carbon films with different Ta contents were synthesized by using a twin-gun magnetron sputtering system. The Ta contents in the deposited coatings were controlled by the magnetron power ratio of pure Ta and graphite cathodes. The nanocrystalline Ta was embedded in the amorphous carbon matrix as a nanocomposite film. 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 Ta doped carbon films were studied. The biocompatibility of Ta doped carbon films were examined in vitro by measuring the mitochondrial dehydrogenase activity (MTT test) of MG-63 Human Osteosarcoma cell lines and human gingival fibroblast (HGF) cells. The adhesive morphology of cells on films was also observed by using SEM. Additionally, the three dimensional (3D) biological structure of MG-63 cell was evaluated by using a confocal microscopy. The results suggested that the Ta doped carbon films can exhibit compatible soft-tissue and hard-tissue biological performances. This indicates that Ta doped carbon films are potential candidates for clinical applications of osseointegration of orthopedic implants.

DP5 Cytocompatibility and Antibacterial Properties of Zirconia Coatings with Different Silver Contents on Titanium, *H.L. Huang*, China Medical University, Taiwan, Republic of China, ***YY Chang*** *(yinyu@mail2000.com.tw)*, National Formosa University, Taiwan, Republic of China, *YC Chen*, MingDao University, Taiwan, Republic of China, *C.H. Lai*, *MYC Chen*, China Medical University, Taiwan, Republic of China

Zirconia and their coatings have been proved to increase their applications in the biomedical fields such as orthopedic devices and dental implants by improving their osseointegration and wear resistance. In this study, doped ZrO_2 coatings containing different proportions of Ag were deposited on bio-grade pure Ti implant materials. A twin-gun magnetron sputtering system was used for the deposition of the ZrO_2-Ag coating. The Ag contents in the deposited coatings were controlled by the magnetron power and bias voltage. The films were then annealed using rapid thermal annealing (RTA) at 450 °C for 2 min to induce the nucleation and growth of Ag particles on the film surface. The crystalline structure and bonding states of the coatings were analyzed by XRD and XPS. The antibacterial behavior will vary, depending on the amount and size of the Ag particles on the coated Ti sample. In this study, S. aureus and Actinobacillus actinomycetemcomitans (A. 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 and bacterial viability agar tests. The cytocompatibility, mRNA expression, and adhesive morphology of human gingival fibroblast cells (HGFs) on the coatings were also determined by using the MTT assay, quantitative real-time polymerase chain reaction with reverse transcription (QRT-PCR), and SEM. It showed that the nanostructure of Ag on the ZrO_2 coatings was correlated with the antibacterial performance and HGF cellular biocompatibility.

DP7 Adhesion and Corrosion Performance of Amorphous Titanium Oxide Films on Stainless Steel, ***V. Garcia-Perez***, Facultad de Odontología, Universidad Nacional Autónoma de México, Mexico, *P. Silva-Bermudez*, Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de Mexico, México, *A. Almaguer-Flores*, Facultad de Odontología, Universidad Nacional Autónoma de México, Mexico, *J. Restrepo*, Universidad Nacional Autónoma de México - Instituto de Investigaciones en Materiales, Mexico, *S. Rodil (ser42@iim.unam.mx)*, Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de Mexico, México

Biomaterials are essential in the development of novel biomedical implants; they have to meet two main characteristics in order to have a potential application: a) To be able to stand the functional demands of the implant; which is normally related to the bulk properties of the material and b) To present a compatible interaction with the biological media; which is mainly driven by the surface properties of the material. It is difficult to find a single material that meets both criteria; functionality and biocompatibility. In this sense, the surface modification of a bulk material, which already meets the functional demands, through the deposition of biocompatible coatings to direct the biological interaction is a promising way to develop successful biomaterials. Thus, in the present work biocompatible TiO_2 thin films were deposited by reactive radio frequency (RF) magnetron sputtering on stainless steel (AISI316L) substrates. The main objective was to improve the coating-substrate adhesion, which is critical for further evaluations and determine the film-substrate resistance to biological environments. Two deposition variables were changed in order to improve the adhesion of the TiO_2 films to AISI316L substrates: a) The deposition of a Ti buffer layer previous to deposition of the TiO_2 film; no Ti layer, a 6nm Ti layer and a 10 nm Ti layer, and b) The substrate temperature during the buffer layer deposition; no substrate heating, the substrate heated at 100 °C and the substrate heated at 250°C. The TiO_2 films were always deposited under the same conditions: from a pure metallic Ti target (99.99%), no substrate heating, using 200 W of RF power and 1800 s of deposition time and under an atmosphere of Ar/O_2 (8:2). The adhesion of the coatings on the AISI 316L was tested by the scratch method using a stainless steel ball with a load speed of 50 N/min, a scratching speed of 10 mm/min and allowing a final load of 40 N after 8 mm. The analysis of the scratch print showed that the first adhesion failure was produced at a shorter scratch distance in the coatings deposited with no Ti buffer layer; the best adhesion seemed to be presented by the coating deposited with the thickest Ti buffer layer (10 nm). The substrate temperature did not show a further important improvement in the adhesion. The optimized TiO_2/10 nm Ti buffer layer/AISI316L system was then submerged into biological fluids for several days in order to verify the adhesion under simulated conditions. The electrochemical response was also evaluated and compared to the bare substrate. Acknowledgements: CONACYT 152995

DP8 Blood Compatibility and Adhesion of Collagen/Heparin Multilayers Coated on Two Titanium Surfaces by a Layer-by-layer Technique, ***C.-C. Chou*** *(cchou@mail.ntou.edu.tw)*, *H.-J. Zeng*, National Taiwan Ocean University, Taiwan, Republic of China, *C.-H. Yeh*, Chang Gung Memorial Hospital, Keelung, Taiwan, Republic of China, *S.-C. Liu*, National Taiwan Ocean University, Taiwan, Republic of China

This paper investigates the blood-compatibility and adhesion of collagen/heparin multilayers on a cp-Ti substrate by a layer-by-layer self-assembly technique. There were two surface polishing processes for the titanium samples: one is mechanical polishing and the other, electropolishing. These samples were pretreated by being immersed in an NaOH solution to obtain a negatively charged surface with hydroxyl groups and then, positively charged in a polyl-L-Lysine one. The repeated treatment of the samples by applying heparin and collagen alternatively determined the number and thickness of the multilayers. The surface topography, chemical composition, and hydrophile of the films were investigated by atomic force microscopy, scanning electron microscopy, Fourier transform infrared spectroscopy, and water contact angle measurement. The study of the multilayers' shear adhesion was conducted by a nano-scratch test as well as a cone-and-plate rheological one. The blood compatibility was evaluated by measuring haemolysis ratio and platelet-covered area in vitro. The uncoated titanium surface was used as the benchmark. The results indicate that the collagen/heparin multilayers on the titanium surface have superior anticoagulation performance than the uncoated titanium surface does. The increase of the multilayers' thickness enhances the adhesion to Ti substrate. The influences of electropolishing process and NaOH pretreatment are also discussed and addressed.

DP11 Effect of Nitrogen Plasma Immersion Ion Implantation Treatment on Corrosion Resistance of Ni-free ZrCuFeAl Bulk Metallic Glass, ***H.M. Huang***, *Y.S. Sun, H.H. Huang (hhhuang@ym.edu.tw)*, National Yang-Ming University, Taiwan

This study was to investigate the corrosion resistance of Ni-free $Zr_{62.5}Cu_{22.5}Fe_5Al_{10}$ bulk metallic glass (BMG) alloy, before and after nitrogen plasma immersion ion implantation (N-PIII), for biomedical application. The corrosion resistance, in terms of potentiodynamic polarization curve and metal ions release measurements, was evaluated in artificial saliva and simulated blood plasma solutions. Commercial biomedical pure Ti was used as the reference group for comparison. Results showed that the N-PIII-treated BMG alloy had lower corrosion rate and higher corrosion potential than the untreated BMG and Ti. The N-PIII treatment significantly improved the pitting corrosion resistance and decreased the metal ions release of BMG alloy. In terms of corrosion resistance, the Ni-free $Zr_{62.5}Cu_{22.5}Fe_5Al_{10}$ BMG alloy has potential for biomedical applications; N-PIII treatment further improves the corrosion resistance of BMG alloy.

DP12 Tribocorrosion and Properties of TiAlN/TiB_2 Coatings Deposited onto Ti6Al4V Alloy by DC/RF Magnetron Sputtering, ***O. Jimenez*** *(omar.jimenez.udg@gmail.com), J. Reyes, M. Flores, E. Rodriguez*, Universidad de Guadalajara, Mexico

Titanium and its alloys are one of the most used materials in many industries such as aerospace, military and biomedical due in part to a combination of properties including low weight and good biocompatibility. One of the low points of this material is the poor wear resistance particularly in sliding conditions. Many PVD coatings are intended to improve the wear resistance by modifying the surface properties of a big variety of substrates while retaining or enhancing existing properties. In this work, ceramic TiAlN/TiB_2 coatings were deposited by DC/RF magnetron sputtering under a selection of parameters. The mechanical properties were measured by nanoindentation techniques, while the structural properties were explored through XRD experiments. The thickness of these coatings and the after deposition roughness were measured by means of profilometry. Tribocorrosion behaviour was evaluated from open circuit potential (OCP) during reciprocating sliding in combined tests using SBF as the electrolyte at 37 °C. Results indicate that hardness values reached more than 20 GPa in all cases, while the thickness was in the range of 3-4 µm. The structural analysis revealed the presence of TiAlN and boron-containing phases. Finally, tribocorrosion results of coated samples showed a considerable change towards positive values in the E_{corr} and slightly lower values were registered in the current density I_{corr} during sliding conditions at 1 and 2N.

DP13 The Tribocorrosion Behavior of CoCrMo Alloys Coated with TIALPtN in Simulated Body Fluid, ***M. Flores*** *(maflores@red.cucei.udg.mx)*, Universidad de Guadalajara, Mexico, *E. Andrade*, Universidad Nacional Autónoma de México, Mexico, *O. Jimenez, E. Rodriguez*, Universidad de Guadalajara, Mexico

The tribocorrosion phenomenon is present in biomedical alloys used in artificial implants to replace natural joints. This damage limit the service life of such implants, the hard coatings can improve the wear and corrosion resistance. The TiAlPtN coatings were deposited on CoCrMo alloys by magnetron sputtering. The structure of coatings was studied by means of XRD and the composition by RBS technique. The tribocorrosion behavior CoCrMo alloys alone and coated with TiAlPtN was studied in simulated body fluid. The tribocorrosion was performed using a ball on plate reciprocating tribometer, the test was conducted in a simulated body fluid at 37 °C of temperature. The loads used were 0.5 N and 1N, the oscillating frequencies was 1Hz. The corrosion and tribocorrosion were studied using open circuit potential (OCP), potentiodynamic polarization, cyclic polarization and potentiostatic polarization measurements. 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. The surface topography and worn surface were studied by means of profilometry. The Pt content in TiAlN films was about 0.5 at. %, the coatings improve the corrosion and tribocorrosion resistance of CoCrMo alloys.

DP14 101 Million Cycle Simulator Wear Characterization of Diamond lLke Carbon Coated CoCrMo Articulating Implants, *K. Thorwarth, U. Müller, R. Figi, B. Weisse*, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland, *G. Thorwarth*, DePuy Synthes Companies, Switzerland, ***R. Hauert*** *(roland.hauert@empa.ch)*, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland

Diamond like carbon (DLC) coatings have been proven to be an excellent choice for wear reduction in many technical applications. However, for successful adaption to the MedTech field, layer performance, stability and adhesion in realistic physiological setups are very important and not consistently investigated. Simulator testing as well as corrosion tests are of great importance to verify the long term stability of such a DLC coated articulating implants in the human body. Commonly one million cycles of simulator testing correspond to 1 year of articulation in the human body. Diamond like carbon coatings were deposited on CoCrMo biomedical implant alloy using a plasma-activated chemical vapor deposition (PACVD) process. As an adhesion promoting interlayer tantalum films were deposited using magnetron sputtering.

It is shown that metal-on-metal (MoM) pairs perform well up to 5 million loading cycles, after which they start to generate wear volumes in excess of 20 times those of DLC-coated implants. This is attributed to the slight roughening observed on unprotected metal surfaces as usually also observed in-vivo. The DLC on DLC inlay pairs show comparable low volume losses throughout the full testing cycle (up to 101 million cycles over a period of three years and two month). To our knowledge this is the first time a simulator test of a DLC-coated articulating implant running for more than 100 million (corresponding to over 100 years of articulation in-vivo) cycles is presented.

Within this time these implants were characterized by high wear resistance, low friction coefficients, high corrosion resistance and low defect growth. These results were obtained by means of optical microscopy, SEM/EDX, FIB cross section and profilometry. The coatings were further analyzed using XRD and XPS.

DP15 Preparation of a Composite Bioceramic HA/Ag Coating and Effect on Insertion Torques of the Coated Ti6Al4V Screws, *T. Cheng, X. Nie (xnie@uwindsor.ca)*, ***Y. Chen***, University of Windsor, Canada

A bioceramic TiO2 coating with Hydroxyapatite (HA) and Silver (Ag) deposited on Ti6Al4V alloy screws was produced by using a combination of electrophoretic deposition coupled plasma electrolytic oxidation (PEO) and anodizing processes. The coatings revealed a relatively rough and porous surface which may potentially promote a higher anchorage as well as more favorable osteointegration properties to the bones. In this paper, an insertion torque (IT) analysis on low (10 pcf, pounds per cubic feet), middle (15 pcf), and high (20 pcf) density sawbones and real pig bones were carried out and compared with the uncoated screws. Higher insertion torques and final seating torques were obtained in the coated screws which may result less micromovement after implantation and thus lower the risk of implant failure. Surface morphological evaluation before and after insertion and removal by SEM and EDS were further performed. The coatings remained adhered to the substrates. No loss of HA and Ag particles from the coating was observed. These results qualitatively implied a good bonding strength between oxide coating and Ti alloy substrate.

DP16 Scratch Resistance of Coated Orthodontic Archwires, ***E. Santos Jr.*** *(emanuel@metalmat.ufrj.br), D. da Silva, A. Ruellas, S. Camargo Jr., C. Mattos*, Federal University of Rio de Janeiro, Brazil

Metallic archwires have been successfully employed in orthodontics for the last decades. Such commercial archwires are made of either stainless steel (CrNi) or NiTi alloys. Both epoxy resin and polytetrafluoroethylyene (Teflon®) thick coatings are commonly used to cover orthodontic archwires exclusively for esthetic purposes. However, some papers have reported the presence of coatings failures in clinical use. Even so, a few works have been published concerning their coating-substrate adhesion, as well as their mechanical and tribological properties. In the present study, five commercialized coated esthetic orthodontic archwires from different manufacturers were studied, as follows: Orthometric (China), Ortho Organizers (USA), TP Orthodontics (USA), Trianeiro (Brazil), and Tecnidente (Brazil). Coatings hardness and elastic moduli were assessed by instrumented indentation tests. For a 2.0 mN load, they presented hardness in the 170 – 250 MPa range, while their elastic moduli varied from 5.5 to 7.7 GPa. Scratch resistance of coatings and their substrates were evaluated by scratch tests. A total of 5 tests were performed on each sample by the ramping load method with loads from 0 to 500 mN, 500 µm scratch length, 50 µm/s scratch velocity, and a diamond Berkovich-geometry tip displaced in the knife-face position. All tests were carried out in air at room temperature. For the tested coatings, the maximum penetration depths of about 12.0 µm were achieved; thereby, the substrates were not reached once the coatings are as thick as 20.0 µm. Despite having elastic recoveries of about 70 - 90%, different failure features could be observed along the scratches by scanning electron microscopy. In some cases, delamination, crack propagation and debris generation were observed. In fact, such failures must be avoided for clinical use. Coating detachment due to poor substrate-film adhesion was not evident. The coatings coefficient of friction (COF) increased linearly up to 0.3 (~ 50 mN load), and then, leveled off in the 0.34 – 0.40 range for higher loads. The COF of the CrNi and NiTi substrates had a different behavior. They increased during all the tests while the loads were ramped. In the beginning, the COF of the substrates were lower than those obtained for coatings for loads up to 250 mN. For the

higher loads, the COF increased until 0.45. The coated archwires most resistant to scratch were those that presented little plastic (permanent) deformation associated with minor damaging features.

DP17 AC Impedance Behavior of HA/TiN Coated Ti-25Ta-xZr Alloy by RF Sputtering and EB-PVD for Dental Implant, ***H.J. Kim***, *Y.H. Jeong, Y.M. Ko,* Chosun University, Korea, *S.W. Eun,* Polytechnic V Colleges, Korea, *H.C. Choe (hcchoe@chosun.ac.kr),* Chosun University, Korea

Cp-Ti and Ti-6Al-4V alloys metallic materials are widely used for dental implant and orthodontic application because of their good properties, however, Ti–6Al–4V alloy can potentially cause some health problems because of the release of toxic metal ions. For improving this problem, Ti alloys with non-toxic elements such as Nb, Ta, Zr, and Hf have been developed, and we have focused on Ti-Ta-Zr alloy system with controlling of Ta and Zr elements. When added to Ti, Ta acts as a β phase stabilizer and lowers the elastic modulus, and Zr, which has similar chemical properties to titanium, provides solid solution strengthening because of its dissimilar atomic radius. The addition of Zr also results in a high level of blood compatibility when used in cardiovascular implants and leads to better corrosion resistance due to the formation of stable ZrO_2. The titanium nitride (TiN) coatings are used widely in many dental and industry fields due to their high hardness, good wear resistance, good adhesion, excellent corrosion resistance, and low friction coefficient. Hydroxyapatite [HA; $Ca_{10}(PO_4)_6(OH)_2$] is a bioactive material that has been used as a bone replacement material in restorative dental and orthopedic implants, and HA can encourage initial bonding between body tissues and an implant surface. However, the bond strength between an HA and substrate can be decreased due to spalling of film in oral environment after long-term use. To overcome, the implementation of a barrier buffer layer on substrate is one way to avoid spalling of HA films, multi-layered coating with TiN and HA showed a fast and stable fusion between the coated implant and the bone. In this study, we investigated AC impedance behavior of HA/TiN coated Ti-25Ta-xZr alloy by RF sputtering and electron-beam physical vapor deposition (EB-PVD) for dental implant. Ti-25Ta-xZr alloys were melted by using a vacuum furnace. Ti-25Ta-xZr alloys were homogenized for 12hr at 1000℃. The microstructures of Ti-25Ta-xZr alloys were analyzed by OM, XRD, and SEM. The TiN coating were obtained by the radio frequency (RF) magnetron sputtering technique. And then, the HA coatings were coated on the samples by EB-PVD method. The surface characteristics were analyzed by field emission scanning electron microscopy (FE-SEM), energy dispersive X-ray spectroscopy (EDX) and X-ray diffractometer (XRD), respectively. Microstructure of Ti-35Ta-xZr alloys changed from α″ to β phase and, a needle-like to an equiaxed structure with Zr content. The AC impedance test showed high value of polarization resistance on HA/TiN coated Ti-25Ta-xZr alloys than that of non coated surface. (NRF: R13-2008-010-00000-0; hcchoe@chosun.ac.kr)

DP18 Hydroxyapatite Precipitation on Nanotubular Film Formed Ti-25Nb-xHf Alloys for Biomedical Application, ***S.H. Kim***, *Y.H. Jeong, Y.M. Ko, H.C. Choe (hcchoe@chosun.ac.kr),* Chosun University, Korea

CP-Ti and Ti–6Al–4V alloy have been studied for the applications of orthopedic and dental implants materials due to its excellent mechanical properties, corrosion resistance, and superior biocompatibility. However, the widely used Ti -6Al-4V is found to release toxic ions (Al and V) into the body, leading to undesirable log-term effects. Recent research on metallic biomaterials has focused on Ti alloys composed of non-toxic elements like Nb, Ta, Mo, Hf and Zr, in order to overcome the long-term health problem caused by the release of toxic metal ions. Moreover, Nb is found to reduce the modulus of elasticity when alloyed with Ti, Hf leads to better corrosion resistance due to the formation of a stable oxide surface layer. The anodization by electrochemical method can be shown highly ordered oxide nanotube layers in fluoride contained acid electrolytes at moderate voltage. Nanotube formation on the surface titanium oxide is conjectured to improve the bone cell adhesion and proliferation in clinical applications of implants. Additionally, hydroxyapatite (HA, $Ca_{10}(PO_4)_6(OH)_2$) has been used as a surface coating material on metallic surface in dentistry and orthopedics due to their bioactive characteristics, which enable their rapid fixation and stronger bonding between the host bone and the metal surface.Therefore, the objective of the present study was to the hydroxyapatite precipitation on nanotube formed Ti-25Nb-xHf alloys for biomedical application. The Ti-25Nb-xHf ternary alloys contained from 0 wt. % to 7 wt. % contents were manufactured by vacuum arc-melting furnace. The formation of nanotubular film was conducted by electrochemical method in mixed electrolytes with 1 M H_3PO_4 + 0.8 wt. % NaF at 30V for 2h. After that, electrochemical deposition for HA precipitation was carried out using cyclic voltammetry (CV) method with scanning potential between 0 V to -1.5 V at scan rate 100 mV/s on 80 ℃ in $Ca(NO_3)_2$ (2.5 - 10 mM) + $NH_4H_2PO_4$ (1.5 – 3 mM) solution. The surface characteristics were investigated using field emission scanning electron microscopy (FE-SEM), x-ray diffractometer (XRD), energy dispersive X-ray spectroscopy (EDS), Fourier transform infrared spectroscopy (FTIR) and contact angle measurement. Microstructures of alloys were transformed from α″ phase to β phase, which showed a needle-like to an equiaxed structure as Hf content increased. Increasing solution concentration, needle-like deposits transferred to the plate-like and micro plate like precipitates in the case of high SBF concentration. (NRF: R13-2008-010-00000-0; hcchoe@chosun.ac.kr).

DP19 HA/TiN Multilayer Coating on the Ti-30Nb-xTa Alloys by RF Sputtering for Biocompatibility, ***E.S. Kim***, *Y.H. Jeong, Y.M. Ko, H.C. Choe (hcchoe@chosun.ac.kr),* Chosun University, Korea

Titanium and its alloys are widely used in biomaterials due to their excellent mechanical properties, high corrosion resistance and good biocompatibility. Ti-6Al-4V alloy has been widely used as a high strength biomedical alloy. However, recent studies have shown the release of both vanadium and aluminum ions to the human body, might cause health problems, such as peripheral neuropathy and Alzhemier diseases. To remove this problem, we have focused on alloying with non-toxic contents such as Ta, Nb and Zr elements. Among these, the additions of Nb and Ta to Ti are usual based on their biological passivity and capacity of reducing the elastic modulus.At HA coating techniques, plasma spraying has shown to be a success in clinical applications since they exhibit enough bioactivity than uncoated ones, but, clinical failures sometimes does occur due to the weak mechanical strength due to the relatively thick coatings (50 - 200 μm). On the other hand, magnetron sputtering is one the most important growth techniques that is applicable to a large variety of materials, providing often the optimum with respect to deposition rate and film quality. Also, the titanium nitride (TiN) coatings are used widely in many dental and industry fields due to their high hardness, good wear resistance, good adhesion, excellent corrosion resistance and low friction coefficient. Especially, the bonding strength of HA/TiN multilayer coating on Ti was markedly improved when compared to that of the TiN and HA single layer coating on Ti. Therefore, this study was performed to fabricate an HA/TiN multilayer coating on the Ti substrate, in order to optimize the biocompatibility of the Ti-30Nb-xTa alloys.In this study, we investigated biocompatibility of HA/TiN multilayer on the Ti-30Nb-xTa alloys coated by RF sputtering. Ti-30Nb-xTa alloys with Ta contents of 0 and 7 wt. % were melted by using a vacuum arc-melting furnace, and homogenized for 12 h at 1000℃. The TiN and HA films were coated on the samples by RF sputtering. The surface of these alloy were analyzed by corrosion test and wettability test in order to observe ion release and hydrophilic property. The phase composition and microstructure were investigated by using field-emission scanning electron microscope (FE-SEM) and energy dispersive X-ray spectroscopy (EDS), X-ray diffractometer (XRD), and optical microscopy (OM). The microstructure of Ti-30Nb-xTa alloys changed α'' phase to β phase, the grain size was increased with Ta content. HA coated Ti-30Nb-xTa alloys surface showed better wettability and higher corrosion resistance than that of non-coated surface. (NRF: R13-2008-010-00000-0; hcchoe@chosun.ac.kr).

DP20 Electrochemical Behaviors of an Interface Between Si/HA Coated Ti-Nb-Zr Alloy and HOB Cell, *Y.H. Jeong,* ***H.C. Choe*** *(hcchoe@chosun.ac.kr),* Chosun University, Korea

Metallurgy materials have a long history in the medical fields but, metals are definitely artificial materials and have not much bioactive that causes to low attraction of metals as biomaterials. The surface modification techniques are developed according to have major purpose to improve hard tissue compatibility or accelerate bone formation. One of bioactive coating technique, HA (hydroxyapatite; $Ca_{10}(PO_4)_6(OH)_2$) coating is widely used for surface modification of metal implants due to the mechanical properties of the metal combined with the excellent bioactivity of the HA, moreover, the silicon substituted hydroxyapatite (Si/HA) coatings are greater than single HA coating for bone on-growth. Meanwhile, β rich Ti-35Nb-xZr alloy system shows significant low elastic modulus and has non-toxic elements, Ti-35Nb-10Zr alloy has appropriate properties of low elastic modulus that consisted with non toxic elements as a substrate for bioactive coating. To confirm a cell attachment on modified surface, electrochemical test between cell and metallic biomaterial is excellent to verify the biocompatibility and corrosion characteristics, especially, the electrochemical impedance spectroscopy (EIS) measurement is also good technique to know the characteristics between true surface and interface without any damages on surface behavior.In present study, the research focused on the electrochemical behaviors of an interface between Si/HA coated Ti-Nb-Zr alloy and HOB cell. The Ti-Nb-Zr alloy was manufactured with 35 wt. % of Nb and 10 wt. % of Zr by arc melting furnace to have a β phase. The Si/HA coatings were prepared by electron-beam physical vapor deposition (EB-PVD) method with variable Si contents between 0.5 and 1.2 wt. %. The surface characteristics were analyzed by field emission scanning electron microscopy (FE-SEM), energy dispersive X-ray spectroscopy (EDS) and X-

ray diffraction (XRD), respectively. To evaluate of cell attachment on Si/HA coated surface, the EIS test was performed after osteoblast like cells (HOB). Numerical parameters of EIS test were compared by a non-parametric method at a significance level of $\alpha = 0.05$. As a result, The EIS measurement could be applied to verify the density of HOB cells on Si/HA coating surface, Si substitution had highly correlation with cell density on their surface to show higher value of corrosion resistance.

DP21 Hydroxyapatite Coating on Micro-pore formed Ti-35Ta-xNb Alloy by Electron Beam-Physical Vapor Deposition, ***C.I. Jo***, *Y.H. Jeong, Y.M. Ko, H.C. Choe (hcchoe@chosun.ac.kr)*, Chosun University, Korea, *S.W. Eun*, Polytechnic V Colleges, Korea

Titanium is an attractive biomaterial for its excellent characteristics such as excellent biocompatibility, corrosion resistance and Ti-6Al-4V alloy is widely used for dental and orthopedic implant. But Ti-6Al-4V alloy concerns about the potential of cell cytotoxic and Alzheimer's disease, because of vanadium and aluminum. Therefore, Ti alloy require to new alloying element such as Nb, Ta, Zr, Hf, Mo, and Sn, as one of β phase Ti alloy, Ti-35Ta-xNb alloys have shape memory property, low elastic modulus, non-allergic and non-toxicity which can be applied to biomaterial. The use of porous Ti and Ti-6Al-4V alloy implants allows a higher degree of bone in-growth and body fluid transport through three dimensional inter-connected arrays of pores, is improving the interactions with bone and the implant fixation. Additionally, anodic oxidation is reported to be one of interesting method for forming rough and porous oxide film and increasing thickness of the native oxide layer. Hydroxyapatite has been widely used as a bioactive coating material in medical and dental applications. Due to the favorable biocompatibility of HA and attractive mechanical properties of metallic structure, HA coated Ti and Ti alloys have become some of the most promising implant materials for dental applications. In this study, we investigated Hydroxyapatite Coating on Micro-pore formed Ti-35Ta-xNb Alloy by Electron Beam-Physical Vapor Deposition. These alloys were prepared from Ti with 35 wt% and Nb which contents of 0, 5, 10, and 15 wt% and were manufacture in arc-melting furnace, and then, homogeneous treatment was carried out at 1000°C for 12h in argon atmosphere. Anodization treatments on Ti-25Nb-xHf alloys were carried out in electrolyte containing typically 1M H_3PO_4 at 200V for this experiment. The HA coating was subsequently prepared by EB-PVD method on micro-pore formed Ti-35Ta-xNb alloys surface. The microstructures, morphology and phase transformation were measured by optical microscope (OM), field emission scanning electron microscope (FE-SEM), X-ray dispersive spectroscopy (EDX), X-ray diffractometer (XRD), roughness test, and wettability test. As results, the Ti-35Ta-xNb alloys transformed α'' to β phase with addition of Nb contents. The XRD peaks showed calcium, phosphate, anatase and rutile phases on HA coating on anodized surface. The micro-pore size depended with Nb content, wettability was highly decreased with HA coating on their surface. (NRF: R13-2008-010-00000-0; hcchoe@chosun.ac.kr [mailto:hcchoe@chosun.ac.kr])

Tribology & Mechanical Behavior of Coatings and Engineered Surfaces
Room: Grand Hall - Session EP

Syposium E Poster Session
Moderator: N.M. Jennett, National Physical Laboratory, UK, T. Scharf, University of North Texas

EP1 Controlled Vacuum Annealing of TiZrN Thin Film on Si (001) and AISI 304 Stainless Steel Deposited by Unbalanced Magnetron Sputtering, ***P-H. Wu***, *J.H. Huang, G.P. Yu (gpyu@ess.nthu.edu.tw)*, National Tsing Hua University, Taiwan, Republic of China

The purpose of this study is to investigate the effect of controlled vacuum annealing of TiZrN thin film at different temperature. After heat treatment, TiZrN thin film was expected to have no apparent changes in the mechanical properties and no oxide on the surface of thin film. A series of TiZrN coatings were deposited on Si (001) and AISI 304 stainless steel substrates using unbalanced magnetron sputtering. Specimens were later annealed respectively at different temperature ranging from 700°C to 1000°C for 1 hour to 4 hours in vacuum($4.5X10^{-6}$torr). X-ray diffraction (XRD) was used to characterize the microstructure of the TiZrN films. The texture coefficient and grain size were both calculated according to the result of θ/2θ scans. Coating thickness was obtained from field-emission gun scanning electron microscope (FE-SEM). X-ray photoelectron spectroscopy (XPS) was used to characterize the bonding state and compositions of the coatings. The hardness of the TiZrN films was measured using nanoindenter. Secondary Ion Mass Spectrometer (SIMS) was used to characterize the compositional depth profiles. The residual stress was determined by laser curvature methods. The electrical resistivity of the TiZrN films was measured using a four-point probe. The corrosion resistance of the TiZrN thin films was obtained from potentiodynamic scanning conducted from -600 to 800 mV in 1M H_2SO_4 +0.05M KSCN solutions respectively. After heat treatment, there is no oxide observed on the surface of TiZrN thin films. The residual stress was relaxed after heat treatment. The grain size increased slightly after heat treatment. T he texture coefficient was still (111). The hardness and the electrical resistivity of TiZrN thin film both were lower.

EP2 Fracture Toughness Measurement of ZrN Hard Coatings, ***Y-H. Chen***, *G.P. Yu, J.H. Huang (jhhuang@ess.nthu.edu.tw)*, National Tsing Hua University, Taiwan, Republic of China

Hardness is one of the important mechanical properties of hard coatings, but toughness is even more crucial in the engineering applications. Many techniques have been developed for assessing fracture toughness of hard coatings; nevertheless, there is still no standard testing method. Although several methods such indentation, buckling, bending, and tension tests can be used to quantitatively measure the fracture toughness of bulk materials, these stress-based methods cannot be directly applied on hard coatings. Owing to the thickness limitation of thin films, specific substrate shape and micro-precracks are difficult to be routinely produced. On the other hand, for thin-film coatings, the energy-based methods may be better than stress-based methods in the measurement of fracture toughness. However, external stress is commonly needed to apply on the specimens in both techniques, which also complicate the experimental setup. Recently, we developed an energy-based technique by controlling the residual stress and film thickness, without applying external stress, to measure the fracture toughness of TiN hard coatings, in which the substrate and size effects were greatly reduced. The results showed that the fracture toughness of random-textured TiN hard coating was 16.7 J/m^2 which is close to previous literature values. Since ZrN coatings have better corrosion resistance, lower resistivity, and higher mechanical properties than TiN coatings, while fewer toughness data of ZrN are available. The purpose of this study was to measure the fracture toughness of ZrN hard coatings. Following our previous testing technique, residual stress was used as the stress source for the toughness measurement, which could be measured by the laser curvature method. By controlling the deposition parameters and film thickness the residual stress of ZrN films could be adjusted. From fracture mechanics, the average storage energy (Gs) can be evaluated by the stress difference before and after crack initiated, and then the toughness of the ZrN coatings can be obtained from Gs, and the critical thickness can also be assessed.

EP3 Producing Thick TiN Films by Controlling Deposition Parameters in Magnetron Sputtering, ***M-L. Cai***, *G.P. Yu, J.H. Huang (jhhuang@ess.nthu.edu.tw)*, National Tsing Hua University, Taiwan, Republic of China

Due to its superior mechanical properties, titanium nitride (TiN) has been widely applied in industry, especially in hard and protective coatings. For the deposition of TiN coatings, people usually focused on adjusting the deposition parameters, such as bias voltage, nitrogen flow rate and substrate temperature, to produce harder and thicker coatings. However, as the film thickness increases to a few μm, the residual stress may increase concomitantly and thereby causing film spallation. The purpose of this study was to develop a deposition method to produce TiN coatings with a thickness larger than 3 μm and above without using Ti interlayer, in other words, to produce a thick TiN coating with low residual stress.

TiN was deposited on p-type (100) Si by unbalanced magnetron sputtering (UBMS). The controlling deposition parameter was either the opening of gate valve between turbomolecular pump (TP) and deposition chamber or the pumping speed of TP. The flux of argon and nitrogen was adjusted at a fixed ratio to maintain the same pressure in the chamber. The film thickness was measured by scanning electron microscopy (SEM). The Hardness of the film was measured using nanoindentation (NIP). X-ray photoelectron spectroscopy (XPS) was used to characterize the bonding state and compositions of the coatings. The preferred orientation of TiN coating was determined using X-ray diffraction (XRD). Laser curvature method was used to measure the residual stress of the TiN film. Using the proposed method, we could successfully produce TiN films with a thickness more than 4 μm and the residual stress was less than -2 GPa. By lowering pumping speed, the lifetime of TP can be effectively prolonged, which would be beneficial to the hard coating industry.

EP4 Wear Behavior and Failure Mechanism of a Solid Lubricant Coating on One Side or Both Sides of Counterbodies, *J. Yang (jiao.yang@ec-lyon.fr)*, ***V. Fridrici***, *P. Kapsa*, Ecole Centrale de lyon, France

Wear is the progressive damage, which occurs on the surface of a component as a result of its motion relative to the adjacent working parts.

To prevent from wear damage, solid lubricants have been introduced to protect the surface of materials and to prolong the service life of element. In the past 40 years, many studies have been done on them, especially for the MoS_2 coating. The experimental studies described in the previous works are all based on the observed trend using the coated flat substrate. Experiments on the comparison of MoS_2 based coating lifetime under one side coated or two side coated counterbodies is, however, lacking, which is popular problems in the linear guidance system and ball screw drives.

Therefore, it is interesting to do some research to explore the effect of coating position on the coating lifetime and friction coefficient. In this study, the coating was sprayed on the ball or cylinder and flat substrate. The FE model was chosen to model the stress distribution for different conditions, to get a better understanding of the wear mechanism of the coating.

In this study, an aerosol sprayed MoS_2 based varnish was deposited on a cleaned and polished 304 stainless steel flat surface and AISI52100 ball or cylinder surface at room temperature. The thickness of the coating is about 10 µm (flat) and 12 µm (ball and cylinder). The normal force is varied from 100 N to 1000 N and displacement amplitude is from ± 10 µm to ± 40 µm.

Some results could be drawn from this study. Firstly, the coating sprayed on substrate will lower contact pressure and enlarge the contact area. The coating on the flat has the similar maximum contact pressure as coating on the cylinder or ball, but they have different contact areas. Secondly, under lower contact pressure of cylinder-on-flat, there is a significant stress gradient between substrate and coating, especially at the interface of coating and substrate. Hence, coating failure occurs easier at the interface, which leads to a lower coating lifetime. In this low contact stress situation, patches of debris appears to be extruded back and forth in steady-state sliding, while in the high contact stress, this debris movement is delayed. The plastic shearing of the junctions forms plucks off the tips of the softer asperities leaving them adhering to the harder surface in the high contact stress, thereby forming the tribo-film and bringing a longer lifetime. Thirdly, the coating on the ball/cylinder has always higher coating lifetime than coating on flat, because the debris generated between two contact bodies could form more easily the transfer film or stay on the wear track.

EP5 Investigation of Internal Stress Levels and Characteristics during Electrocodeposition of Ni-MoS_2 Composite Coatings, *E. Saraloglu Guler (esaraloglu@gmail.com), İ. Karakaya,* Middle East Technical University, Turkey, *E. Konca,* Atilim University, Turkey, ***M. Erdoğan***, Middle East Technical University, Turkey

Internal stress in plated deposits has been a common problem that may affect the functionality of coatings. Coatings may develop cracks, blisters, distortions and peel away from the substrate material when the stress levels are high. Electrodeposition parameters, such as; current density, coating thickness, pH and temperature of the bath affect the levels and the characteristics of internal stress of coatings. Furthermore, insoluble particles in electrocodeposition are also expected to make contributions. The influence of the electrocodeposition parameters and their interaction effects on the internal stress during the electrodeposition of Ni and Ni-MoS_2 composite coatings were studied by fractional factorial design. The parameters studied and their ranges were; MoS_2 particle concentration (0-5 g/l), temperature (30-50ºC), pH (2-4), current density (1.2-4.8 A/dm^2), and coating thickness (25-50µm). MoS_2 addition into Watts bath resulted in the decrease of the tensile internal stress values of the composite coatings or even changed the stress character from tensile to compressive. Moreover; low stress values were obtained when pH was low and coating thickness was high. The temperature of the Watts bath did not show a significant effect. However, the effect of current density was seen to depend on other electroplating parameters.

EP6 Impact Wear Resistance of CrN, CrAlN and TiAlN PVD Coatings on Cemented Carbide and M2 Steel Substrates, ***J.L. Mo*** *(jlmo@swjtu.cn), M.H. Zhu*, Southwest Jiaotong University, China, *S. Banfield*, University of Sheffield, UK, *J. Housden*, Tecvac Ltd, UK, *A. Leyland, A. Matthews*, University of Sheffield, UK

The impact wear resistance of CrN, CrAlN and TiAlN coatings deposited on cemented carbide and M2 steel substrates by an electron-beam (EB) plasma-assisted (PA) Physical Vapour Deposition (PVD) technique were evaluated by dynamic ball-on-plate impact wear testing. The test is used to assess the resistance of coatings to dynamic, high-cycle loading caused by the repeated impact of a 6 mm diameter tungsten carbide ball at a impact frequency (*f*) of 9 Hz. After the wear tests, the wear craters were studied by stylus profilometry, SEM and EDX, to investigate wear behaviour. It is shown that all the three coatings on cemented carbide substrates exhibited good impact wear resistance. The impact wear mechanisms were mainly adhesive wear. No interface failure was found and the impact wear process of the coatings can be described as a gradual process of reduction in coating thickness by repeated impact loading. The maximum depths of the wear craters of the three coatings on M2 steel substrates were much higher than the coating thickness as soon as the coatings were subjected to 10^3 impact cycles; however, the coatings still remained on the surface in good condition until a certain much higher impact cycles when the coatings were damaged by main impact wear mechanisms of micro-cracking and micro-spallation.

EP7 Examples for the Time Dependent Effective Indenter Concept, ***N. Bierwisch*** *(n.bierwisch@siomec.de),* Saxonian Institute of Surface Mechanics, Germany, *N. Schwarzer*, Saxonian Institute of Surface Mechancis, Germany, *A. El Seweifi*, Forum Zehlendorf, Germany, *M. Griepentrog, P. Reinstädt*, BAM Berlin, Germany

The effective indenter concept was introduced by Bolshakov et al in 1995 [1]. It's well known that this concept is the theoretical basis of the standard analysis method for nanoindentation measurements, the Oliver & Pharr method [2]. With some extensions this concept is also applicable to more complex mechanical contact experiments on layered or viscose materials for normal and multi-axial loading conditions. This was shown in many papers in the last 15 years [e.g. 3,4].

This work will focus on presenting examples for these extensions, mainly the extension for time dependent material behaviour. So analysis results for viscose materials (like polymers or soft metals) for different test methods (indentation, scratch and tribotests) will be presented.

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EP8 Effect of Implant Diameter and Length on Stress Distribution for Titanium and Zirconia İmplants with 15° Angled Abutment by using Finite Element Analysis (FEA), ***F. Karabudak*** *(filizkbudak@atauni.edu.tr), R. Yesildal, F. Bayindir*, Atatürk University, Turkey

The purpose of this study was to analyze stress distribution patterns in implant restorations created in different length and diameter made of titanium and zirconia with 15° angled abutment by using three dimensional finite element analysis. For Titanium models; Ti-6Al-4V for implant fixture, connection element and abutment, yttrium tetragonal zirconium polycrystal (Y-TZP) for zirconium framework, feldsphatic porcelain for superstructure material and for zirconia models; Y-TZP for implant fixture, connection element, abutment and zirconium framework, feldsphatic porcelain for superstructure material were used. A comparison of the areas between titanium and zirconium implants with maximum stress for implants of the same length but different diameters and same diameters with different lengths showed different variances.**Key Words:** Zirconia, Titanium, MIMICS, feldsphatic porcelain, Stress analaysis, implant lenth, implant diameter

EP9 Coated Polymers for Low Friction and Wear of Roller Bearing Cages in Lightweight Design, ***T. Sander*** *(sander@mfk.uni-erlangen.de), B. Vierneusel, S. Tremmel, S. Wartzack*, Friedrich-Alexander-University Erlangen-Nuremberg, Germany

Solid cages made of polymer materials are often used in high-speed rotary bearings to keep the inertial forces small. The freedom in geometric design due to the injection molding process allows the realization of sustainable cage shapes. The material polyamide PA 66 is already being used in mass-produced bearings, often glass fiber reinforced to increase strength, modulus of elasticity and maximum operating temperatures. To improve the tribological properties of PA 66, particles of the solid lubricant MoS_2 can be added to the plastic granulate. However, the mechanical properties are deteriorated by these particles since they are usually the starting point of cracks and fractures. As an alternative to these composite materials, the friction between cage and rolling elements can be reduced by the use of PTFE, having a substantially higher density, lower strength and a lower modulus of elasticity, in comparison with PA 66. The wear on the cage has a significant influence on the cage pocket clearance or rib guidance clearance. Dynamic bearing analyses show that this in turns has influence on the hydrodynamic pressure buildup in the gaps. Consequently, a suitable cage material must provide a variety of positive characteristics in a balanced relationship with each other. The PVD thin film technology allows the combination of a suitable substrate material with low density, high strength and stiffness with the excellent tribological sliding properties of the coating material, without affecting the tolerances uncontrollably. This poster gives an overview of conventional cage materials and layer combinations on fiber reinforced polyamide substrates regarding friction and wear on the basis of model tests. The possibility of variation of the sputtered solid lubricant

molybdenum disulfide by modification of the microstructure and by doping elements is in the focus of the investigations. The tribological and mechanical properties are compared with sputtered a-C (amorphous carbon film) and conventional materials for roller bearing cages. The coating adhesion is determined by a modified scratch test for polymer substrates.

EP10 Tribological Properties of Hard a-C:H:F Coatings, *C. Jaoul (jaoul@ensil.unilim.fr)*, Université de Limoges - CNRS, France, *O. Jarry*, Sulzer Sorevi, *P. Tristant*, Université de Limoges - CNRS, France, *E. Laborde*, Université de Limoges - CNRS, *M. Colas*, *J.P. Lavoute*, Université de Limoges - CNRS, France, ***L. Kilman***, Sulzer Sorevi, *H. Ageorges*, *C. Dublanche-Tixier*, Université de Limoges - CNRS, France

Hydrogenated amorphous carbon (a-C:H) thin films are among the best coating solutions for the reduction of automotive fuel consumption because of its very good tribological properties. Quite high values for hardness are required to withstand high contact pressure occurring for example in the cam-tappet contact in automotive motorsport engine. Commercial coatings exist with adapted sub-layers to obtain a good adhesion of highly stressed DLC (Diamond-Like Carbon) on the steel substrate. Since wear can occur, the development of wear-resistant coating is still necessary.

Each deposition process lead to a DLC film with specific properties correlated with hydrogen content and sp^3/sp^2 bonded carbon ratio. Many elements have been introduced in the a-C:H matrix to modify and improve some properties of this material. For fluorine containing DLC, friction and wear properties improvement can be observed [1] but hardness is strongly decreasing with fluorine introduction [2]. Objective is thus to obtain hard a-C:H:F with enhanced tribological properties compared to standard a-C:H without changing deposition parameters.

DLC films are produced by radio-frequency PECVD with different combinations of precursors in order to explore various F/H ratios. ERDA-RBS measurements are performed to determine the chemical composition of the films. Chemical bonding is observed by Raman spectroscopy and X-ray photoelectron spectroscopy (XPS). Then, Young modulus and hardness are measured by nanoindentation. To conclude, tribological tests are performed with a ball-on-disc tribometer to measure wear resistance and friction coefficient in dry conditions. Fluorine introduction led to a decrease of hydrogen content and hardness. Coatings with less than 6 at.% of F kept a hardness superior to 28 GPa and wear resistance was improved.

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EP11 Microtribological Properties of Extremely Thin Diamond-like Carbon Films Deposited using Bend-type Filtered Cathodic Vacuum Arc and Electron Cyclotron Resonance Chemical Vapor Deposition Techniques, ***S. Yamazaki*** *(syamazaki9503@gmail.com)*, *S. Miyake*, Nippon Institute of Technology, Japan

In magnetic storage devices, nanometer scale wear and minute fluctuations in friction degrade equipment performance. Therefore, an improvement in the nanotribology of the magnetic head medium is important for the advancement of the fast growing magnetic recording industry. Thus, extremely thin protective films play an important role in realizing higher reliability magnetic storage devices. In this study, m icrotribological properties such as nanoscratching, nanowear, and low load reciprocating friction of extremely thin diamond-like carbon (DLC) films deposited using bend-type filtered cathodic vacuum arc (FCVA) and electron cyclotron resonance chemical vapor deposition (ECR-CVD) techniques were evaluated. The structure and composition of these DLC films were evaluated using Raman spectroscopy, transmission electron microscopy, and auger electron spectroscopy (AES). These analyses showed that the FCVA-DLC films have tetrahedral structures, while the ECR-CVD-DLC films have a-CH structures. The AES measurements showed that the actual thickness after deposition matched the target thickness. The nanoindentation hardness and nanowear resistance were evaluated by atomic force microscopy. The nanoindentation hardness of the 100-nm-thick DLC films deposited by FCVA and ECR-CVD were 57 and 25 GPa, respectively, at a 40 mN load. However, it was difficult to evaluate the hardness of DLC films with a thickness of a few nanometers by this nanoindentation test. In contrast, nanometer scale wear tests could be used to evaluate the extremely thin DLC films. The wear depths of 1.0- and 2.0-nm-thick FCVA-DLC films were extremely low at less than 1.0 nm, even after 20 sliding cycles. The wear depths of 0.8-, 1.0-, and 2.0-nm-thick ECR-CVD-DLC films were nearly 1.0 nm after only one sliding cycle and exceeded the film thicknesses after a few sliding cycles. These results reveal the differences in the nano wear resistance between these extremely thin DLC films and the superior nano wear resistance of FCVA-DLC thin films. In a 10 mN load reciprocating friction test, the friction coefficients of nanometer-thick ECR-CVD-DLC films fluctuated, and the damage caused to these films was greater than that caused to the FCVA-DLC films. On the basis of the dependence of the friction properties on the film thickness, we can conclude that the friction coefficients of FCVA-DLC films are low and stable. In contrast, the friction coefficients of ECR-CVD-DLC films that are thinner than 1.0 nm are as high as those of Si (100) substrates. Therefore, these results reveal the excellent wear resistance of extremely thin films deposited by FCVA.

EP12 Deposition and Tribological Properties of Multilayer and Mixed Films Composed of Gold and Diamond-like Carbon, ***S. Takanori*** *(tokuiti.1017@gmail.com)*, *M. Shojiro*, Nippon Institute of Technology, Japan

To improve the tribological properties of materials for use in various fields, the application of solid lubricant films that lower the friction coefficient is desirable. Among solid lubricant materials, although soft metals have a higher friction coefficient and poorer durability than other solid lubricants such as graphite and MoS_2, these metals are currently used in electrical and mechanical parts such as electrical contacts owing to their high electrical conductivity. Therefore, low-friction, wear-resistant electroconductive solid lubricant films are desired. In contrast, diamond-like carbon (DLC) films have low friction and high wear resistance. Coating with hydrogen-free DLC films is highly advantageous. Lubricants such as polyalphaolefin (PAO) with and without glycerol monooleate (GMO) are capable of significantly reducing the friction of hydrogen-free DLC films under boundary lubrication conditions. Research on the development of nanometer period multilayer films for improving film hardness has thus been carried out. To apply these multilayer films as solid lubricants, we proposed a nanoperiod multilayer solid lubricant film with friction lower than that of conventional solid lubricants. This study aims to realize lower friction and electroconductive solid lubricant films on the basis of a nanoperiod multilayer solid lubricant model. To develop electroconductive solid lubricant films, multilayer and mixed films composed of gold and DLC layers were deposited using bias radio frequency sputtering. Then, the electroresistivity and tribological properties of the deposited films were evaluated. The electroresistivities of 80 at% gold-DLC multilayer and mixed films were low at values less than 0.03 Ω cm, while the electroresistivities of 50 at% gold content multilayer and mixed films were low at 15–18 Ω cm. The 50 at% gold content multilayer films had a higher Young's modulus and hardness than the gold monolayer films and values similar to those of DLC films.

The friction coefficient of the nanoperiod multilayer film was the lowest of all the tested samples. In addition, the wear depths of the multilayer films were smaller than those of the gold and DLC mixed and monolayer films in air. The friction coefficient and wear durability were considerably improved for the multilayer films among the samples tested under water boundary lubrication conditions. Under PAO boundary lubrication conditions with and without GMO, the wear durability of the multilayer films was superior, and the damage to the multilayer films was less than that for the gold monolayer film and similar to that for the DLC film.

EP14 Deposition and Characterization of Bismuth Containing Hard Coatings, ***R. Mirabal*** *(mirabalroberto@yahoo.com)*, *S. Rodil*, *P. Silva-Bermudez*, *S. Muhl*, *G. Ramirez*, Universidad Nacional Autónoma de México - Instituto de Investigaciones en Materiales, Mexico, *J. Oliveira*, *A. Cavaleiro*, Faculdade Ciencias E Tecnologia Da Universidade De Coimbra, Portugal

Bismuth is a soft semimetal with a rhombohedral graphite-like quasi-layered structure and a low melting point of 271°C. These characteristics point to the use of Bi or Bi-compounds for self lubrication applications where low friction and low wear rates are required. However, pure Bi and its compounds are very soft. Therefore our proposal is the inclusion of Bismuth into a hard coating using the methodologies developed for nanocomposite thin films; either as nano-sized particles into a hard matrix or as a lamellar structure, alternating a bismuth layer with a hard-coating layer. Then, the excellent frictional properties of Bismuth could be exploited in combination with materials that provide mechanical resistance. Bismuth sputtered films for mechano-tribological applications and its addition into metal nitride coatings have been poorly studied, therefore there is a strong need to define the deposition conditions adequate to achieve a stable and adhered coating. In this work, we report the deposition of Bismuth containing niobium nitride coatings using a confocal dual sputtering system. Both targets (2") were ignited simultaneously, but using different powers; 400 W direct current for the Nb target (99.95 %) and 6,10 and 20 W radio frequency for the Bi target (99.999%). The coatings were deposited on Silicon at 200 °C using a mixture a fixed Ar/N_2 (14/6) flow ratio. The deposition pressure was 3 mTorr starting from a backing pressure below $5x10^{-6}$ Torr. The composition of the coatings was obtained by both X-ray photoelectron, to clearly detect the presence of oxidized phases, and

energy dispersive spectroscopy, in order to detect the presence of segregated bismuth. The Bi segregation and NbN structure were also studied by X-ray diffraction. The coefficient of friction of the coatings was measured by pin-on-disk tests using a load of 5 N and a sliding distance of 500 m.

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EP15 A Laboratory-scale Pin-sliding Instrument for Triboluminescence Measurement, ***S. Leelachao***, *S. Muraishi (muraishi.s.aa@m.titech.ac.jp)*, Tokyo Institute of Technology, Japan

A report on the design and construction of an inexpensive, compact triboluminescence measuring setup is presented. The system simply composes of a rotating stage and a stainless steel sliding pin. The counter pin is interchangable. An optical fiber, being connected to spectrophotometer, is used for detecting the generated light signal from the luminescent materials. A visible emission is measured from the bottom of the contact area. Any experimental parameters, such as an external load or rotation speed, are able to be adjusted. ZnS-based phosphor powders are selected as a reference sample. A characteristic emission from substitutional Mn^{+2} ions at wavelength of 580 nm is able to be recorded even the load is 0.5N. Further information of the equipment with the results on triboluminescence of the phosphors are also included and discussed.

EP16 An Overview of Interfacial Fracture Energy Predictions for Stacked Thin Films Using Four-Point Bending Framework, *C.C. Lee (changchunlee@cycu.edu.tw)*, ***Y.J. Lai***, Chung Yuan Christian University, Taiwan, Republic of China, *C.C. Huang*, National Nano Device Laboratories, Taiwan, Republic of China

Adhesion of stacked thin films in advanced devices becomes significantly important as the concerned characteristic dimensions continue scaling down to the regime of several nanometers. The occurrence of interfacial fracture is easily examined during the manufactured process with thermal cycles and the inherent poor adhesions of stacked films. Therefore, developing a robust predicting methodology regarding interfacial fracture energy of dissimilar materials is necessary and urgent to meet the mechanical requirements of investigating novel material and subsequent device structures. For this reason, in according with interfacial fracture mechanics, this research overviews several useful approaches, such as J-integral method, modified virtual crack closure technique (VCCT), and analytical solutions derived from the relation between stress field of delaminated tip and crack tip opening displacements (CTOD). Through the testing vehicles of four-point bending framework, the validations of foregoing predicted approaches by using finite element analysis (FEA) are acquired as comparing the simulated results with related experimental data. The critical energies of 18J/m2, 78.53J/m2, 52.01J/m2, and 71.02J/m2 for the bonded interfaces of SiO2/SiLK, Ta/SiLK, TaN/SiLK, and Si3N4/SiLK stacked thin films are precisely judged, respectively. Predicted results of J-integral method match well with the estimation of modified VCCT. As the interfacial crack length increases, the results reveal that opening fractured mode is dominant at the beginning of crack advances along bonded interface of Ta/SiLK, TaN/SiLK, and Si3N4/SiLK stacked film. All the results shown in this research could be regards as a design guideline of interfacial fractured behavior for stacked films utilized in the developments of advanced device technologies.

EP17 Thermo-mechanical Failure Behavior of Copper TSV Induced by Transient Selective Annealing Technology, *C.C. Lee (changchunlee@cycu.edu.tw)*, ***Y.H. Lin***, Chung Yuan Christian University, Taiwan, Republic of China, *C.C. Huang*, National Nano Device Laboratories, Taiwan, Republic of China

For the purpose of providing multi-functions in a complicated microsystem, the use of three-dimensional (3D) integrated circuit (IC) technology with through silicon via (TSV) interposers is regarded as a promising framework to meet the foregoing requirements. However, managing the related process stability of 3D-IC manufactured integration is still a thorny issue, especially for the thermo-mechanical behavior of copper filled TSV interposer during the annealing operation. In this work, a transient annealing process is successfully applied on the filled copper only, that is, one selective heating technology. To address this concerned problem, a transient thermal-structural coupling analysis by using a nonlinear finite element simulation is proposed. As compared with the experimental data, the present simulated methodology is validated to be highly reliable. The analytic results show that high temperature deteriorates from the top surface of copper TSV to other regions within a silicon-based TSV interposer. Via a transformation of the above-mentioned thermal load in a mechanical analysis, the maximum thermal stress is examined to occur on the exposed top surface of silicon interposer close to interface between copper TSV and Ta thin barrier film when the power keeps supply for the annealing of copper metal. In other words, the phenomenon of stress-induced fracture among bonded films is prone to be observed so as to worsen subsequent mechanical reliability of 3D-IC devices. In accordance with the results presented in this investigation, the improvement could be suggested and acquired by optimizing the fabricated parameters in annealing processes. The technology provides a high throughput and reliable process on TSV manufacturing.

EP18 Global Elastic Anisotropy of Polycrystalline Metallic Thin Films and Multilayers, ***D. Faurie*** *(faurie@univ-paris13.fr)*, *P. Djemia*, LSPM-CNRS, Université Paris 13, Sorbonne Paris-Cité, France, *E. Le Bourhis*, *P.O. Renault*, Institut P' - Universite de Poitiers, France, *O. Castelnau*, PIMM, ENSAM Paris, France, *R. Brenner*, UMPC, Paris, France, *P.O. Goudeau*, Institut P' - Université de Poitiers, France

Elastic properties of anisotropic metallic thin films were investigated experimentally by several complementary techniques, namely in-situ tensile testing under X-ray diffraction (XRD), nanoindentation, and Brillouin light scattering (BLS). Specimens were probed along different directions to reveal the strong effects of elastic anisotropy at the (local) grain and (global) film scales. XRD allows the investigation of both local and global anisotropies, while BLS and nanoindentation are limited to global analyses. A micro-mechanical model, based on the Self-Consistent scheme, and accounting for the actual microstructure of the films, is applied to interpret experimental data. Although different kind of elastic constants can be determined with the used experimental techniques (static/dynamic, local/global), a good agreement is obtained, showing that comparison of these techniques is feasible when carried out carefully.

In the case of nanometric multilayers, a three-scale transition model is proposed for estimating the effective elastic constants from the intrinsic properties of elementary constituents (grains), taking into account the thickness ratio of each sublayer (in the case of multilayers) and the grains orientation distribution in each kind of layers. We show that the elastic anisotropy at the sample scale can be greater in the case of multilayers than in the case of single-layers, as confirmed experimentally by Brillouin light scattering.

EP19 On the Meaning and Requirements of the Concept of an Effective Indenter, ***M. Fuchs*** *(marcus.fuchs@s2003.tu-chemnitz.de)*, Chemnitz University of Technology, Germany

The Oliver & Pharr method [1] is probably the most widely used methodology for the analysis of nanoindentation measurements in order to mechanically characterize thin films and coatings. It is based on the implicit assumption of the concept of an effectively shaped indenter which was introduced later by Bolshakov [2]. This concept implies certain model assumptions (e.g. a flat surface and a monolithic half space) which may not be met by sophisticated coating structures. Nevertheless, the Oliver & Pharr method is frequently used in literature to analyze such sophisticated coating structures (e.g. multi-layer coatings, thin films, gradient coatings), even though extensions to this method allowing a proper analysis of such sophisticated surface structures have already been developed by Schwarzer [3]. This work will explain the model assumptions in order to help understanding them by means of adapted schemata of the “effective indenter” concept and examples which illustrate the significant differences in the analysis results (e.g. elastic modulus *E*, hardness *H*, yield strength *Y*, stress profiles, etc.) between the original Oliver & Pharr method and the extended one by Schwarzer.

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EP21 Friction Characteristics Degradation of Cup Anemometer used for Wind Energy Potential Measurements, ***M. Zlatanovic*** *(jzlatanovic@beotel.net)*, School of Electrical Engineering, Serbia, *D. Romanic*, Republic Hydrometeorogical Service, Serbia

The first step in order to minimize the error in predicting a wind farm production is to improve the wind measuring technique and long term wind climate prediction methods. Wind speed sensors based on different measuring principles are used but cup anemometers invented nearly 170 years ago still serves as a reference instrument. The angular velocity of this anemometer is directly proportional to the wind speed. Since the instrument contains moving parts some degradation of performance may occur during long term operation at open field conditions. Several material pairs for manufacturing the shaft and bearing as a tribological pair used for cup anemometer construction were selected. Special lubricants were applied to lower the friction coefficient in case of metal contact surface, but in some

cases self lubricated tribological pairs were used. Long term field operation of NRG #40 cup anemometer with the shaft made of fully hardened beryllium copper and self-lubricating modified teflon bearings was analyzed. Sensor performance degradation due to dry friction whip was found and analyzed in details in several papers. In this paper the degradation of anemometer performance detected after three years of continuous operation was investigated and recalibration was carried out in an aerodynamic tunnel. A significant change of calibration curve was found with increased offset value. The origin of calibration offset is mostly due to the aerodynamic torque, but in considered case the friction torque influence not clearly related to dry friction whip was found. A method to recognize the friction torque change during sensor field operation was suggested which allows for friction characteristics prediction and correction of wind speed data.

EP22 Characterization of Zr-Ti-Fe Thin Film Metallic Glasses Containing Different Fe Contents, ***L.T. Chen***, National Taipei University of Technology, Taiwan, Republic of China, *J.-W. Lee (jefflee@mail.mcut.edu.tw)*, Ming Chi University of Technology, Taiwan, Republic of China, *Y.C. Yang*, National Taipei University of Technology, Taiwan, Republic of China

Recently metallic glass thin films represent a class of promising engineering materials for structural applications. In this work, the Zr-Ti-Fe thin film metallic glasses (TFMGs) with different Fe contents were prepared by magnetron co-sputtering system using pure Zr, Ti and Fe targets. The influence of iron contents on the amorphous state, microstructure and mechanical properties of Zr-Ti-Fe thin film metallic glasses was investigated. The thermal behavior of each TFMG was determined using a differential scanning calorimeter (DSC). The crystal structure of the samples was determined by grazing incidence X-ray diffraction (GIXRD). The compositions of the films were analyzed by field emission electron probe X-ray micro-analysis (FE-EPMA). Surface and cross-sectional microstructure of the films were observed by scanning electron microscope (SEM). The surface roughness of thin films was explored by atomic force microscopy (AFM). A nanoindenter, a scratch tester and ball-on-disk wear tests were used to evaluate the hardness, adhesion and tribological properties of TFMGs, respectively.

EP23 Enhanced Wear Resistance and Mechanical Properties of the WC-12%Co HVOF Thermally Sprayed Coatings Doped with MWCNTs, ***M. Rodriguez*** *(m.rodriguez.ucv@gmail.com)*, Universidad Central de Venezuela (UCV), Venezuela (Bolivarian Republic of), *J. Caro*, Fundació CTM Centre Tecnològic, Spain, *E. Anglaret, N. Fréty*, Université Montpellier II, France, *L. Gil*, Universidad Nacional Experimental Politécnica (UNEXPO), Vicerrectorado Puerto Ordaz, Venezuela (Bolivarian Republic of)

WC-Co is widely used as a tribological coating material requiring a combination of high toughness, high hardness, and good strength. Herein, an attempt has been made to further enhance the mechanical and wear properties of tungsten carbide cobalt coatings by reinforcing multi wallet carbon nanotubes (MWCNTs) using thermal spraying. In this work 0.35% w of MWCNTs were mixed by jar-milling in ethanol solution with WC-12%Co microcrystalline powders at different blended times. The mix was thermally spayed using HVOF process onto a plain steel substrate. Also, coatings deposited with both WC-12%Co microcrystalline and nanostructured powders, using the same thermal spray process, were evaluated and compared with samples doped with MWCNTs. The microstructures of the coatings were characterized using scanning electron microscopy, energy dispersive spectroscopy (EDS), Raman test and X-ray diffraction (XRD). The mechanical properties were assessed using micro-Vickers hardness, nanoindentation and wear measurements by two different tests. Effects of doping times of MWCNTs on the phases, microstructure, wear and mechanical properties of the coatings were investigated. The results showed that the best results were obtained when using a blending time of 36 hours. MWCNTs reinforcement improved the hardness of the coating by almost 18 % and decreased the abrasion wear rate of the coating by almost 70%. WC-Co reinforced with 0.35 wt.% CNT blended during 36 hours had an elastic modulus 260 ± 8 GPa, hardness of 16.6 GPa ± 0.64 and a coefficient of friction of 0.24. It was concluded that the CNT reinforcement increased the wear resistance by forming intersplat bridges while the improvement in the hardness was attributed to the deformation resistance of CNTs under indentation.

EP24 Evaluations of the Residual Stress in the Plasma Sprayed Multi-layer Electrodes of the Solid Oxide Fuel Cell, *Y.C. Yang (ycyang@ntut.edu.tw)*, ***Y.C. Wang***, National Taipei University of Technology, Taiwan, Republic of China, *C.S. Hwang*, *C.H. Tsai*, Institute of Nuclear Energy Research

The advantage of porous metallic supported solid oxide fuel cell (MSC) produced by APS process is to have a SOFC cell applied in the harsh environment with large cell area and effective production cost. However, through the spraying process, residual stresses are unavoidably developed in coatings due to the differences in thermal expansion coefficients, and different cooling conditions between the coating and the substrate. In this study, we investigated the residual stress of each membrane electrodes, which under the cyclic redox treatments. The results show that all of the components of MSC (LSCM buffer, NiO/LDC anode, LDC buffer, LSGM electrolyte, LSCF cathode) reveal compressive residual stress after plasma spraying. However, the stress states of these components become complicated and irregular after the redox treatments. The strain state of both LSCM buffer layer and anode were changed from compressive to tensile. We also found that the original stress state was changed when the upper component was deposited. For example, the original stress state was 0.78% in compressive; after the NiO/LDC anode deposited on the LSCM buffer, the anode side of LSCM revealed the compressive strain with 3.34% and the matrix side of LSCM revealed the tensile strain with 10.65%. Two strain states coexisted in a layer resulted in the coating failure occurred in the interface between the opposite stress states. Therefore, the redox treatments indeed affect the strain state of the MSC components and the influences on the cell durability should not be ignored. The more research results will be described in detail.

EP25 Microstructure and Properties of WC-Co Carbides Coatings Obtained by Different Methods of High Velocity Thermal Spray Process, *K. Szymański, G. Moskal (grzegorz.moskal@polsl.pl),* ***H. Myalska***, Silesian University of Technology, Poland

Microstructural characterization of WC - based coatings obtained by standard and modified HVOF method was showed in this article. Two different standard feedstock powders of WC-Co 88-12 and 83-17 (by Amperit) type was used to deposition of coating o steel substrate. The aim of investigation was related to comparison of microstructure and basic mechanical properties of coatings depending of applied method of deposition. The range of investigations included characterization of feedstock powders by SEM, EDS, XRD and EBSD method and their technological properties as well. In second step the characterization of deposited coatings were made, especially evaluation of theirs overall quality, porosity, micro-hardness distribution, adhesion of coatings to substrate alloys and theirs tendency to cracks. To characterization of coatings microstructure the same methods were used. Adhesion to substrate alloy and tendency to crack of coatings were characterized by bend test and Brinell hardness measurement on polished top surface of carbide coatings.

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 acknowledged.

EP27 Characteristics of Structure and Selected Properties of High Velocity Oxy-fuel Thermal Sprayed WC-Co Type Coatings with the use of Ultra-fine Powders, ***A. Iwaniak*** *(aleksander.iwaniak@polsl.pl)*, Silesian University of Technology, Poland, *G. Wieclaw, K. Rosner*, Certech Sp. z o.o., Poland

The use of the of high velocity oxy-fuel method and classic powders of graining 45µm in the process of thermal spraying allows to obtain coatings resistant to abrasiveness and having porosity of 1%. Devices having the minimum burner power of 45 kV are needed. In the study, the structure of thermally sprayed WC-Co coatings was analyzed. The coatings were sprayed with the use of ultra-fine powders of graining ranging from 1 to 10µm and nanostructure. For spraying ultra-fine powder, the burner with power 20÷40 kW was used. The structure of coatings obtained from classic powders (45µm) and ultra-fine ones of graining 1÷10µm were compared. Structural tests were done with the use of light microscopy (LM), High Resolution Scanning Electron Microscope (EDS), phase composition (XRD) and electron probe micro-analyzer (EPMA) together with chemicals mapping. The coatings spayed with the use of ultra-fine powders were characterized by porosity smaller than 0.1% and high hardness of 1200 HV0.3. The tests for erosive wear showed better resistance of the coatings obtained with the use of smaller graining powders.

This research was conducted as a part of Innotech program founded by The National Centre for Research and Development in Warsaw (Poland).

EP28 Deformation and Failure Mechanisms of Magnetron Sputtered Cu/TiN Multilayers, *R. Raghavan (rejin.koodakal@empa.ch), D. Esqué-de los Ojos, A. Montagne*, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland, *E. Almandoz, G. Fuentes*, AIN-Centre of Advanced Surface Engineering, Spain, ***J. Michler***, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland

Multilayered films of Cu and TiN were deposited by magnetron sputtering on Si (100) with a thickness ratio of 1:2 and individual layer thicknesses varying across two orders of magnitude from 500 to 5 nm. The mechanical

behavior of all the Cu/TiN multilayers was studied by compression of micro-pillars FIB machined within the multilayered film with the Si (100) substrates forming the base of micro-pillars, whose heights were chosen equal to the film thickness. The stress-strain curves obtained from the micro-pillar compression experiments reveal that at the length scales close to 500 and 50 nm, corresponding to the individual layer thicknesses of Cu, the yielding of the overall multilayer is governed by the size dependent yield stress of Cu. On the other hand, the failure of the multilayer is governed by the inter-columnar shear strength of the TiN columns formed within the individual TiN layers. An interesting change in flow and failure response is observed at the smallest individual layer thicknesses of Cu (5 nm) and TiN (10nm). While the yield stress of this multilayer is higher than the 500 nm Cu and 1000 nm TiN multilayer and lower than the 50 nm Cu and 100 nm TiN multilayer, the failure stress is highest among all the multilayers. Thus, while a transition in the yield stresses occurs when the interlayer thicknesses are smaller than 50 nm, a continuous increase in failure stresses and a change in failure mechanism is observed. The transition in yield stress of the multilayers is discussed in terms of potential inverse Hall-Petch behavior, change in strain hardening of the Cu and potential plasticity of TiN. The increase in failure stress is explained in terms of the increase in inter-columnar shear strength of the TiN columns. These observations and arguments are reinforced with FEM simulations. A 2D axisymmetric model is used during simulations where length and mesh sensitivity are avoided by properly defining the model. A piecewise elastic-power law plastic relation is used to capture the uniaxial behavior of Cu, while TiN is considered as a perfectly elastic material. Size dependence of yield stress and residual stresses obtained from present experimental results and literature are used during simulations to obtain the experimental trends. In summary, the findings and analysis suggest that a multilayer with optimal individual interlayer thicknesses could be designed to obtain the desirable merger of strength and toughness.

New Horizons in Coatings and Thin Films
Room: Grand Hall - Session FP

Syposium F Poster Session

Moderator: A.P. Ehiasarian, Sheffield Hallam University, U. Helmersson, Linköping University, IFM, Plasma and Coatings Physics, Sweden, S. Kodambaka, University of California, Los Angeles

FP1 Mechanical Properties of Patterned Oxide Structures on Compliant Substrates for Flexible Optoelectronics, *K. Sierros (kostas.sierros@mail.wvu.edu)*, West Virginia University, ***T. Bejitual***, *N. Morris, D. Cairns*, West Virginia University, US

There is currently great interest to design and fabricate novel flexible devices for solar cell, solid-state lighting, biomedical and energy harvesting applications. Such devices require the use of electrode components. Desired electrodes must exhibit structural integrity, low electrical resistivity and, in most cases, high optical transparency in the visible range.

Despite growing efforts to replace them, transparent conducting oxides layers deposited on polymer compliant substrates are still enjoying a dominant role as the electrode material. This is because of their excellent electrical and optical properties. However, their performance when they are subjected to externally applied mechanical stresses is limited. Such performance has been extensively investigated for the case of continuous brittle oxide films on polymer substrates. However, there is relatively little work reported to date on the mechanical behavior of patterned conducting layers on compliant substrates. Patterned brittle structures may be able to accommodate higher mechanical strains because of their controlled shape, size and edge definition.

In this study we report on the mechanical behavior of various patterned indium tin oxide (ITO) shapes on polyethylene terephthalate. Micron-sized shapes include lines, circles, squares and zigzag-based structures. Uniaxial tensile and buckling experiments are performed in-situ using an optical microscope in order to monitor critical strains and potential failure mechanisms. In addition, in-situ electrical resistance measurements are conducted during mechanical deformation. We also report on the effect of ITO etching time and edge definition. Furthermore, ex-situ characterization using scanning electron and atomic force microscopies is conducted. Finally, experimental results are compared with modeling studies.

We believe that this work is providing an improved understanding that will aid towards designing patterned flexible device platforms with enhanced structural integrity.

FP2 Influence of H-radical Irradiation on the Properties of a Ge/SiC Nanodot/SiC Stacked Structure, *K. Satou, Y. Anezaki*, Nagaoka University of Technology, Japan, *M. Suemitsu*, Tohoku University, Japan, *H. Nakazawa*, Hirosaki University, Japan, *Y. Narita*, Yamagata University, Japan, *A. Kato, T. Kato*, Nagaoka University of Technology, Japan, ***K. Yasui*** *(kyasui@vos.nagaokaut.ac.jp)*, Nagaoka Univeversity of Technology, Japan

Semiconductor quantum dots can confine carriers such as electrons and holes in three-dimensions and exhibit unique electronic and optical properties. For highly efficient IR light-emitting devices using Ge nanodots, a high density of small Ge nanodots, less than 10 nm in diameter, is required. It has been reported that a density of 2×10^{11} cm^2 nanodots was achieved by the pregrowth of submonolayer carbon.[1] In this case, carbon atoms were incorporated into a Si(001) substrate and surface strain was induced, leading to the formation of a Si(001) c(4×4) reconstruction structure at the surface layer, which changed the Ge growth from the Stranski–Krastanov (SK) mode to the Volmer-Weber (VW) mode and resulted in formation of a high density of nanodots. Strong repulsive interaction can operate between Ge and C; therefore, Ge atoms deposited on the SiC layer do not interdiffuse. The c(4×4) surface was expected to function as a template substrate for the formation of a high density of Ge nanodots. We have previously reported that the c(4×4) structure is formed by the reaction of monomethylgermane (MMGe) on the Si(001) 2×1 surface. The Ge nanodots embedded in the SiC structure are expected to strongly confine carriers, due to the difference in the bandgap between Ge and SiC. Ge nanodot formation using MMGe resulted in the formation of SiC and Ge nanodots after the appearance of the c(4×4) reconstructed surface. Using a pulse-controlled nucleation method, the formation of a high density (1.3×10^{11} cm^{-2}) of nanodots (6 nm) with a small standard deviation (1 nm) was achieved. We have previously reported reflection high-energy electron diffraction (RHEED) and scanning tunneling microscopy (STM) results for the surface structure of Ge and SiC nanodots fabricated using MMGe.[2] Photoluminescence (PL) spectra of Ge nanodots capped with a SiC layer were also measured at low temperatures.

In this study, the influence of H-radical irradiation on the photoluminescence properties of Ge/SiC nanodots was investigated. The apparatus configuration and conditions for the growth of Ge/SiC nanodots were the same as those reported previously, except for the addition of a tungsten wire. The tungsten wire (0.2 mm diameter) was heated at 2073 K to generate H-radicals after the growth of Ge/SiC dots and after deposition of the SiC capping layer. The substrate temperature was maintained at 473K-673 K according to the temperature for H-desorption from the Ge-H surface.[3]

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FP3 Shape Controllability and Photoluminescence Properties of ZnO Nanorods Grown by Chemical Bath Deposition, ***T. Terasako*** *(terasako.tomoaki.mz@ehime-u.ac.jp)*, *T. Murakami*, Graduate School of Science and Engineering, Ehime University, Japan, *M. Yagi*, Kagawa National College of Technology, Japan, *S. Shirakata*, Graduate School of Science and Engineering, Ehime University, Japan

Much attention has been given to the fabrication of ZnO nanostructures because of their potential applications in opt-electric devices. Chemical bath deposition (CBD) method permits low growth temperatures suited for the fabrication of the nanostructures on the flexible substrates, such as metal foils and polymers. In this paper, shape-controllability and photoluminescence properties of ZnO nanorods (NRs) grown by the CBD method using the aqueous solution of zinc chloride ($ZnCl_2$) and the mixed aqueous solution of zinc acetate dehydrate (ZnAc) and hexamethylenetetramine (HMT) will be discussed.

Glass slides, Au films and (Mg,Zn)O/glass films prepared by chemical spray pyrolysis were used as substrates. The concentration of $ZnCl_2$ in the aqueous solution was changed in the range from 0.02 to 0.24 M. The pH value of the $ZnCl_2$ solution was adjusted to 10.0 by adding ammonia water. The concentration of ZnAc was changed in the range from 0.01 to 0.02 M and the molar ratio of HMT to ZnAc was kept at 1:1. The temperature of the water bath was kept at 90°C during the deposition process. Growth time (t_g) was varied in the range from 15 to 240 min.

X-ray diffraction (XRD) measurements and scanning electron microscope (SEM) observations revealed the successful growth of vertically aligned ZnO NRs with preferred c-axis orientation on the Au and (Mg,Zn)O seed layers. When t_g increased from 15 to 180 min, the average diameter of the NRs grown using the $ZnCl_2$ solution of 0.17 M increased from 150 to 1000 nm together with the change in shape from cones to hexagonal prisms. For

the ZnAc solution of 0.03 M, the diameter increased from 100-400 nm for t_g=60 min to 550-1000 nm for 240 min.

PL spectra from the as-grown NRs were composed of an orange (OR) emission and a near-band-edge (NBE) emission. The appearance of the OR emission suggests that the NRs have the high density of interstitial oxygen atom in their surface regions. For the NRs grown using the $ZnCl_2$ solution, the relative intensity of the NBE emission to the OR emission was independent of tg. For the NRs grown using the ZnAc solution, however, the relative intensity of the NBE emission to the OR emission became larger with increasing t_g, suggesting the improvement of the crystalline quality. PL excitation (PLE) measurements for the NRs grown using the ZnAc solution revealed that the OR emission was effectively excited at the photon energy corresponding to the A free-exciton energy. However, PLE spectra for the OR emission from the NRs grown using the $ZnCl_2$ solution showed that the secondary phase $Zn(OH)_2$ formed at the surface regions of the NRs contributed to the excitation process for the OR emission.

FP4 Optical Properties of La_2O_3 Thin Films Deposited by RF Magnetron Sputtering, *S.B. Brachetti-Sibaja (bbrachetti@hotmail.com), M.A. Domínguez-Crespo, A.M. Torres-Huerta*, Instituto Politécnico Nacional, Mexico, ***S. Rodil***, Universidad Nacional Autónoma de México, Mexico

In spite of the high potential applications of lanthanum oxide thin films, only few studies have investigated the correlation between deposition conditions and optical properties. La_2O_3 films have been deposited by different physical thin film growth methods such as electron-beam evaporation, pulsed-laser evaporation and vacuum evaporation, but not by sputtering.

In the present work, lanthanum oxide films were deposited by radiofrequency magnetron sputtering from a La_2O_3 target in an Argon atmosphere (20 mTorr). The films were deposited onto Si(100) and glass substrates. Two different RF-powers were tested (60 and 90 watts) and for each power, the deposition time was changed from 25, 40 and 60 minutes, as well as the substrate temperature (ambient and 200°C). The film thickness was measured by profilometry obtaining variations between 102 nm for the 60 W with 25 minutes and ambient temperature and 1097 nm for 90 W with 60 minutes and 200 ºC of temperature. The structure, morphology and chemical composition was studied by X-ray Diffraction (XRD), X-ray Photoelectron Spectroscopy (XPS), and Scanning Electron Microscopy (SEM), respectively. The optical properties were estimated by modeling the ellipsometric spectra (1.5 to 5 eV) using Tauc-Lorentz dispersion models. The results from the ellipsometric model were compared with the transmission spectra obtained in the UV-VIS range for the films deposited on glass.

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FP5 ZnO Nanostructures as Efficient Antireflection Layers in High Efficiency Non-selenized Cu(In,Ga)Se2 Solar Cells, *B.T. Jheng*, National Tsing Hua University, Taiwan, Republic of China, ***P.T. Liu*** *(ptliu@mail.nctu.edu.tw)*, National Chiao Tung University, Taiwan, Republic of China, *Y.P. Chang*, Nan Kai University of Technology Nantou, Taiwan, *M.C. Wu*, National Tsing Hua University, Taiwan, Republic of China

Non-selenized Cu(In,Ga)Se2 (CIGS) thin-film solar cells with a zinc oxide (ZnO) nanorod/ Al and Y codoped ZnO(AZOY)/ ZnS/ CIGS/ Mo/ SLG structure have been fabricated using an aqueous synthesis solution method-ZnO nanorod arrays layer and high quality CIGS absorber layers grown using sputtering system.The use of ZnO nanorod arrays antireflection (AR) coating, which is a higher light-trapping probability than dielectric MgF2, improved the reflectance of fabricated cells at UV–visible wavelengths, leading to an increase in the short-circuit current. In the work, we successfully applied ZnO nanorod arrays in the production of non-selenization CIGS thin-film solar cell devices, to achieve the low reflection incident light and to better the solar cell device conversion efficiency to around 10%.

FP7 Phase Stability of Bi_2O_3 Thin Films prepared by Reactive Magnetron Sputtering, ***O. Depablos-Rivera*** *(osmarydep@yahoo.com), P. Silva-Bermudez, S. Rodil*, Universidad Nacional Autónoma de México - Instituto de Investigaciones en Materiales, Mexico, *E. Camps*, Instituto Nacional de Investigaciones Nucleares de Mexico

Bismuth oxide thin films were deposited by reactive magnetron sputtering from a Bi_2O_3 target (99.95 at%) using RF and an Ar/O_2 atmosphere (80/20). The films were deposited on silicon and glass substrates at 120 W and 150ºC. Under these conditions, the films were stoichiometric and showed the cubic delta phase, which is usually the stable phase of bismuth oxide at high temperatures (725-850ºC). However, as a thin film, it has been shown that the delta-phase can be obtained even at room temperature conditions. The delta Bi_2O_3 is the high ionic conductivity, which is searched for solid oxide fuel cell applications, as the solid electrolyte. The objective of this work is to study the structural stability of the delta-phase films as a function of the both the storage-time and thermal treatments in air. The films were storage under environmental conditions (25ºC, 760 Torr). The film structure was obtained by X-ray diffraction and Raman spectroscopy, which is a very useful technique to identify the presence of the disorder inherent to the delta phase. Similarly, the optical properties have been measured by both transmission and spectroscopic ellipsometry. The films kept at ambient conditions have been analyzed periodically, after a year no changes in the structure have been observed, which is a good indication. Annealing experiments were done in air from 120ºC to 500ºC, in order to identify the temperature at which phase transition occurs. The results indicated that the film structure is stable up 210ºC where the d-phase remained unchanged. Higher temperatures lead to phase transitions into the beta phase up to 360ºC, above this temperature, some regions started to show the alpha-phase. The optical transmission increases with the annealing temperature.

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FP8 Photocatalytic Activity of Bismuth Oxide Thin Films, ***J.C. Medina*** *(21.juancarlos@gmail.com), S. Rodil, M. Bizarro, P. Silva-Bermudez*, Universidad Nacional Autónoma de México - Instituto de Investigaciones en Materiales, Mexico

Bismuth oxide (Bi_2O_3) thin films were deposited by Magnetron Sputtering technique under different deposition conditions; substrate temperature and RF power in order to obtain films having different crystalline phases. X-ray diffraction, profilometry, scanning electron microscopy, and optical transmission were used to characterize the films. The results indicated that it was possible to obtain oxide films in the alpha, beta and delta phase, depending on the deposition conditions. The photocatalytic activity for each one of the Bi_2O_3 phases was evaluated testing the degradation of methyl orange dye ($C_{14}H_4N_3SO_3Na$) under different light energies (ultraviolet, white and solar light). The photocatalytic activity was measured as a function of the irradiation time, light-energy, concentration and pH of the solution. The colorant degradation and the kinetic of the reaction were estimated using the variation of the corresponding absorption band situated at 508 nm (acid media) and 461 nm (neutral and basic media). For the UV light (380 nm and power of 9 W), the results pointed out that the photocatalytic effect was only activated under acidic conditions, for the other pHs, the activity was negligible. Moreover, it was also found that the delta-phase films presented larger photocatalytic efficiency reaching almost 100% of degradation of the dye solution in only 60 minutes, which was an remarkable result considering the photocatalytic performance of other oxides in similar conditions. The rate of reaction of the delta-phase samples was almost twice than that obtained for the other phases. The rate of reaction was used to compare the efficiency of the catalytic reactions and to correlate it with other physicochemical properties, such as the band gap. These results suggest that the Bi_2O_3 films are a rather new and promising photocatalytic material for water treatment application.

Acknowledgement: The research leading to these results has received funding from the European Community Seven Framework Programme (FP7-NMP-2010-EU-MEXICO) and CONACYT under grant agreements nº 263878 and 125141, respectively.

FP9 Synthesis and Characterization of Copper Nanoparticles by Solution Plasma Processing, ***S.M. Kim***, *S.C. Kim, S.H. Jin*, Korea Aerospace University, Republic of Korea, *G.J. Yoon, S.W. Nam, J.W. Kim*, University of InCheon, Republic of Korea, *S.Y. Lee (sylee@kau.ac.kr)*, Korea Aerospace University, Republic of Korea

Copper nanoparticles were synthesized with various discharge durations in the presence of amide and acid capping agent using solution plasma processing (SPP), and the effects of the discharge duration between 60 and 600 s on the size and shape of the copper nanoparticles were investigated using UV–Vis NIR spectrophotometry, X-ray diffactometer (XRD), and transmission electron microscopy (TEM). The results showed that discharge duration had a strong effect on the formation of copper nanoparticles. Using high voltage power supply, copper nanoparticles was rapidly formed after discharge at 60 sec and the size and shape of copper nanoparticles were dependent on discharge time, indicating a strong effect of capping agent under various discharge media characteristics (pH and temperature). With long discharge time, copper nanoparticle size tended to decrease with the formation of various particle morphologies, spherical, cubic, hexagonal, triangular, and rod–like shapes. The decrease in size as a function of discharge time could be explained by the dissolution of copper nanoparticles in lower pH solution at higher temperature. After discharge at 300 sec, the role of capping agent evidently showed the shape control and oxidation protection of the synthesized copper nanoparticles. The desirable

size and shape of copper nanoparticles without the undesirable oxidation could be controlled by adjusting discharge time of solution plasma. Detailed experimental results will be presented.

FP10 A Study of Microstructure and Electrical Properties of Strontium Doped Ceria Thin Films Deposited by High Power Impulse Magnetron Sputtering, ***C.T. Chang***, National Taipei University of Technology, Taiwan, Republic of China, *J.-W. Lee (jefflee@mail.mcut.edu.tw)*, Ming Chi University of Technology, Taiwan, Republic of China, *Y.C. Yang*, National Taipei University of Technology, Taiwan, Republic of China

The high power impulse magnetron sputtering (HIPIMS) technology is a promising coating technology, which has been intensively studied recently. In this study, the HIPIMS technique was adopted to deposit the electrolyte of solid oxide fuel cell (SOFC). The strontium doped ceria thin films were fabricated to replace the yttria stabilized zirconia (YSZ) coating, which was the high-temperature electrolyte layer in SOFC. Effects of strontium contents on the microstructure and electrical properties of ceria thin films were explored. The HIPIMS parameters, including duty cycle and pulse frequency were adjusted to grow strontium doped ceria thin films. The proper strontium concentration and suitable HIPIMS fabrication parameters were also reported in this work.

FP12 Effect of Substrate Bias and Hydrogen Addition on the Residual Stress of Hexagonal Boron Nitride Film Prepared by Sputtering of B_4C Target with Ar/N_2 Reactive Gas, ***J.K. Park*** *(jokepark@kist.re.kr), J.H. Lee, W.-S. Lee, Y.J. Baik*, Korea Institute of Science and Technology, Republic of Korea

cBN (cubic boron nitride) shows outstanding mechanical properties such as hardness and wear resistance. Despite of the excellent properties, high stress developed during the deposition of cBN film deteriorates adhesive strength of the film and restricts the application for coating material. Recently, addition of hydrogen [1,2] was reported to be useful technique to reduce the residual stress of cBN film prepared by sputtering of B_4C as well as hBN targets. Ar incorporation between (0002) planes of hBN (hexagonal boron nitride) was suggested to be the main origin for the residual stress observed in boron nitride film, which could be suppressed by the hydrogen addition through the formation of sp^3 bonding at the growing hBN (0002) plane edge. In this study, we have investigated systematically the effect of substrate bias and hydrogen addition on the residual stress of hBN film prepared by magnetron sputtering of B_4C target. The deposition was performed on Si (100) substrate under the chamber pressure of 0.27 Pa with substrate bias from -200V to -300V. After the deposition of B_4C layer, hBN film was deposited with a step-wise increase of nitrogen flow rate from 0 sccm to 4.5 sccm in Ar/N_2 mixed gas with a constant Ar flow rate of 25 sccm. Hydrogen (5 sccm) was added to a gas mixture of argon and nitrogen flowing 25 sccm and 5 sccm, respectively to investigate hydrogen effect on the residual stress. The compressive residual stress of hBN film was observed to be decreased from 5.0 GPa to 2.8 GPa, with increasing substrate bias voltage from -200V to -300V. The hydrogen addition reduced the compressive residual stress value of hBN film further. The decreasing behavior of the compressive residual stress observed in the hBN film with increasing substrate bias is difficult to be explained only by the effect of lattice defect and distortion induced by ion bombardment. In this presentation, the stress variation with substrate bias and hydrogen addition was discussed in terms of the relation between the penetration probabilities of argon ions into the film.

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FP13 In-situ Biaxial Loading During X-Ray Diffraction and Digital Image Correlation Measurements: Application to Metallic Thin Films Supported by Polyimide Substrates, ***P.O. Renault*** *(pierre.olivier.renault@univ-poitiers.fr), E. Le Bourhis*, University of Poitiers, France, *D. Faurie*, University of Paris 13, France, *G. Geandier*, University of Lorraine, France, *P.O. Goudeau*, University of Poitiers, France, *D. Thiaudière*, Synchrotron SOLEIL, France

The objective of the present work is to study the co-deformation of composite exhibiting strong mechanical contrast components: nanostructured metallic thin film deposited onto polymeric substrate. The mechanical characterization of such composite structures and the relationship with the microstructure still required for further understanding both for fundamental and technological applications. In order to mimic the stress field of thin films in actual applications, we used a biaxial tensile device dedicated to the DiffAbs beamline at the French synchrotron SOLEIL. The machine allows for controlling equi- or non-equi-biaxial loading onto thin films supported onto compliant substrates, e.g. polyimide substrates. The applied strains are measured in situ both by X-ray diffraction (XRD) and by digital image correlation (DIC). Those two methods are non-destructive: XRD strain is related to the shift of Bragg peaks and DIC strain is obtained from photography of the surface or the backside of the sample. The inherent phase selectivity of XRD technique is a useful tool to get a deeper understanding of the mechanical behaviour of a composite, e.g. the load transfer between the different crystallographic phases and between different orientation grains. The in-situ mechanical testings have been performed onto metallic thin films (produced by Physical Vapor Deposition technique) deposited at the center of a cruciform-shaped polyimide substrate (Kapton ®). In order to verify the accuracy and the feasibility of the combination of the two techniques, the first in situ coupling correlation-diffraction techniques have been performed on W based thin films. Indeed the mechanical modeling using homogenization methods is quite specific for thin films; it has to take into account both the crystallographic texture and morphology of the metallic films. The grain interaction model is very simple in the case a perfect local elastic isotropy such as W. W based thin films allows for directly comparing lattice strains (measured at the microscopic grain scale by X-ray diffraction) to macrostrains (measured at the macroscopic scale by DIC).

FP14 Antimicrobial Brass Coatings Prepared on Poly(ethylene terephthalate) Textile by High Power Impulse Magnetron Sputtering, ***Y.H. Chen*** *(tieamo2002@gmail.com), G.W. Chen, J.L. He*, Feng Chia University, Taiwan, Republic of China

Silver coating, particularly prepared by magnetron sputter deposition, has been proven to be antimicrobial and on the way towards commercialization for application in textile industry. However, the expensive raw material and unsatisfactory film adhesion has limited its usage. Copper, on the other hand provides good enough antimicrobial efficacy of all the metals, is considered for silver substitution, but unfortunately suffers poor corrosion resistance in form of thin film coating. Brass, known to be good corrosion resistance, is a good candidate material for antimicrobial coating. The purpose of this study is to obtain an antimicrobial coating starting with brass alloy as target material to grow onto poly(ethylene terephthalate) (PET) textiles by high power impulse magnetron sputtering (HIPIMS), which is known to provide high plasma density, so as to produce strongly adhered film and high quality films at a reduced deposition temperature.

The results show that under a peak target power density of 0.6 kW/cm2, the obtained brass film exhibited layer-by-layer growth mode in the initial stage, followed by island growth mode and reached a film thickness of 238 nm for 10 min deposition. Film composition retained their Cu/Zn ratio (1.86) close to that of brass target, and the phase structure of the film was found to be mainly α-brass. From the results of color fastness to rubbing tests, the film ultimately reached graded 5 and graded 4-5 at dry and wet rubbing, respectively, indicating strong adhesion of the obtained film. Antimicrobial efficacy test show that simply 1 min deposition time can achieve good bactericidal (> 0) and bacteriostatic (> 2.0) efficacy according to the JIS Standard.

Keywords: antimicrobial, poly(ethylene terephthalate), textile, high power impulse

FP16 Influences of Various Feedstocks on Characteristics of the Plasma Sprayed NiO/YSZ Anode in Solid Oxide Fuel Cell, *Y.C. Yang (ycyang@ntut.edu.tw)*, ***H.C. Tseng***, *C.T. Cheng*, National Taipei University of Technology, Taiwan, Republic of China

In the present study, porous electrode coating of NiO/YSZ on the stainless steel was made by the plasma-spraying. By introducing the Na_2CO_3 as the pore former into the composite feedstock powder (NiO/8YSZ/Na_2CO_3), the porous structure of SOFC anode was obtained. Two kinds of feedstocks from various synthesis processes were employed. The powder made by the spraying-dry method reveal more porous than that from the hand made granulated method. The porosity of porous anode after Na_2CO_3 dissolved and reduction in 5% hydrogen could be varied from 30 to 40%. The results suggest that the method exhibits the potential to manufacture the porous ceramic/metal anode of SOFC to achieve the large triple phase boundary. Moreover, the plasma spraying technique for SOFC fabrication could avoid the thermal failure between the components of SOFC which made from the traditional sintering method at high temperature.

FP17 Effect of Mo Content on Structure and Corrosion Resistance of Arc Ion Plated Ti-Mo-N Films on 316L Stainless Steel as Bipolar Plates for Polymer Exchange Membrane Fuel Cells, ***M. Zhang*** *(m.zhang@live.com)*, Liaoning Normal University, China, *K. Kwang Ho*, Pusan National University, Republic of Korea, *S. Zhigang*, Dalian Institute of Chemical Physics, *P. Yunli*, *H. Xiaogang*, *H. Ye*, Liaoning Normal University, China

Bipolar plates are one of the most important components in PEMFC stack and have multiple functions, such as separators and current collectors, distributing reactions uniformly, mechanically supporting the cell stack and managing the heat and water of the cells. Stainless steel is ideal candidate for bipolar plates owing to good thermal and electrical conductivity, good mechanical properties etc. However, stainless steel plate still cannot resist the corrosion of working condition.

In this work, solid solution Ti-Mo-N films were fabricated on 316L stainless steel (SS316L) as a surface modification layer to enhance the corrosion resistance and conductivity. A hybrid system, which combines arc ion plating and magnet sputtering, was employed to prepare the Ti-Mo-N films. Mo content in the Ti-Mo-N films is controlled by adjusting the sputtering power of Mo target. The effect of Mo content on structure and corrosion resistance of the Ti-Mo-N films was investigated by means of XRD, EPMA, and anode polarization tests.

Mo content in the Ti-Mo-N films increases linearly from 0 to 48 at% when the sputtering current increases from 0 to 1.0 A. XRD results show the films are solid solution, crystallize in TiN phase, and the preferred orientation changes from (111) to (200) plane as Mo content increases. The corrosion resistance of the coated SS316L bipolar plates becomes worse as Mo content increases, and the TiN (Mo content is 0) coated plates show the best corrosion resistance. Compared to the bare SS316L bipolar plates, the coated plates show improved corrosion resistance and lower ICR, i.e. for the TiN coated plates, corrosion and passivation current density reduces by one and four orders of magnitude, respectively; the ICR decreases by two orders of magnitude. The improved corrosion resistance and conductivity of the TiN coated bipolar plates is attributed from the integrate lattice and a (111) preferred orientation in the TiN film, which is the close-packed plane in body-centred cubic TiN phase.

FP18 The Smoke Density Evaluation of Acrylic Emulsion and Intumescent, *Z. Li (zslee999@gmail.com), H. Wang*, ***W. Zhao***, *W. Lu, J. Zhao*, Marine Chemical Research Institute, State Key Lab of Marine Coatings, China

The emulsion based coatings have induced pollutions to the environment, eliminate the fire dangerous, and saving resources. More and more investigations are focused on the emulsion based coatings. Herein, we fabricated a novel kind of intumescent fire resist coatings with acrylic emulsion, and discuss the smoke density feathers of both acrylic emulsion and intumescent. Initially, the static smoke density of both acrylic emulsion and intumescent is measured, and the capability influence of acrylic emulsion to intumescent is discussed. Meanwhile, the thermal decomposition kinetics of both acrylic emulsion and intumescent are investigated. Results show that acrylic emulsion has a quite higher smoke density comparing to intumescent during burning process. The thermogravimetric (TG) and derivative thermogravimetric (DTG) curves of both acrylic emulsion and intumescent are obtained. Through multiple peaks fitting of intumescent DTG curve, every step of thermal decomposition could be separated, and be identified to each ingredient of intumescent. Combining with the smoke density data, the smoke contribution of acrylic during the intumescent burning process could be estimated. Approximately, acrylic emulsion is decomposed 13.1% for whole, that's the 3.51% of intumescent. These results can be deduced that acrylic contributes 51.57% in smoke density during the intumescent burning process. The intumescent exhibits lower smoke density while comparing to acrylic emulsion. The reason of such phenomenon could be speculate that during the burning process, the fire retardant system may restrain the decomposition of intumescent, cause the total smoke density reduce.

Keywords emulsion, smoke density, acrylic, intumescent

FP19 Effects of Duty Cycle and Pulse Frequency on the Fabrication of AlCrN Thin Films Deposited by High Power Impulse Magnetron Sputtering, ***Y. C. Hsiao***, National Taipei University of Technology, Taiwan, Republic of China, *J.-W. Lee (jefflee@mail.mcut.edu.tw)*, Ming Chi University of Technology, Taiwan, Republic of China, *Y.C. Yang*, National Taipei University of Technology, Taiwan, Republic of China

High power impulse magnetron sputtering (HIPIMS) is a novel coating technology, which is characterized for its high peak power density to achieve unique thin film properties, such as high hardness, good adhesion and tribological performance. The aim of this work was to systematically study the microstructure evaluation and mechanical properties of AlCrN coatings as a function of duty cycle and pulse frequency evolutions. The experimental results showed that the peak power density increased linearly as the duty cycle decreaseing from 5% to 1.5%. A maximum peak power density of 2.06kW/cm^2 was achieved at the duty cycle of 1.5 %. The AlCrN coatings that exhibited a dense microstructure and excellent mechanical properties was fabricated by using the HIPIMS technology under optimal duty cycle and pulse frequency in this work.

FP20 Enhancing the Thermal Stability and Oxidation Resistance of the Cr Zr N Films by Adding Oxygen, ***D.J. Kim***, *J.H. La, S.M. Kim, Y.S. Hong, S.Y. Lee (sylee@kau.ac.kr)*, Korea Aerospace University, Republic of Korea

CrZrON coatings were produced by reactive magentron sputtering at different N_2/O_2 flow ratios on the Si wafer substrate and H13 tool steel substrates. The structure, and mechanical properties of the coatings depend strongly on their oxygen content. T he coatings crystallize in the rhombohedral Cr_2O_3 structure and CrZrN cubikc stricture . The morphology of the samples, as studied by scanning electron microscopy (SEM), is columnar. The hardness of the CrZrN coatings (31.6±0.8 GPa) decreases with increasing oxyzen content in the coatings and the hardness decreased down to 15.5±0.8 Gpa in CrZrO coatings. Higher oxygen contents lower the hardness of the coatings. X-ray powder diffraction (XRD) studies were performed in air and t he increase of the oxygen content leads to an enhancement of the (002) preferred orientation and CrZrO coatings became amorphous structure. The Cr Zr ON coatings showed an improved thermal stability against oxidation with increasing oxygen contents in the coatings, which could be attributed to the protective oxide layer on the surface of the coatings and the experimental details will be presented.

FP21 Novel Synthesis of Conductive Nano-crystalline Carbon Film by Advanced Magnetron Sputtering, ***JeonG. Han*** *(hanjg@skku.edu), SungI. Kim, J.D. Nam*, Sungkyunkwan University, South Korea

Conductive carbon film attracts a great interest for application as electrode materials with its inherent chemical stability in various energy devices such as fuel cell and capacitor etc.. It is well known that conventional deposition processes by plasma including magnetron sputtering and PECVD at low temperature have been limited to synthesize carbon films with high conductivity comparable to that of conductive bulk or powder carbon materials with graphite structure. The design of film structure and process for synthesis of conductive carbon film is performed by energy model deposited onto the surface by control of various plasma parameters in magnetron sputtering, which is closely associated with process parameters. Nano-crystalline(nc) graphite clusters are then synthesized in the matrix of amorphous carbon, and conductivity of the film is therefore significantly enhanced. The conductivity is closely associated with proportion of nc graphite clusters and can be enhanced down to 2x10E-3 ohm.cm in our study.

This paper will discuss on the mechanism of energy deposition at the substrate surface during magnetron sputtering and corresponding changes of nucleation and growth of film with variation of process parameters during magnetron sputtering by integrated plasma diagnostics.

The mechanism of nc carbon film control is then discussed based on the film nucleation and growth theory for designed microstructure of various porosity and corresponding film properties in comparison with empirical data measured for the films deposited by magnetron sputtering with plasma control .

FP22 Reactive Sputtering Al2O3 and Cr2O3 Coatings using Arc Free High Power Pulsed Magnetron Sputtering, ***J. Lin*** *(jlin@mines.edu), W. Sproul, B. Wang, Y. Ou*, Colorado School of Mines, US

Deep oscillation magnetron sputtering (DOMS) is an alternative high power pulsed magnetron sputtering technique which offers virtually arc free depositions for reactive sputtering of insulating films at high target powers and currents. In this study, DOMS has been used to deposit Al2O3 and Cr2O3 coatings from either flow control or partial pressure control of the reactive gas with or without applying a RF substrate bias voltage. The hysteresis effects for the deposition process have been measured. The effects of the substrate temperature on the crystal structure of the coatings were investigated. It was found that dense and well crystallized Cr2O3 coatings can be obtained by DOMS without using external substrate heating. The coatings exhibited high hardness values between 25 GPa to 30 GPa and smooth surface. Approaches for obtaining crystalline Al2O3 coatings using DOMS at elevated substrate temperatures will also be presented. The microstructure, optical properties, mechanical and tribological properties of the oxide coatings deposited by DOMS were characterized and compared to those deposited using traditional pulsed dc magnetron sputtering.

Applications, Manufacturing, and Equipment
Room: Grand Hall - Session GP

Symposium G Poster Session
Moderator: D. Pappas, EP Technologies, LLC, K. Yamamoto, Kobe Steel Ltd.

GP2 Preparation of Phosphor-doped TiO_2 Particle/Passivating Layer and their Applications in Dye-sensitized Solar Cells, *T.S. Eom, K.H. Kim, C.W. Bark,* ***H.W. Choi*** *(chw@gachon.ac.kr)*, Gachon University, Republic of Korea

The Dye-sensitized solar cell (DSSC) are composed of a dye-adsorbed nanoporous TiO_2 layer on a fluorine-doped tin oxide (FTO) glass substrate, redox electrolytes and a counter electrode. DSSC were constructed by application of phosphor-doped and TiO_2 nanoparticle composite particles with various percentages. phosphor-doped TiO_2 nanoparticle have been synthesized by introducing a trace amount of silicate phosphor to the reaction system. TiO_2 passivating layer was deposited on the substrate by hydrolysis of $TiCl_4$ aqueous solution. TiO_2 layer was coated on FTO glass by screen printing method. The crystal structure and the morphology were characterized by X-ray diffraction (XRD), and a Scanning Electron Microscope (SEM). The transmittance and the absorbance of TiO_2 films and phosphor scattering were characterized by UV-vis. The TiO_2 films were calcinated by the conventional method and a Rapid Thermal Annealing system. It was found that the conversion efficiency of the DSSC was highly affected by the crystalline structure of the scattering layer.

GP3 Dual Frequency ICP Discharge: Effect of Pressure and Gas Ratio on EEDF and Discharge Parameters, ***A. Mishra*** *(anurdi@gmail.com), T.H. Kim, K.N. Kim, G.Y. Yeom*, Sungkyunkwan University, Republic of Korea

Using a radio frequency compensated Langmuir probe, pressure and gas ratio dependent effects on plasma parameters and electron energy distribution functions (EEDFs) are investigated in Ar/CF_4 discharge produced by dual frequency/dual antenna large area (450 mm) inductively coupled plasma (ICP) source, at an operating in the pressure range from 1 to 25 mTorr. A tungsten probe tip of 10 mm in length and 100 µm in diameter is located at the center of the substrate and 70 mm away from the plasma source.

It is observed that increasing pressure reduces energy spread of electron energy probability functions (EEPFs), due to increasing electron energy loss via collisions, from 20 eV at 1 mTorr to 13 eV at 25 mTorr. At a constant RF power, plasma density (n_e) increases linearly with pressure between 1 to 10 mTorr and then (> 10 mTorr) decreases. The same trend has also been observed for electron temperature.

It has also been found that increasing Ar gas proportion in Ar/CF_4 mixture significantly increases plasma density (n_e), however plasma temperature and plasma potential influences marginally.

GP4 Failure Behavior of Thick Single and Multilayered TiSiCN Coatings under Impact-sliding Forces, ***J.F. Su****, X. Nie (xnie@uwindsor.ca), H. Hu*, University of Windsor, Canada, *R.H. Wei*, Southwest Research Institute, US

With plasma-enhanced magnetron sputtering (PEMS) technology, a series of thick single and multilayered TiSiCN coatings have been successfully deposited on H13 steels. The thick TiSiCN coatings have been investigated in severe sliding wear, erosive and corrosion conditions. However, there is a lack of study on failure behavior of the coatings when subjected to cyclic impact-sliding loads. An impact-sliding coating fatigue wear testing method was used to evaluate the failures behavior of the coatings under high contact stress conditions caused by impact and sliding forces. The impact-sliding wear tracks were observed at both top view and cross-section view using scanning electron microscopy. The effects of thickness, multilayer structures, surface topography on failure mechanisms were particularly discussed.

GP5 Evolution of Reliability on Electroplated and Sputtered Ni-Zn films for Under Bump Metallization with Sn-3.0Ag-0.5Cu Solder Attached During Liquid Reactions, ***H.M. Lin****, J.G. Duh (jgd@mx.nthu.edu.tw)*, National Tsing Hua University, Taiwan, Republic of China

The suitable Ni-rich alloy films could be fabricated by controlling parameter of electroplating, and the alternative Ni-Zn, Ni-Fe and Ni-Co films which act as under bump metallization (UBM) layer have been developed in flip chip electronic design. Flip chip structures are the better ideal to enhance the reliability of solder joint and pursue the small size, low cost, and multiple functionalities in electronics. Regarding the suppression of both intermetallic compounds (IMCs) formation and UBM consumption rates in the flip chip design of the solder joints, Ni-based films UBM with the slower elemental diffusion should be selected. This study aims to investigate and to evaluate the feasibility of electroplated Ni-Zn, Ni-Fe, Ni-Co films UBM. The doped Zn, Fe, Co might inhibit and affect the elemental diffusion in the solder joints. After fabricating these suitable Ni-rich alloy films, the intrinsic properties, i.e. residual stress, roughness, microstructure, texture were analyzed by curvature measurement, atomic force microscopy (AFM), field-emission scanning electron microscopy (FE-SEM), and X-ray diffractometry (XRD), respectively. Furthermore, the extrinsic properties of the IMC formation and composition re-distribution in those solder joints via different Ni-based films UBM attached with Sn3.0Ag0.5Cu (SAC305) solder were evaluated by a field emission electron probe microanalyzer (FE-EPMA) during various reflow time. Besides, the reliability of the SAC305/Ni-Zn, SAC305/Ni-Fe, and SAC305/Ni-Co joints was evaluated by high speed impact tests. This study demonstrated that the binary Ni-Zn, Ni-Fe, and Ni-Co film might be the potential alternatives for under bump metallization application. The possible mechanisms for correlation between intrinsic properties of these novel Ni-based films UBM and related extrinsic interfacial reaction were discussed and proposed.

GP6 Improvement of Air Plasma Spraying Parameters for the Fabrication of Thermal Barrier Coatings, ***S. Liscano*** *(sliscano@unexpo.edu.ve), L. Gil, M. Romero*, UNEXPO, Venezuela (Bolivarian Republic of)

In this research, ZrO_2–10%Y_2O_3–18%TiO_2,Al_2O_3–13%TiO_2 thermal barrier coatings (TBCs) with $NiCrAlCoY_2O_3$ bond coats were sprayed by employing an air plasma thermal spray (APS) technique following factorials design experiments in order to obtain the best favorable spraying conditions able to enhance their properties. The powders particle size distribution analysis was obtained by mesh analysis using sonic sifter equipment. The morphology and microstructure of composites powders were analyzed by SEM (EDS) and X Ray Diffraction techniques. The effect of the spraying parameters on the porosity, microhardness, microstructure and morphology of coatings were determined by using different techniques such as optical microscopy (OP) with image analysis, Vickers indentation and scanning electron microscopy (SEM) technique, this latter coupled with X-Ray microanalysis (EDS). The adhesive strength of each TBCs System was measured according to the ASTM C633. It was found that both variables evaluated the arc voltage and the arc current, as well as their interaction, had a significant effect on the microstructure and mechanical properties of the coatings.

GP7 Surface Recrystallization of Tungsten Carbide by MPCVD due to Controlled Oxidation and Deoxidation in an Equilibrium Process, ***M. Mee*** *(manuel.mee@iwm.fraunhofer.de), S. Meier*, Fraunhofer IWM, Germany

Diamond coatings for hard metal tools have been used for years, but usually only inadequate adhesion appears. The approach to remove cobalt from the surface by a two-step chemical etching pretreatment has led to good results, but at the same time a strong weakening of the underground structure is a result of this approach. A newly developed process causes surface regeneration due to a balance of coincidental oxidation and deoxidation.

GP8 Understanding of Wear Mechanisms of Coated Solid Carbide Endmills During Machining of Ti-Al6-V4, *S. Stein,* ***R. Rachbauer*** *(richard.rachbauer@oerlikon.com), M. Arndt*, OC Oerlikon Balzers AG, Liechtenstein

State-of-the-art cutting operations for difficult-to-cut materials, e.g. Ni- or Ti-based alloys, represent a challenging topic for research and development efforts of tool manufacturers and coating designers. Conventional process conditions involve high temperatures up to 1000°C at the cutting edge, which mostly stem from the low thermal conductivity of the workpiece materials. Moreover, the high-temperature toughness and high material strength of Ni- and Ti-based alloys at elevated temperatures demand optimized process conditions and coating solutions.

In order to understand the apparent wear mechanisms during solid carbide milling of Ti-Al6-V4 in more detail, the present work explores the complex interaction of the tool micro and macro geometry, including edge and corner shapes, as well as different coating systems and the impact of liquid coolants. The adhesive wear behaviour during the machining of Ti-Al6-V4 is analyzed by experimental work, utilizing optical and electron microscopy. Furthermore, currently available coating concepts, that only exhibit marginal benefits in comparison to uncoated tools, are discussed with special focus on roughing operations.

The present contribution emphasizes the importance of a holistic process knowledge and gives a contribution to the understanding of wear mechanisms in context of cooling lubrication and coating design.

Topical Symposia
Room: Grand Hall - Session TSP

Syposium TS Poster Session
Moderator: C. Muratore, University of Dayton

TSP1 Fine Micro- and Nano-Imprinting onto DLC Coating via Controlled Oxygen Plasma Etching, ***T.A. Zho*** *(taizawa@sic.shibaura-it.ac.jp)*, Shibaura Institute of Technology, Japan, *K.M. Mizushima*, Shibaura Institute of Tchnology, Japan, *T.F. Fukuda*, Mitsue Mold Engineering, Co. Ltd.

Thick diamond-like carbon (DLC) coating has a potential to be used as a mold die for micro- and nano-imprinting onto metallic sheets and optical oxide-glasses. In the previous paper, our developing high-density oxygen plasma etching processing had been introduced to make micro-patterning onto DLC-coating with aid of chromium masking. Aiming at further applications, this oxygen plasma etching process must be improved by instrumentation via quantitative plasma diagnosis. In addition, masking technique had to be advanced to deal even with nano-patterns.

In the present study, resin-base masking technique is proposed as an initial patterning procedure onto DLC coated mold-die substrates. Spectroscopic measurement and Langmuir probe method are combined not only to describe the population of activated oxygen species but also to measure the transients of electron density in plasmas. Through optimization of processing conditions, high etching rate was attained up to 8 to 10 micro-meter per hour, or, 2.2 to 3.0 nm/s. Both line and grid patterns were first employed to describe anisotropic etching behavior via SEM and leaser-microscopic measurement, and, to discuss this microscopic etching with reference to reactive ion etching process. In addition, macroscopic etching behavior was also in-situ monitored by spectroscopic plasma diagnosis for rational termination of etching when the monitored peak intensity became minimum. This termination of etching provided us the stepwise depth profile of micro- and nano-grooves and grids as the three dimensional pattern onto DLC coating.

In final, this etching method was applied to make three dimensional micro-grid patterning onto DLC-coated WC (Co) mold dies. Geometric accuracy of 5.2 x 5.2 μm squared grid as well as the depth of 5 μm was attained onto the 50 x 10 mm^2 mold-surface of DLC coated WC (Co) through SEM observation and laser reflection profilometer. This surface-engineered mold die was applid to duplicate these patterns onto aluminum shee via mold-stamping and to fabricate heat-radiation devices.

TSP2 Comparison of Flow Curves of Thin Films Determined by Different Finite Element Models and Nanoindenter Geometries, ***K. Bobzin***, *N. Bagcivan, R.H. Brugnara, J. Perne (perne@iot.rwth-aachen.de)*, Surface Engineering Institute - RWTH Aachen University, Germany

Plastic properties of thin coatings are difficult to quantify. The substrates influence on the growing films as well as the specific production environment in physical vapor deposition (PVD) leads to mechanical properties of the coatings incomparable with macroscopic scaled samples. The determination of flow curves of thin coatings using nanoindentation is intensively investigated. In this paper an approach to determine flow curves using nanoindentation with spherical indenters coupled with finite element method is introduced. The finite element model is complemented by an analytic method providing information about the initial yield strength thereby reducing the number of possible solutions for the flow curve. The approach uses an FEM model to calculate the force-displacement-curve of the nanoindentation out of an arbitrary given flow curve for the sample material. The calculated force-displacement curve is compared with the measured one to adjust the modeled samples material model. This procedure is repeated iteratively until simulated and measured force-displacement curves match. This approach is realized with models for indenters with 10 and 1 μm radius. The models are verified on reference materials with known flow curves and used to analyze different $Cr_xAl_{x-1}N$ coating systems applied using direct current and high power pulse magnetron sputtering physical vapor deposition. The chemical composition of the coatings varies from 23 to 95 at.-% chromium.

TSP3 Micro-chemical and -morphological Features of Heat Treated Plasma Sprayed Zirconia-based Thermal Barrier Coatings, ***B. Cortese*** *(barbara.cortese@ismn.cnr.it), D. Caschera, T. De Caro, G.M. Ingo*, CNR, Italy

Zirconia-based plasma-sprayed coatings are widely used in jet and land-based engines as thermal barriers coatings (TBCs) for protecting and insulating gas turbine metal components from the extreme temperature in the hot gas thus extending the engine life capabilities and service performances as well as to reduce fuel consumption. Zirconia-based thermal barrier coatings (TBCs) of nominal chemical composition 8 wt% Y_2O_3–ZrO_2 and 25.5 wt% CeO_2–2.5 Y_2O_3–ZrO_2 were prepared by means of atmospheric plasma spray (APS) and low pressure plasma spray (LPPS) and thermal treated at different temperature (up to 1460°C, treatment time 200 hours). The heated materials have been then fractured and the resulting surfaces have been studied by means of X-ray photoelectron spectroscopy (XPS), field emission scanning electron microscopy (FE-SEM) combined with energy dispersive spectrometry (EDS) and secondary ion mass spectrometry (SIMS) in order to study the surface micro-chemical composition and morphology The results disclose the variation of the stabilising oxides amount, the occurrence of valence states modifications of cerium, impurities segregation phenomena and sintering. These information confirm that chemical and morphological aspects in plasma sprayed TBCs must be known in order to understand and predict relationships between the parameters of plasma spray process and TBC features, properties and performances for a better design of reliable TBCs.

TSP6 Deposition, Structural and Optoelectronic Properties of Bi_2O_3 Thin Films Deposited by Magnetron Sputtering, ***C.L. Gomez*** *(zethli83@hotmail.com)*, Universidad Nacional Autonoma de Mexico, Mexico, *S. Rodil, P. Silva-Bermudez*, Universidad Nacional Autónoma de México, Mexico, *M. Lejeune, S. Charvet, A. Zeinert*, Universite de Picardie Jules Verne, France, *E. Camps*, Instituto Nacional de Investigaciones Nucleares de Mexico

Bismuth oxide thin films were deposited by magnetron sputtering using an α-Bi_2O_3 target, under an Ar/O_2 (80:20) atmosphere. The power and substrate temperature were varied from 100-180 W and 125-250 °C. The films were simultaneously deposited on glass and silicon substrates; therefore spectroscopic optical characterization was done by both transmittance and ellipsometry. The film structure was studied by X-ray diffraction, obtaining strong differences in the predominant phase (mainly delta, beta and alpha) as the power or substrate temperatures were increased, which were also reflected in the deposition rate, the variations in the structure were also confirmed by Raman spectroscopy. The XPS analysis confirms that for all the conditions the composition was nearly 2:3 (Bi:O), except for minor traces of metallic bismuth found in some samples.

The electrical properties of the films were measured in planar mode for samples deposited on glass using two concentrical Pt electrodes. The measurements were done as a function of the temperature from RT to 600 °C. It was clearly shown that for all samples, the resistivity decreased as the T increased, showing an Arrhenius variation which allow us to estimate the values of the activation energy (optical gap) and the intrinsic surface conductivity. The results from the electrical properties are correlated to both the deposition conditions and the structure of the samples.

The optical properties, n and k as a function of the energy (E) from 1.5 to 5 eV, of the films were obtained by modeling the ellipsometric spectra by means of a Tauc-Lorentz dispersion model. From the k vs E curve, the absorption coefficient was calculated and compared to the data obtained from the transmission experiments. By doing this process iteratively, it was possible to have consistent parameters of the optical properties for each of the films and therefore of the Bi_2O_3 phases.

Acknowledgement: The research leading to these results has received funding from the European Community Seven Framework Programme (FP7-NMP-2010-EU-MEXICO) and CONACYT under grant agreements nº 263878 and 125141, respectively.

TSP8 Relationship Between the Microstructure and Thermoelectric Properties of n-type Bi-Se-Te by Using RF Sputtering, ***T.S. Chen***, *C.C. Shih, H.D. Fu, M.S. Leu (menson@itri.org.tw)*, Industrial Technology Research Institute, Taiwan

The thermoelectric thin films have attracted great interest due to solid state operation, high reliability and zero emission. Bismuth-telluride based alloys have excellent thermoelectric properties at room temperature. In this study, we have investigated the relationship between the microstructure and thermoelectric properties of the n-type Bi-Se-Te films, which were deposited at room temperature by magnetron RF sputtering using $Bi_2Se_{0.3}Te_{2.7}$ alloy targets and electric stressing annealed by rapid thermal annealing (RTA) at 300 °C for 5 min. Then, X-ray diffraction, energy dispersive spectroscopy, scanning electron microscopy, Hall, Seebeck and 3ω measurement were utilized to characterize the evolution of microstructure, composition and thermoelectric properties of Bi-Se-Te films as function of RF power, working pressure and annealing temperature. XRD results show that each film exhibits polycrystalline microstructure. The intensity of (0 1 5) peak at 27.8∘increases with increasing power and decreasing working pressure. In addition, the intensity of diffraction peaks appears to increase after electric stressing annealing. Consequently, the composition of as-deposited film is closely about target stoichiometry and after annealing films at 300°C was conserved. The surface of Bi-Se-Te film exhibits sheet-like morphology and the feature size was larger as the (0 1 5)

preferred orientation. The microstructure and composition and morphology concur with the change in thermoelectric properties. The Seebeck coefficient and resistivity increase with increasing working pressure and decreasing RF power and the impact of the resistivity rather than the Seebeck lead to low power factor. However, the power factor was substantially enhanced after rapid thermal annealing due to the reduction of defect or carrier concentration and more crystallization orientation. The relationship between the microstructure and thermoelectric properties of n-type Bi-Se-Te films is discussed and established.Key words: Thermoelectric, Thin film, Seebeck, Bi-Se-Te (Bismuth selenium telluride), RF sputtering.

TSP9 Surfactant-assisted Dispersion of Polyimide/multi-walled Carbon Nanotube Nanocomposites Films with Ultrahigh Electrical Conductivity, ***H.P. Yu***, National Chin-Yi University of Technology, Taiwan, Republic of China, *Y.C. Huang*, National Chiao Tung University, Taiwan, Republic of China, *I.H. Tseng, Tsai (tsaimh@ncut.edu.tw)*, National Chin-Yi University of Technology, Taiwan, Republic of China

A facile approach to disperse and stabilize high loading of multi-walled carbon nanotubes (CNTs) in polyimide (PI) matrix is presented. PI/CNT nanocomposite films were synthesized by in situ polymerization of pyromellitic acid dianhydride (PMDA) and 4,4'-oxydianiline (ODA) in N,N'-dimethyl acetamide (DMAc) with the presence of various amounts of CNTs and the surfactant polyvinylpyrrolidone (PVP) and sodium dodecyl benzene sulfonate (SDBS). The FTIR spectroscopy proved that the surfactant did not hinder the polymerization of PI. The experimental results showed that the dispersion of CNT was significantly improved by increasing the ultrasonication temperature to 60 ^{o}C. Accordingly, The electrical conductivity of PI/CNT was increased to 41.5 S/m for the hybrid film containing 40 wt% of CNT.

TSP10 Poly(amide-imide) / Graphene Oxide Nanocomposite Films for Anticorrosion Application, ***C.W. Chang***, *I.H. Tseng, M.-H. Tsai (tsaimh@ncut.edu.tw)*, National Chin-Yi University of Technology, Taiwan, Republic of China, *J.M. Yeh*, Chung-Yuan Christian University, Taiwan, Republic of China

A series of advanced anticorrosive hybrid films comprising of polyimide (PI) or poly(amide-imide) (PAI) matrix dispersed with various content of graphene oxide (GO) nanosheets have been successfully synthesized through the solution dispersion process of GO in PI or PAI. PAI was synthesized by mixing 4,4'-oxydianiline (ODA), 3,3'-4,4'-benzophenonetetracarboxylic dianhydride (BTDA), trimellitic anhydride chloride (TMAC) in N-Methyl-2-pyrrolidone (NMP) solvent. The content of hydroxyl groups in PAI affects the dispersion of GO in PAI matrix. The water-vapor-transmission-rate (WVTR), oxygen-transmission-rate (OTR) and corrosion resistance in saline condition of PAI/GO films were comprehensively studied and correlated with the content of GO. The PAI/GO nanocomposite films exhibit improved corrosion inhibition compared to pure PI and PAI .

TSP11 Aberration-corrected HRSTEM Characterization of Nanolaminate Copper Diffusion Barriers Grown by PEALD, ***C.N. Hsiao*** *(cnhsiao@itrc.narl.org.tw)*, *B.H. Liou*, National Applied Research Laboratories, *G.S. Chen*, Feng Chia University, Taiwan, Republic of China, *Y.J. Cheng*, National Chi Nan University, *Y.S. Y. S. Lai*, National Applied Research Laboratories

Ru/TaN nanolaminate barriers and Cu interconnect were sequential directly grown on dual damascene nano-porous dielectrics (PMSQ**,** k < 2.3) by plasma enhanced atomic layer deposition (PEALD) for the application of 28 nm node and below. The PEALD processes for TaN, Ru and Cu employed argon/ammonia (Ar/NH_3) and hydrogen (H_2) plasmas. $Ta(NC_2H_6)_5$ and $RuEt(Cp)_2$ was used as the precursor source for tantalum and ruthenium while $Cu(hfac)_2$ was used as the copper precursor source. Liner dependency of the growth rate on the precursor pulse time with different self-limited PEALD cycle number were analyzed from thickness measurements using high resolution scan transmittance electron microscopy. The growth rate of TaN was 0.05 nm/cycle as 1.5 s pulse time, 0.02 nm/cycle for Ru as 0.2 s pulse time, and 0.03 nm/cycle for Cu at the 2 s pulse time, respectively. Moreover, resistivity of nanolaminate barriers was dependent on the microstructural features by grain size and crystalline which characterized by atomic-resolution aberration-corrected HRSTEM (C1, A1, A2, B2, and C3 corrected), EDS mapping, X-ray and the sheet resistance measured by four-point probe. Additionally, various materials properties including conformability, diffusion gradient and electro-thermal stress of Ru/TaN nanolaminate barriers on dual damascene structure have been evaluated. Furthermore, the integration PEALD processes at lower substrate temperature with porous low-k dielectric and pore-sealing effect by plasma and ion beam on voiding treatment of PMSQ are also discussed.

TSP12 Kinetics of Spinodal Decomposition in Au-Ni Nanolaminates near Room Temperature, ***A. Jankowski*** *(alan.jankowski@ttu.edu)*, Texas Tech University, US

The kinetics of spinodal decomposition are affected by several factors including the alloy composition and the depression of the coherent spinodal below chemical spinodal within the miscibility gap. Within the spinodal, phase separation leads to the formation of characteristic composition wavelengths from a solid solution. In the gold-nickel (Au-Ni) alloy system, nanolaminates were used to initially create an artificial composition fluctuation with unique nanoscale wavelengths. Although the decomposition reaction has been well documented for Au-Ni in the literature, the direct measurement of the diffusivities at low temperatures, i.e. at room temperature, would require time durations on the order of several decades. This has been accomplished by now examining sputter deposited films that were synthesized in a thermalized condition 25 years ago. In addition to the aging at room temperature, the effects of strain energy are accounted for in accommodating lattice misfit in this superlattice system. For this purpose, the results of x-ray diffraction to assess the state of short-range order at grazing incidence angles are compared with scans at high angle reflections that evidence the effects of lattice distortions.

TSP13 Synthesis of CdS Thin Films with Hexagonal Orientation Through an Ammonia-free System, ***K.Y. Chen***, *S.C. Hsiao, B.J. Yang, L.H. Chou (lhchou@mx.nthu.edu.tw)*, National Tsing Hua University, Taiwan, Republic of China

Cadmium sulfide (CdS) is a n-type semiconductor material which is known to be a window layer of high efficiency thin film solar cells such as copper indium gallium diselenide (CIGS) and cadmium telluride (CdTe). Chemical bath deposition (CBD), a low-cost and scalable technique, was often used to synthesize CdS films. Traditional CBD synthesis, which is predominantly based on one-step process, usually use ammonia as the complexing agent, though it is environmentally harmful. The films as-produced are deposited in a growth solution containing cadmium chloride, ammonia, KOH and $CS(NH_2)_2$ (thiourea) and accompanied with several disadvantages such as porous films, $Cd(OH)_2$ byproduct and hard-controlling thickness.

In this work, a process with ammonia replaced by sodium citrate was employed for producing a more continuous, compact, homogeneous CdS thin film with controlled thickness. Cadmium acetate, instead of cadmium chloride, was used for its low-cost and not under regulation. First, $Cd(OH)_2$ particles were deposited on the substrate, thiourea was then added to the solution and the CdS uniform thin film was formed finally. Phase determination was carried out by X-ray diffraction (XRD). It was reported that the CdS synthesized using cadmium chloride had a preferred (002) hexagonal orientation and the crystal quality produced by cadmium acetate was not as good. However, an (002) hexagonal crystal orientation was obtained in this work applying cadmium acetate by controlling the pH value in the beginning of reaction. Surface morphology of the films was observed by scanning electron microscopy (SEM). Hall measurement and optical transmission spectroscopy will be applied to determine the carrier mobility and band gap. The reaction mechanism will be discussed in this paper and the as-formed CdS films are expected to be beneficial for solar cell applications for its probable high carrier mobility and reduced carrier recombination.

TSP14 Electrical Characteristics and Stability of Metal Electrodes for Pyrite Ultra-thin Film Solar Cells, ***B.K. Chen***, *S.C. Hsiao, L.H. Chou (lhchou@mx.nthu.edu.tw)*, National Tsing Hua University, Taiwan, Republic of China

FeS_2 (pyrite) is catching the attention gradually because of its promising potential for optoelectronic applications. It possesses a suitable band gap and very high absorption coefficient ($5x10^5$ cm^{-1}) that makes pyrite to be one of the candidates for thin film solar cell, especially ultrathin and flexible cell, absorption material. Pyrite's environmental compatibility and elemental abundance further assures its sustainable applications.

It is known that ohmic metal contact is essential for solar cell devices application. However, few studies has been reported for pyrite thin film devices. Schieck et al. [1] reported that platinum showed good ohmic contact characteristic on thick pyrite crystal film and R. J. Soukup et al. found the low-cost Ni metal also showed ohmic characteristic on pyrite thin film with higher resistivity. In order to get good and cheaper ohmic metal contacts for our ultrathin pyrite films, various metals were tested and stability study will be performed for the best electrode obtained in this report.

Various metals including Au, Mo, Cu, Ag, and Ni were tried in this study to find out their ohmic contact characteristic on our pyrite ultrathin films. The metal layers with thickness of 1 μm were deposited onto glass substrates by direct current magnetron sputtering under argon atmosphere. Pyrite thin film with ~50 nm thickness produced by spin coating pyrite nanoparticles ink was covered on these metal layers. Layers stacked by this sequence may

avoid the destruction of the pyrite absorption layer resulted from the post deposited metal layers. For optimal choice of contact metal, a current-voltage (I-V) measurement was employed on sandwich-structured electrodes. The top metal electrodes were sputtered on the pyrite film applying a mini-pores mask so as to eliminate the plasma damage to the absorption layer. The devices were then annealed at 400 °C in sulfur ambient to improve the crystallinity of the spin-coated pyrite thin films.

Grazing incidence x-ray diffraction (GIXRD) diffractometer will be utilized to detect if phases other than pyrite and metals are present. The metal with best I-V characteristic will be adopted for further interface diffusion study. Depth profiles from nano Auger will reveal the interface diffusion between the metal layer and pyrite thin film after prolonged annealing.

Reference:

[1] R. Schieck, A. Hartmann, S. Fiechter, R. Konenkamp, and H. Wetzel, J. Mater. Res., 5 (1990) 1567.

TSP15 Nanostructure Formation of Al_2O_3 Layer Carried Out in a Three-Component Electrolyte, ***M. Kubica*** *(mkubica@us.edu.pl),* University of Silesia, Poland, *M. Bara, W. Skoneczny*, Univesrsity of Silesia, Poland

It has been reported that the size and shape of the pores depend on the structure of the base metal, the type of electrolyte and the conditions of the anodizing process. The paper presents thin Al2O3 oxide layer formed under hard anodizing conditions on a plate made of EN AW-5251aluminium alloy. The oxidation of the ceramic layer was carried out for sixty minutes in a three-component SFS electrolyte at a temperature of 303K, electric charge 180A*min and the current density of 3A/dm2. Presented images taken with a scanning microscope for: base material (aluminium alloy), breakdown voltage, beginning of the oxidation, five, ten and sixty minutes layer growth. A computer analysis of the binary images showed the average surface of a pore and different shapes as: triangle, rhombus, pentagon and hexagon. The structure of ceramic Al2O3 layers is one of the main factors determining chemical, physical, surface and mechanical properties. The resistance to wear of polymer-oxide coating layer depends on porosity, morphology and roughness of the ceramic layer surface. A 3D oxide coating model, based on the computer analysis of images from a scanning electron microscope (SEM), was proposed. Special computer program that shows morphology of the layer was programmed in C++ language.

TSP16 Performance Characterisation of Metallic Substrates Coated by HVOF WC-Co, ***A. Venter*** *(Andrew.Venter@necsa.co.za),* Necsa Limited; DST/NRF Centre of Excellence in Strong Materials, South Africa, *P. Oladijo*, DST/NRF Centre of Excellence in Strong Materials, South Africa; University of the Witwatersrand, South Africa, *V. Luzin*, ANSTO (Australian Nuclear Science & Technology Organisation), Australia, *L. Cornish*, *N. Sacks*, DST/NRF Centre of Excellence in Strong Materials, South Africa; University of the Witwatersrand, South Africa

The high-velocity oxygen-fuel (HVOF) thermal spray technique is extensively used by in-dustry to produce thin coatings on substrates to enhance their functional properties such as wear resistance linked to adhesion and residual stress enhancement, or to act as thermal or chemical barriers. Our research interest is the systematic characterisation of the performance of metal substrates subjected to the different processing steps associated with their HVOF coating with WC-Co.

A number of substrates that have coefficients of thermal expansion covering a range of values different to that of the coating material have been considered to assess the potential role of thermal misfit as mechanism in improving the coating performance. Both the as-coated and stress annealed conditions (40% of the respective melting temperatures) have been investigated.

The different annealing temperatures influence the final coating microstructural properties [1,2]. Depth resolved studies of the in-plane residual stresses in the coatings and substrates have been investigated using, X-ray, synchrotron and neutron diffraction techniques in con-junction with sub millimetre sized gauge volumes [1-3]. The abrasive wear performance of the coatings were characterised using an ASTM-G65 three body abrasive wear machine. Steep stress gradients have been observed in the near surface regions of all the as-coated substrates, extending to approximately 0.5 mm from the interface. It has been identified to originate primarily from the shot blast surface preparation step. Annealing had the effect of completely removing the cold work contribution and triggering the differences in the CTE's between coating and substrates that introduced beneficial residual stresses. Differences ob-served in the wear behaviour are related to the residual stresses resulting in the coatings ow-ing to the thermal mismatch between the coatings and substrates.

[1] O.P Oladijo. A.M. Venter, L.A. Cornish, N. Sacks, X-ray diffraction Measurement of Residual Stress in WC-Co Thermally Sprayed Coatings onto Metal Substrates, Surface & Coatings Technology (2012) 206 4725

[2] A.M. Venter, T. Pirling, T. Buslaps, O.P. Oladijo, A. Steuwer, T.P. Ntsoane, L.A. Cornish, N. Sacks, Systematic investigation of the residual strains associated with WC-Co coatings thermal sprayed onto metal substrates, Surface & Coatings Technology (2012) 206 4011

[3] V. Luzin, A.M Venter, O.P. Oladijo, L.A. Cornish, N. Sacks, Residual stress in WC-Co coated systems studied by high resolution neutron diffraction, 5th Asian Thermal Spray Conference, 26 –28 November 2012, Japan. To be submitted to Journal of Thermal Spray Technology

TSP17 Micromechanical Characterisation of a-C:H Coating Systems with Si-based Adhesion Layers, ***C. Schmid*** *(christoph.schmid@ww.uni-erlangen.de), C. Schunk, M. Krottenthaler, V. Maier, M. Göken, K. Durst*, University of Erlangen-Nürnberg, Germany

A common technique to enhance the adhesion of hydrogenated amorphous carbon (a-C:H) coatings especially on steel substrates is the use of adhesion layers based on different elements like W, Cr or Si. These layers normally show a complex microstructure with chemical gradients and their thickness is less than one micron. Relating the local chemical composition to the microstructure and the mechanical properties is therefore not an easy task.

In this work two a-C:H coating systems with an Si-based adhesion layer deposited with different process parameters on steel substrates were investigated in terms of chemical composition, local mechanical properties and residual stresses. Nanoindentations across small angle cross-sections of the coating systems result in a complex hardness and Young`s modulus depth profile over the adhesion layer. Additionally, auger electron spectroscopy revealed the corresponding chemical composition. A direct correlation between the local mechanical properties and the chemical composition of the two different adhesion layers was observed.

In addition, residual stresses of the two a-C:H coating on steel substrates were determined by means of focused ion beam (FIB) milling and digital image correlation (DIC). For this a H-bar geometry which is commonly used for TEM lamella preparation was FIB milled in the a-C:H coating which causes the residual stresses to relax locally. The residual stresses can be quantified by tracking the relaxation strain with DIC. At this the H-bar geometry enables a simple evaluation of the residual stresses using Hooke's law. For the two a-C:H coatings similar residual compressive stresses of about - 2 to -3 GPa were found.

Tribology & Mechanical Behavior of Coatings and Engineered Surfaces
Room: Golden West - Session E3-2+G

Tribology of Coatings for Automotive and Aerospace Applications
Moderator: S. Dixit, Plasma Technology Inc., A. Gies, OC Oerlikon Balzers AG, Liechtenstein, G.L. Doll, University of Akron

8:00am **E3-2+G-1 Tribological and Mechanical Analysis of the Interest of DLC in Cold Rolling of High Carbon Steel Strips**, ***C. Choumad-Ould*** *(could.hefrd@hef.fr)*, HEF, CEMEF, France, *X. Badiche*, HEF, France, *P. Montmitonnet*, CEMEF, France, *Y. Gachon*, HEF, France

Two types of rolls are widely used in high carbon steel strips cold rolling: HSS steel rolls and chromium-electroplated rolls. Lower costs and replacement of chromium, criticized because of its effects on health, are two reasons to look for another coating solution for rolling mill rolls. To be economically viable, it must maintain surface quality in accordance with customer requirements, allow larger strip reduction per pass, work at higher rolling speed or resist wear better so as to roll more coils between roll changes. Different phenomena, strongly related to the nature of roll surface, must be controlled if one wishes to benefit from such improvements:

The severe adhesive wear of strip ("pick up", "roll coating"), which limits the maximum reduction per pass at a given rolling speed;

Abrasive wear of rolls, which limits the lifetime of rolls;

Adhesive transfer, which both limits the lifetime of the rolls by reducing their roughness and can trigger the phenomenon of severe adhesive wear.

DLC coatings are widely used in various tribological applications. Their resistance to wear and adhesion gives them a high potential in rolling. The interest of a hydrogenated DLC coating (20% of H) has therefore been studied for this application. The proposed paper analyzes its tribological and mechanical characteristics using two well adapted tests. Its resistance to transfer, severe adhesive wear, abrasive wear and fatigue is evaluated and compared with reference materials used in the rolling industry, uncoated HSS and chromium but also with other PVD coatings (TiN, CrN, TiBN) already described in previous studies [1] [2] [3]. **Keywords**: Strip rolling; Mill roll; PVD Coating; Tribological properties; DLC; Adhesive wear; Transfer; High carbon steel **References:** [1] Ould C, Gachon Y, Montmitonnet P, Badiche X (2011) Tribological Testing of Anti-Adhesive coatings for Cold Rolling Mill Rolls – Application to TiN-Coated Rolls. In: Proc. ESAFORM Conf. (April 27-29, 2011, Belfast, Northern Ireland) 1747-1752. [2] Ould C, Badiche X, Montmitonnet P, Gachon Y (2011) Feasibility of TiBN PVD Coating for Mill Rolls – Laboratory Testing of Anti-adhesive and Fatigue Resistance Properties. In: Proc. ICTP Conf. (September 25-30, 2011, Aachen, Germany), 9-14. [3] Ould C, Badiche X, Montmitonnet P, Gachon Y (2012) PVD Coated Mill Rolls for Cold Rolling of Stainless Steel Strips: Tribological and Mechanical Laboratory Tests, JMP (Accepted September 12, 2012).

8:20am **E3-2+G-2 Formation and Characterization of Reconstructive Coatings**, ***H. Liang*** *(hliang@tamu.edu)*, Texas A&M University, US **INVITED**

Reconstructive coatings have attracted great attention in recent years thanks to the advancement of active materials. In addition to be highly wear resistant and thermally stable, reconstructive coatings are self-generated. In this presentation, we discuss about these coatings through tribofilm formation and those containing solar-activated nanoparticles. In a lubricated system, it was found that lubricants with high polarity enhanced the formation of a transfer layer on the steel surface, whereas nonpolar failed to do so. Lubricants with high polarity are effective to prevent metal hardening and to bond debris particles to the metal surface. Those with nonpolar components, on the other hand, generate abrasive nanoparticles during sliding. Active reconstructive coatings can protect and repair surfaces. An example is given on a coating containing solar-activated nanoparticles as electron donors. When encapsulated with inhibitors, the coating provides protection and repair of damaged surfaces with improved triboloical properties.

9:00am **E3-2+G-4 Plasma Electrolytic Oxidation for Surface Treatment of Engine Cylinder Bores**, ***H. Eiliat*** *(eiliat@uwindsor.ca)*, *X. Nie*, University of Windsor, Canada

Automotive industry thrives to discover new practical technologies in order to reduce total weight and reduce fuel consumption. Aluminum alloys are a good choice in terms of weight reduction however they are susceptible to wear and corrosion once introduced to the combustive environment of the engine. Many methods has been used and applied to tackle these disadvantages however each have their own drawbacks. Plasma Electrolytic Oxidation (PEO) treatment is an alternative technique for surface modification of aluminum silicon cylinder bores. The goal of this paper is to study the coating composition and surface profiles of PEO treated Al 319 cylinders and their influence on coefficient of friction (COF) on the surface of the bores and the wear rate on the counterface piston rings. Thin coatings (< 10 μm) on cylinder bores with different surface roughness were produced. The coated bores were then machined by a brushing technique. Tribotests on the brushed coatings were conducted under designed lubrication modes. The correlation of coating surface profiles vs. COFs and piston ring wear were discussed.

9:20am **E3-2+G-5 Understanding Wear of Diamond-like Carbon Coatings for use in High-pressure Diesel Injection Engines**, ***U. May*** *(ulrich.may2@de.bosch.com)*, *M. Djoufack*, Robert Bosch GmbH, Diesel Systems, Germany **INVITED**

The reduction of CO_2 emissions is one of the global challenges of our modern industrialized society. It is the challenge of the automobile industry to develop engine technology that is even more energy and fuel efficient than today. Because of their superior efficiency relative to gasoline-operated engines, Diesel-operated engines play a key role. Efficient combustion of Diesel fuel is realized using high-pressure fuel-injection technology, through which the Diesel fuel is injected into the combustion chamber at a pressure of up to 2000 bar and even more in the future. Due to the high pressures and requirements on size and weight of the components, the stresses are concentrated on very small contact areas. In addition the amount of injected Diesel fuel must be controlled with high precision and low drift over lifetime. For wear protection coatings are applied on these highly loaded parts. Diamond-like carbon coatings (DLC) play a special role here due to their superior tribological properties, such as high wear resistance and low wear of the counterbody in contact with the coated component. This paper presents coated machine elements of Diesel injection systems together with the requirements on the wear-protection coatings. For robust design of the coated contacts the wear has to be taken into account with the help of appropriate wear models. Influence factors on DLC and counterbody wear are discussed together with wear mechanisms leading to a physically motivated wear model for lubricated DLC-steel contacts.

10:00am **E3-2+G-7 Characterization and Tribological Investigations of Arc Evaporated Mo-based Coatings**, *J. Becker*, Oerlikon Balzers Coating Germany GmbH, Germany, *M. Döbeli*, Ion Beam Physics ETH Zürich, Switzerland, *A. Gies*, *T. Huben*, ***J. Ramm*** *(juergen.ramm@oerlikon.com)*, *H. Rudigier*, *F. Seibert*, *B. Widrig*, OC Oerlikon Balzers AG, Liechtenstein

Future engine development needs the selection of new coating materials which support the functional design of complex tribological systems. PVD coatings may be utilized to control wear in low viscosity lubricants, to protect standard materials in high temperature and oxidizing environment and to adapt the wear between different materials. Coating design must consider possible chemical reactions with formulated oils and additives in lubricants. Reactive cathodic arc evaporation has the flexibility to synthesize new and very different thin film materials. Mo-N, Mo-O-N and other MoN-based coatings were produced at different substrate types and were characterized with respect to their stoichiometry (RBS,EDX), morphology (SEM, TEM), mechanical properties (Nanoindentation) and the microstructure of the layers was investigated by X-ray diffraction. The reciprocating wear test was used to compare the wear behavior for these coatings under dry and lubricated condition with 100Cr6 as counter-part. The test allows a classification of the coatings with respect to material transfer similar to scuffing or fretting and may be utilized for a pre-selection of coatings for engine tests. Very low friction coefficient and very low counter-part wear were observed under lubricated conditions.

10:20am **E3-2+G-8 Development of New Oxidation Resistant Coating for Dry Hobbing**, ***M. Abe*** *(abe.maiko@kobelco.com)*, *K. Yamamoto*, *Y. Yamamoto*, Kobe Steel Ltd., Japan

In the field of gear cutting, long-cutting tool life with high precision, and efficiency has been increasingly required. In addition, use of difficult-to-cut materials is also increasing for the realization of high-strength components.

Wet machining which uses lubrication medium is conventional way in order to enhance cutting accuracy and longer tool life, whereas dry machining which does not use lubricant is becoming more popular due to environmental concern recently. Increase of cutting temperature by dry machining reduces the tool life. Therefore extending tool life for cost reduction or increasing cutting speed for improved productivity is demanded by developing of high performance coatings. As the cutting temperature of the hob is expected to be increased by dry and high speed cutting, more oxidation resistance is also well required. TiN and TiAlN coating is commonly used for hobs [1].

In this study, in order to achieve the improvement in the cutting performance at higher cutting temperature, TiCrAlSiYN film which contains Si and Y was developed. In the presentation, the result of the cutting test of hobs coated TiCrAlSiYN and comparison with standard TiAlN will be shown. TiCrAlSiYN films with different deposition conditions were deposited by arc ion plating (AIP) process. Cutting tests were done by comparing the difference in wear width using simulated hobs. Cutting conditions were the same for TiAlN and TiCrAlSiYN coated hobs: cutting speed 180-220 m/min and cutting feed 2.88m/rev under dry conditions.

Cutting test using SCM420 (HV290), TiCrAlSiYN coated hobs showed that the flank wear is decreased by 25% less than conventional TiAlN at the cutting length of 45m. We will run additional test using different work piece and analyze the wear mechanism of the cutting edge by the TEM.

[1] M Zlatanovic, Vacuum Vol. 39,No. 6(1989)557

10:40am **E3-2+G-9 Third Body Behavior During Dry Sliding of Al-Al_2O_3 Composite Coatings: *in situ* Tribometry and Microanalysis**, *J.M. Shockley*, McGill University, Canada, *S. Descartes*, Université de Lyon - CNRS, INSA-Lyon, France, *E. Irissou, J.-G. Legoux*, National Research Council Canada, ***R. Chromik*** *(richard.chromik@mcgill.ca)*, McGill University, Canada

Aluminum matrix composite coatings containing 0, 10, and 22 wt.% Al_2O_3 particulate reinforcements were deposited via the cold spray process. Reciprocating dry sliding wear experiments were conducted on the coatings using a custom-built *in situ* tribometer, such that the third body activity at the sliding interface was directly observed through the transparent sapphire counterface. Higher Al_2O_3 contents in the coatings led to greater stability of the transfer films (third bodies adhering to the slider), as well as greater stability of the friction coefficient, lower mean friction coefficient, and lower wear rates.

Wear tracks and transfer films from 0 and 22 wt.% coatings were analyzed *ex situ* via optical interferometry, scanning electron microscopy, focused ion beam cross-sectioning, x-ray diffraction, and nanoindentation to reveal the morphological, microstructural and mechanical properties associated with the change of transfer behavior. Third bodies in the wear tracks of the 0 wt.% Al_2O_3 coating exhibited near-surface grain refinement and cracks corresponding to the formation of wear debris particles. Wear tracks on the 22 wt.% Al_2O_3 coating consisted of a coherent, nanocrystalline third body, typically referred to as a mechanically mixed layer (MML). The MML exhibited elevated oxygen content, grain sizes below 100 nm, and higher hardness than the 0 wt.% coating wear track third bodies. Transfer films formed during wear of the 0 wt.% Al_2O_3 coating exhibited bimodal microstructures consisting of patches of aluminum with grain sizes of 0.2 - 1 μm intermixed with lamellae of nanocrystalline aluminum with grain sizes below 100 nm. Transfer films formed during wear of the 22 wt.% Al_2O_3 coatings consisted of nanocrystalline material similar to that found in the MML in its wear track.

In situ tribometry observations revealed that the dynamic changes in the transfer films contributed to increased wear and friction, and played a greater role than is commonly reported for metals tribology. Reduced wear in the 22 wt.% Al_2O_3 coating was attributed to mechanical stability of the transfer film, which was also connected to more uniform microstructures in the transfer film and wear track third bodies. The Al_2O_3 particles allowed for localization of the deformation and modified the third body flows, consequently leading to the formation of uniform microstructures. From this study, a new understanding was gained regarding the role of third bodies in the tribology of cold sprayed Al-Al_2O_3 composites, and the mechanisms described may have implications for the tribology of metals and metal matrix composites beyond the present system.

New Horizons in Coatings and Thin Films
Room: Sunrise - Session F6-1

Coatings for Fuel Cells & Batteries
Moderator: G.V. Dadheech, General Motors Research and Development Center, L. Lei, Shanghai Jiaotong University

8:00am **F6-1-1 Prototyping Solid-Oxide Fuel Cells with Pulsed Laser Deposition**, ***S. Mao*** *(ssmao@me.berkeley.edu)*, Lawrence Berkeley National Laboratory, US **INVITED**

Among various approaches to depositing thin films, pulsed laser deposition is a mature technique that has been utilized for prototyping and optimizing energy conversion devices, such as solid-oxide fuel cells, particularly their electrolytes and electrodes. With pulsed laser deposition, thin films in good contact with the substrate can be grown at lower temperature, which also suppresses chemical reactions between the electrode and the electrolyte for fuel cells. This presentation will start with an overview of the state-of-the-art pulsed laser deposition technology, in particular an advanced high throughput thin film material screening and discovery platform; followed by a discussion of recent progress in the development of prototype high performance solid-oxide fuel cells where pulsed laser deposition has played an important role.

8:40am **F6-1-3 High Performance Nano-Coatings for Ferritic Stainless Steel Strips used as Solid Oxide Fuel Cell Interconnects**, ***J.G. Grolig*** *(jan.grolig@chalmers.se), J. Froitzheim, L.G. Johansson, J.E. Svensson*, Chalmers University of Technology, Sweden

Solid oxide fuel cells (SOFCs) are seen as promising concerning decentralized electricity and heat production. To reach a marketable product - SOFCs have to be improved concerning their long term stability, efficiency, and most of all less cost intensive materials need to be developed. The use of metallic interconnect materials, mainly ferritic stainless steels has reduced costs substantially compared to ceramic interconnect materials. To achieve sufficiently low corrosion rates special alloys such as Crofer 22 APU, Crofer 22 H or Sanergy HT have been developed. These materials are characterized by a chromium content of approximately 22 wt % which leads to a chromia protection layer and a manganese content of about 0.5 wt % to form a chromium manganese spinel layer on top which lowers chromium evaporation. Even though the corrosion performance of these special steels is improved, coatings against Cr evaporation on top these steels are needed to reach acceptable performance.

The above mentioned high performance alloys are relatively expensive compared to mass manufactured 441 stainless steel. This work investigates 441 in combination with a multifunctional coating, that inhibits Cr evaporation and also leads to lower corrosion rates and higher electrical conductivity. Therefore 10 nm thin reactive element coatings of cerium or lanthanum have been applied to increase corrosion resistance and were later combined with a 640 nm thick cobalt coating to minimize chromium evaporation. Samples were exposed to a cathode side environment (air, 850 °C, 3 % water) and a recently developed "Denuder Technique" has been used to measure chromium evaporation in a time resolved manner. Scanning electron microscopy is used to investigate the evolved microstructure and analyze the corrosion performance. Simple ASR characterization has been performed to monitor influences of the coatings.

It has been observed that the uncoated stainless steel 441 suffers relatively high corrosion in a cathode side environment and even spallation has been observed. The reactive element coatings decreased the corrosion significantly. Cobalt coated samples showed slightly higher corrosion, which can be linked to the oxidation of cobalt and successfully reduced chromium evaporation about 90 %. Finally, coating combinations of reactive elements with cobalt showed a superior corrosion and chromium evaporation performance.

9:00am **F6-1-4 Strontium Diffusion in Magnetron Sputtered Gadolinia-doped Ceria Thin Film Barrier Coatings for Solid Oxide Fuel Cells**, *S. Sonderby, P. Lunca Popa, J. Lu*, Linköping University, Sweden, *BH. Christensen, KP. Almtoft, L. Pleth Nielsen*, Danish Technological Institute, Denmark, ***P. Eklund*** *(perek@ifm.liu.se)*, Linköping University, Sweden

Strontium diffusion through sputtered Gd_2O_3-doped CeO_2 (CGO) thin films is investigated by in-situ and ex-situ X-ray diffraction (XRD) and electron microscopy. A model system consisting of a screen printed $(La,Sr)(Co,Fe)O_{3-\delta}$ (LSCF) layer and magnetron sputtered thin films of CGO and Y_2O_3-ZrO_2 (YSZ) were prepared with the CGO sandwiched between the LSCF and YSZ. This system simulates a solid oxide fuel cell setup and allows Sr diffusion to be probed by XRD by tracing the formation

of $SrZrO_3$ upon annealing. CGO films were prepared with different thicknesses and at different substrate bias voltage. For CGO barriers with thicknesses up to 600 nm, $SrZrO_3$ formation was observed at temperatures above 900 °C. However, by use of substrate bias the temperature could be increased to 950°C. Observation of $SrZrO_3$ precipitates by transmission electron microscopy (TEM) confirmed the observation done by XRD and proved the use of XRD as a suitable method for assessing the quality of CGO barrier coatings. Furthermore, the combined XRD and TEM study yielded understanding of the Sr diffusion mechanism. Sr was found to diffuse along grain/column boundaries in the CGO film. By modifying film thickness and microstructure, the Sr diffusion could be decreased.

9:20am **F6-1-5 High Performance Duplex Coatings for PEMFC Metallic Bipolar Plates by CFUBMSIP and HIPIMS Technology**, ***H. Sun*** *(hailin.sun@miba.com), K. Cooke, P. Hamilton*, Teer Coatings Limited, Miba Coating Group, UK, *P. Hovsepian, A.P. Ehiasarian, A. Sugumaran*, Sheffield Hallam University, UK

Coatings are essential to maximise performance and longevity of metallic Bipolar Plates (BPPs) in Polymer Electrolyte Membrane Fuel Cells (PEMFC). Thin stainless steel foils, around 0.1mm thick, are attractive for automotive PEMFC stacks, providing mechanical and structural integrity, and minimisation of size and weight. However, the intrinsic chromium-oxide passivation on the stainless steel surface raises interfacial contact resistance (ICR) and will not withstand long term exposure in the aggressive electrochemical environment of the cells, leading to corrosion with further degradation of the electrical conductivity and the release of metal ions, which can poison the cell's membrane. In order to meet such challenging performance, economic and serial manufacturing requirements, thin, sub-micron duplex coatings consisting of a transition metal nitride and a highly conductive carbon top coat have recently been demonstrated to dramatically improve both the ICR and the corrosion resistance of the plates. TiN+C & CrN+C have been deposited by industrially compatible, magnetron-based PVD techniques.In this research, closed field unbalanced magnetron sputter ion plating (CFUBMSIP) and High Power Impulse Magnetron Sputtering (HIPIMS) are used to produce dense, well adhered coatings, of transition metal nitrides and non-hydrogenated amorphous carbon. CFUBMSIP coatings include a thin metallic adhesion layer, followed by a graded interface with increasing nitrogen content and modulus, supporting the main stoichiometric nitride and the topmost amorphous carbon contact surface. HIPIMS utilises a high energy bombarded interface region resulting in intimate, extremely dense, and fine structured coating without the need for a separate gradient layer. HIPIMS coatings have also been shown to provide exceptional corrosion resistance. The critical characteristics of the coatings produced by both processes have been determined and their relative merits are discussed.Duplex coatings improve the ICR of the metallic plates, compared to a single transition nitride coating, achieving ICR close to that of thin (e.g. >20nm) Au, which is widely regarded as an industry benchmark. Their corrosion resistance has been assessed ex-situ by potentiostatic and potentiodynamic tests under simulated anode and cathode conditions and exceeds the requirements of the relevant industry specifications at both low and high potentials. Surface roughness, coating structure and composition have been assessed by profilometry, SEM and TEM.Finally, the potential for the future industrial exploitation of the duplex coatings is discussed.

9:40am **F6-1-6 Industrial, Low Cost Ceramic MaxPhase™ Protective Coatings for Stainless Steel Bipolar Plates**, ***H. Ljungcrantz*** *(henrik@impactcoatings.se), K. Nygren, M. Samuelsson*, Impact Coatings, Sweden

Bipolar plates (BPP) provides cell separation, gas distribution, current collection, and structural integrity of the fuel cell (FC) stack. While typically made from graphite, this makes the BPP heavy, bulky, fragile, and costly. Producing plates from stainless steel circumvents the aforementioned shortcomings. However, uncoated steel cannot withstand the corrosive environment in the FC, which will result in deterioration of the membrane from corrosion products and subsequent cell failure. Noble metal coatings, such as Au, will not deteriorate during operation, but they fail to meet the US Department of Energy (DOE) cost target. The lack of available coatings that meet the cost target and that are chemically stable under FC operation conditions impedes the transition from graphite to stainless steel BPP.

Impact Coatings offers Ceramic MaxPhase™ (CMP) coatings as a low cost material suitable for stainless steel BPP, in conjunction with the InlineCoater™ deposition system which provides high throughput, short cycle times, and simultaneous two-sided coating. In the present work, CMP deposited by physical vapor deposition is compared to Au coatings. Ex-situ evaluations of chemical stability and electrical properties of CMP coated stainless steel show high oxidation resistance and low contact resistance (<10 mΩcm2). Moreover, the electrical properties were not affected by the corrosion treatment. Life-time tests in commercial PEMFC systems show equal stack performance of CMP coated plates as compared to Au coatings for at least 2,000 hours of operation. In addition, cost calculations for high volume production of the coatings were performed, showing that the cost target of the DOE is within reach. Thus, the CMP coatings and the production concept enable the transition from graphite to stainless steel BPP for use in PEMFC and DMFC.

10:00am **F6-1-7 Pre-coated Steel Stripes for PEMFC and SOFC Interconnects**, *G.V. Dadheech (gayatridadheech@gmail.com)*, General Motors Research and Development Center, US, *H. Holmberg*, Sandvik Coromant R&D Materials and Processes, Sweden, ***M. Schuisky***, Sandvik Machining Solutions, Sweden

Metal interconnects are getting widely popular due to their fast and easy high volume manufacturing. One of the metals of choice is stainless steel materials which have good corrosion stability due to the naturally occurring native oxide on its surface. However, stainless steel offers a high contact resistance when connected in series, mainly due to the passive oxide surface layer, which is the sole reason behind the corrosion resistance of stainless steels. Typical interfacial contact resistance (ICR) values for stainless steels at the compaction pressures of interest for PEMFC bipolar plates, are at least an order of magnitude higher than the DOE target of 10 mΩ cm^2. The use of uncoated stainless steel leads to undesirable high electrical contact resistance and significant fuel cell stack performance loss. In this talk we would review reducing the ICR and improving corrosion resistance using graphite like carbon (GLC) coatings precoated on stainless steel strips for easy high volume production.

10:20am **F6-1-8 R.F. Magnetron Sputtered Li-Mn-O Thin Films**, *J. Fischer (Julian.Fischer@kit.edu), T. Bergfeldt*, Karlsruhe Institute of Technology, Germany, *K. Chang*, RWTH Aachen University, Germany, *H. Leiste, T. Scherer*, ***S. Ulrich***, *H.-M. Bruns*, Karlsruhe Institute of Technology, Germany, *C. Ziebert*, Karlsruhe Institute of Technology, Germay, *H.J. Seifert*, Karlsruhe Institute of Technology, Germany

The increasing demand on lithium ion batteries (LIB) and more efficient energy storage solutions for portable consumer electronic devices like Smartphones, Camcorders and Tablet-PCs makes thin film technology more and more interesting as an serious alternative to conventional produced micro battery applications. With thin film and nano-technology it is possible to develop electrochemical storage systems that are both, small and powerful. While the most conventional liquid-electrolyte-based lithium ion secondary batteries hold the risk of leakage, burning and undesirable side-reactions, these problems can be completely eliminated with all solid state technology. Like in the liquid based systems the diffusion of the lithium ions through the cathode material is one of the most limiting factors and makes additional studies on the understanding and improvement of intercalation compounds desirable and necessary.

This work is about the investigation and development of environmental friendly manganese oxide based thin film cathodes. R.f. magnetron sputtering was used in combination with furnace annealing to produce amorphous and crystalline Li-Mn-O thin films. All samples were investigated on their elemental ratios Li:Mn:O by inductively coupled plasma optical emissions spectroscopy (ICP-OES) and carrier gas heat extraction (CGHE). Atomic force microscopy (AFM) and scanning electron microscopy (SEM) techniques were used to investigate thin film surface roughness and morphology of the surface and cross-section. Further a structural investigation was carried out by X-ray diffraction (XRD), Raman-spectroscopy and transmission electron microscopy (TEM) in combination with focused ion beam (FIB) produced TEM-lamella. The distribution of the elemental compositions in the as deposited and annealed films was investigated with time of flight secondary ion mass spectroscopy (TOF-SIMS) depth profiles. To complete these measurements finally electrochemical battery tests in Swagelok half-cells were carried out to investigate both the electrochemical reactions and the galvanostatic cycling behavior.

10:40am **F6-1-9 The Effect of Reactive Element Coatings on the Oxidation Properties of Ferritic Steels for Solid Oxide Fuel Cell Interconnect Applications**, ***R. Sachitanand*** *(rakshith@chalmers.se), J. Froitzheim, J.E. Svensson, L.G. Johansson*, Chalmers University of Technology, Sweden

Ferritic stainless steels are used as interconnector materials in solid oxide fuel cells owing to their combination of low cost, compatible mechanical properties and electronically conductive oxide scales. The applicability of these materials is however limited by their unsatisfactory high temperature oxidation resistance and chromium volatilization of the oxide scale leading to catastrophic cell degradation. Solid oxide fuel cell interconnectors operate in dual atmospheres wherein the oxygen partial pressure differs significantly on either side of the bipolar interconnector plate. This entails oxidizing conditions on one side and reducing on the other, which throws

up varying material challenges on the same piece of steel under operating conditions.

This study investigates the effect of metallic thin films of Ce and La on the oxidation properties of the commercial interconnector material Sanergy HT (Sandvik Materials Technology) in a typical cathode side SOFC environment.Exposures are carried out in tubular furnaces at 850°C, with 6l/min airflow and 3% H_2O to simulate the cathode side atmosphere in a SOFC. Test durations range from 1 minute to 1000 hours .In addition to the oxidation tests, in-situ chromium evaporation measurements are carried out using a novel denuder technique to investigate the effect of these coatings on chromium volatilization. The surface morphology and microstructure of the oxide scales are characterized using scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX). Secondary ion mass spectroscopy (SIMS) and X-ray photoelectron spectroscopy (XPS) are applied to better understand the effect that these coatings have on near surface chemistry.

Applications, Manufacturing, and Equipment
Room: California - Session G5-2

Coatings, Pre-Treatment, Post-Treatment, and Duplex Technology
Moderator: T. Takahashi, KCS Europe GmbH

8:00am **G5-2-1 Surface Modification for Metal using a Newly Developed Atmospheric Controlled Induction-heating Fine Particle Peening (AIH-FPP) System**, ***J.K. Komotori*** *(komotori@mech.keio.ac.jp)*, Keio University, Japan **INVITED**

An atmospheric controlled induction-heating fine particle peening (AIH-FPP) treatment system was developed. Using the system the surface of structural steel with carbon content of 0.45%C was modified with Cr shot particle at room temperature, 500 C, 700 C and 900 C in atmosphere of argon and air. The treated surfaces were characterized using a scanning electron microscope (SEM) an energy dispersive X-ray spectrometer (EDX), an X-ray diffractometer (XRD) and an X ray photoelectron spectroscope (XPS). In the case of specimen treated in argon atmosphere, a relatively thick and uniform Cr diffused layer was formed at the surface. The thickness of the layer was changed with an increase in temperature, the higher the temperature, the thicker the layer. In the case of the specimen treated in air, however, an oxidized scale was formed on the treated surface instead of a Cr diffused layer. The results of the experiments prove that AIH-FPP treatment successfully creates a Cr diffused surface layer.

By introducing *design of experiment* (DOE), we examined the effect of processing parameters, such as peening pressure, particle supply rate, peening time, and heating time, on the characteristics of modified layers. The surface of structural steel was modified by IH-FPP with Cr shot particles at 900℃ in an argon atmosphere. Results showed that the peening time strongly affected the levels of oxygen concentration at the treated surface; the longer the peening time, the higher the oxygen concentration. Heating time also affected the Cr concentration at the surface; the longer the heating time, the higher the Cr concentration. Corrosion tests were performed using a three-electrode electrochemical cell connected to a computer driven potentiostat. The specimens with Cr diffused layers showed higher corrosion resistance compared to other specimens. This is because of the existence of passive films on treated surfaces.

8:40am **G5-2-3 Number of Passes and Thickness Effect on Mechanical Characteristics of Cold Spray Coating**, ***A. Moridi***, *S.M. Hassani-Gangaraj, M. Guagliano (mario.guagliano@polimi.it)*, Politecnico di Milano, Italy, *S. Vezzù*, Associazione Civen, Italy

Nowadays with the severe competitive business environment, limited material sources and high cost of manufacturing, the importance of maintenance and repair is self-evident. One of the potential applications of cold spray coating is dimensional recovery of damaged structural parts. In most cases thick coatings are necessary for this demand. Thick coatings can be deposited in single or multiple numbers of passes giving different thermal and stress contribution to the components and coatings itself. The thermal input, the amount and the type of residual stresses (compressive or tensile) confer appreciable or depreciable characteristics to the coatings mechanical property. In this study single and multi-pass deposition of a desired thickness of Al 6082 coting on the same substrate is studied. In addition one pass deposition of different deposition thicknesses are also investigated. Micro-structural observation, micro-hardness measurements and X-Ray diffraction (XRD) measurement of residual stress were performed on all groups of sprayed material. Tubular coating tensile test tests were also carried out to characterize the cohesion of the coating in different cases. Observation of fractured surface was used to investigate the failure mechanism of the cold-sprayed materials. A critical discussion on the effects of thickness and number of passes on mechanical behavior of coated specimens is presented.

Key words: cold spray, residual stress, cohesion, Al 6082, multi-pass.

9:00am **G5-2-4 Effects of Intermediate Surface Treatments on Corrosion Resistance of Cathodic Arc PVD Hard Coatings**, ***S. Abusuilik*** *(Saleh_Abusuilik@hitachi-tool.co.jp)*, *K. Inoue*, Hitachi Tool Engineering, Ltd., Japan

Cathodic arc PVD CrN-based coatings offer excellent tribological and corrosion properties. However, adoption of these coatings in industrial applications, particularly at corrosive environments, is limited by growth defects of the coatings such as droplets, pores, and pinholes. This study reports on the effects of intermediate treatments and their role in improving corrosion resistance of CrN-based PVD coatings, aiming to minimize the negative effects of coating defects. Different intermediate treatments were examined including Ar and metal etching, lapping and polishing, and shot blasting. CrN-based monolayer and multilayer coatings were deposited on refined AISI D2 tool steel substrates and were characterized. Corrosion behavior of the coatings was studied by immersion tests in 10 % sulfuric acid aqueous solution and pitting potential measurements in 5 % sodium chloride solution. Observation of the coatings and their cross sections was made using scanning electron microscope and optical microscope. Immersion tests results showed that applying intermediate treatments enhanced the corrosion resistance of CrN-based coatings. Particularly, intermediate lapping and polishing of the coatings surfaces help in removing droplets and other inclusions before deposition the second layer. This may lead to suppression of penetrated pinholes and thus preventing formation of corrosion cells. Based on the findings of this study, intermediate treatment of arc PVD coatings may be a promising solution to improve corrosion resistance of coatings operating under severe environments.

9:20am **G5-2-5 Microstructure and Dielectric Nature of Plasma Sprayed Ultra Purity Aluminum Oxide Coatings**, ***S. Dixit*** *(sdixit@ptise.com)*, Plasma Technology Inc., US

Plasma sprayed acid washed aluminum oxide coatings are prepared and their microstructural and dielectric properties are measured. The coatings are compared with that of commercial grade Aluminum oxide coatings. Coating thickness variation and use of various sealers is assessed to see their effect on improvement of the dielectric strength. Application of various sealers such as Metco AP, Metco ERS, and Dichtol and the effect of thickness variation on dielectric strength will be evaluated. Coatings will be characterized for their microstructure, dielectric properties, bond strength, porosity, and sealer percolation. Coating characteristics on various electronic substrates such as alumina, stainless steel, pure aluminum etc. will be evaluated and reported.

9:40am **G5-2-6 The Fracture Toughness of Boride Coating Improved by a Diffusion Annealing Process**, *I. Campos-Silva (icampos@ipn.mx), M. Flores-Jiménez, G. Rodriguez-Castro*, Instituto Politecnico Nacional, Mexico, *E. Hernandez-Sanchez*, Universidad Autonoma Metropolitana-Azc, Mexico, ***J. Martínez-Trinidad***, *L. Jiménez-Tinoco*, Instituto Politecnico Nacional, Mexico

Boriding is carried out with the purpose of increasing the hardness, wear and corrosion resistance in engineering components for industrial applications. The boriding of different steel grades results in the formation of either a single-coating (Fe_2B) or double-coating (FeB/Fe_2B). 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.

This study proposes a diffusion annealing process to increase the fracture toughness of boride coating formed at the surface of the AISI 1045 borided steel. First, the boriding of AISI 1045 steel was developed by the powder-pack method at a temperature of 1223 K in the range of exposure times of 8 – 12 h. The evolution of the FeB/Fe_2B coating as a function of the exposure time was estimated in the range of 238 to 301 microns. Vickers microindentation tests were conducted at 50 microns from the surface of the borided steels, where the indentation loads in the FeB coating ranged between 0.098 and 9.8 N for the set of experimental parameters of the boriding process. In addition, the magnitude of the indentation size, and the cracks emanated from the corners of the indentation marks were measured for the different applied loads.

Second, the diffusion annealing process was carried out on the borided samples at a temperature of 1273 K with 8 h of exposure. The borided steels were embedded in a closed-cylindrical container with a powder mixture of

silicon carbide and bentonite with the absence of inert gases into the furnace. Before the process, the presence of a single Fe_2B coating was observed at the surface of the borided steels with thicknesses between 285 to 363 microns. The mechanical characterization of the borided samples exposed to the diffusion annealing process was similar to those applied in the boriding conditions.

The behavior of the hardness as a function of the indentation load for both conditions (FeB/Fe_2B and Fe_2B coatings, respectively) showed the presence of the indentation size effect (ISE) at 50 microns from the surface; the load-independent hardness value (H_o) of the boride coatings was estimated by the proportional specimen resistance (PSR) model.

Finally, considering that the hardness is independent of the applied load, the fracture toughness evaluated in the Palmqvist crack regime for the borided samples exposed to the diffusion annealing process showed a reduction of the brittleness around 30% in comparison with the estimated values over the FeB/Fe_2B coating.

Topical Symposia
Room: Royal Palm 4-6 - Session TS1-1

Surface Engineering for Thermal Transport, Storage and Harvesting

Moderator: B. Cola, Georgia Technical Institute, US, C. Muratore, University of Dayton

8:00am **TS1-1-1 Direct Thermal Conductivity Measurement of Nanostructured Coatings Using a Modified Photoacoustic Technique**, ***T. Bougher*** *(tbougher@gatech.edu)*, Georgia Institute of Technology, US, *B. Cola*, Georgia Technical Institute, US

The photoacoustic (PA) technique was used to measure the thermal conductivity of nanostructured materials without the use of a metal foil or transducer layers to absorb laser energy. Using the sample material as the absorption layer eliminates the need to bond the nanostructured material to a metal foil or deposit a metal film on the sample, which creates an unknown contact resistance between the sample layer and the metal. Because of the elimination of the additional contact resistance, the bare sample measurement has a much higher theoretical sensitivity to the thermal conductivity of the sample compared to the sensitivity when a metal foil or film transducer is used. The measurement technique is demonstrated on vertical forests of carbon nanotubes (CNTs), polymer nanotubes, graphite, and polymer films. Bare graphite and CNT samples were measured and compared directly with graphite and CNT samples with deposited metal film transducers and metal foil transducers. The accuracy of the thermal conductivity measurements was found to be significantly better without metal foils or deposited films atop the sample . Measurements of the thermal conductivity of graphite and polymer films without metal transducers were in good agreement with reference values. To compliment the experimental results, a theoretical analysis was conducted to show how to best increase the sensitivity of the measurement to the sample thermal conductivity while minimizing the error due to uncertainty in the optical absorption length. Some limitations to the direct absorption PA technique are also discussed.

8:20am **TS1-1-2 Thermo-Mechanical Modeling of Carbon Nanotube Arrays for Thermal Interface Applications**, ***S. Sadasivam***, *S. Hodson, T. Fisher (tsfisher@purdue.edu)*, Purdue University, US

A growing interest has developed in the past decade on the use of carbon nanotube (CNT) arrays as thermal interface materials (TIM). This interest on CNT-based thermal interfaces stems primarily from two factors – the high intrinsic thermal conductivity of individual CNTs and mechanical compliance of the CNT array. Innovative methods for the measurement of mechanical and thermal properties of CNT arrays have been developed by many others. However, modeling of CNT TIMs have mostly been limited to semi-empirical methods without detailed consideration of the CNT array microstructure, primarily due to the inherent randomness of the microstructure and the computational complexity involved in full atomistic modeling of CNTs. A compelling need exists for developing physics-based models in order to move from interpretation of experimental data to prediction and optimization of mechanical and thermal characteristics of CNT arrays. In this work, we report combined thermo-mechanical modeling of CNT arrays with coarse-grain methods. The coarse graining of CNTs allows us to model reasonably large numbers of CNTs at practical engineering scales within a reasonable computational time. Parametric studies include the effects of CNT height, diameter and volume fraction on important mechanical properties such as the Young's modulus and buckling load of CNT arrays. A mesoscopic thermal network model couples with the coarse grain mechanics model and uses parameters derived from the various atomistic transport studies reported in prior literature. The thermal network model is used to estimate the diffusive and tip contact resistances of CNT arrays. We also report the pressure dependence of thermal resistance, tip contact area and compare our predictions with experimental values. Other useful information for thermal interface applications such as the effects of surface roughness and fillers such as wax are also predicted within the framework of the thermal network model.

8:40am **TS1-1-3 Heat Transfer in Encased Graphene**, ***C. Dames*** *(cdames@berkeley.edu)*, University of California, Berkeley, US **INVITED**

Although suspended graphene has been reported to have very high in-plane thermal conductivity, most applications will require graphene to be encased within, or supported by, dielectric layers. To understand the thermal performance of graphene in this important configuration, I will describe two measurements of the thermal transport in graphene and ultrathin graphite encased within silicon dioxide. First, the thermal contact resistance between graphene and SiO2 was measured using a differential 3-omega method, revealing significantly better thermal contact than previous reports for carbon fibers and carbon nanotubes. Second, the in-plane thermal conductivity of encased graphene sheets was measured using a novel "heat spreader" method, which fits a measured temperature profile using a finite element method (FEM) with one free parameter. The results show that the constraints of the encasing layers reduce the in-plane thermal conductivity by at least a factor of 10 as compared to bulk graphite.

9:20am **TS1-1-5 Limited Thermal Conductance of Metal-carbon Interfaces**, *J. Gengler*, Spectral Energies, LLC/Air Force Research Laboratory, Materials and Manufacturing Directorate, Nanoelectronic Materials Branch, USA, *S. Shenogin*, UES/Air Force Research Laboratory,Materials and Manufacturing Directorate, Nanoelectronic Materials Branch, USA, *J. Bultman*, UDRI/Air Force Research Laboratory, Materials and Manufacturing Directorate, Nanoelectronic Materials Branch, USA, *A. Roy*, *C. Muratore*, ***A. Voevodin*** *(andrey.voevodin@wpafb.af.mil)*, Air Force Research Laboratory, Materials and Manufacturing Directorate, Nanoelectronic Materials Branch, USA

The thermal conductance for a series of metal – graphite interfaces has been experimentally measured with time–domain thermoreflectance (TDTR). For metals with Debye temperatures up to ~ 400 K, a linear relationship exists with the thermal conductance values. For metals with Debye temperatures in excess of ~ 400 K, the measured metal–graphite thermal conductance values remain constant near 60 MW m^{-2} K^{-1}. Titanium showed slightly higher conductance than aluminum, despite the closeness of atomic mass and Debye temperature for the two metals. Surface analysis was used to identify the presence of titanium carbide at the interface in contrast to the aluminum and gold – carbon interfaces (with no detectable carbide phases). It was also observed that air–cleaved graphite surfaces in contact with metals yielded slightly higher thermal conductance than graphite surfaces cleaved *in vacuo*. Examination of samples with scanning electron microscopy revealed that the lack of absorbed molecules on the graphite surface resulted in differences in transducer film morphology, thereby altering the interface conductance. Classical molecular dynamic simulations of metal – carbon nanotube thermal conductance values were calculated and compared to the TDTR results. The upper limit of metal – graphite thermal conductance is attributed to the counteracting effects of decreased coupling and heat capacity for higher vibrational frequency modes of the lighter metals studied.

9:40am **TS1-1-6 Thermoreflectance Microscopy of Thin Films**, ***A. Schmidt*** *(schmidt@bu.edu)*, Boston University, US **INVITED**

Engineering and testing thin films requires sensitive characterization tools. Optical techniques based on thermoreflectance have emerged as reliable way to measure thermal transport in nanoscale thin films and across their interfaces. We discuss the challenges and benefits of extending time-domain and frequency-domain thermoreflectance measurements into scanning microscopy tools that can create maps of thermal conductivity, thermal interface conductance, and several other properties. Calibration methods and resolution limitations are presented along with measurements of several thin-film systems.

10:20am **TS1-1-8 Hydrogen Absorption and Desorption Properties of Pd/Mg/Pd Tri-layers Prepared by Magnetron Sputtering**, *Y.K. Gautam, R. Chandra (ramesfic@gmail.com)*, Indian Institute of Technology Roorkee, India, ***M. Kumar***, Indian Institute of Technology Delhi, India

Hydrogen storage materials are one of the important key materials for the futuristic clean energy sources. To achieve high hydrogen absorbing capacity and suitable absorption/desorption temperature, the study on nanostructured multilayer hydrogen absorbing materials is very important. A study on hydrogenation and dehydrogenation of Pd/Mg/Pd tri-layers,

prepared by DC/RF magnetron sputtering has been conducted using XRD, FE-SEM and AFM. Hydrogenation of the films was carried out at (50-150°C) temperatures in a fix amount of hydrogen gas (1bar). Hydrogen contents in as-deposited and hydrogenated thin films have been estimated by Elastic Recoil Detection Analysis (ERDA) technique with 120 MeV $_{107}Ag^{+9}$ ions. The maximum hydrogen absorption (8.4×10^{17} H atoms/cm^2) has been observed for 125°C among all samples studied. The hydrogen desorption kinetics has been enhanced by cooperative phenomena in Pd/Mg/Pd tri-layers system due to elastic interactions between nanostructured Mg and Pd interface. Low desorption temperature (80° C) has been observed for Pd/Mg/Pd tri-layer system.

10:40am **TS1-1-9 Interface Engineering for Optimized Thermal Transport in Copper/Diamond System**, ***V. Sinha***, UES/Air Force Research Laboratory,Materials and Manufacturing Directorate, US, *J. Gengler*, Spectral Energies, LLC/Air Force Research Laboratory, Materials and Manufacturing Directorate, Nanoelectronic Materials Branch, US, *C. Muratore (cmuratore1@udayton.edu)*, Air Force Research Laboratory, Materials and Manufacturing Directorate, Nanoelectronic Materials Branch, US, *J. Spowart*, Air Force Research Laboratory, Materials and Manufacturing Directorate, US **INVITED**

The high thermal conductivity *(λ)* and low coefficient of thermal expansion (CTE) of copper-diamond composites lead to their selection for several high-performance thermal management applications. In this research, thermal properties of Cu-diamond composites with different types of interfacial carbides were studied. The interface thermal conductance *(h_c)* was calculated with Maxwell mean-field and differential effective medium schemes. The value of h_c is intimately related to the morphology and thickness of the interface carbide layer. Furthermore, copper thin film was sputter-deposited on diamond substrate and subsequently analyzed with time-domain thermoreflectance (TDTR) technique to more directly measure the h_c of Cu/diamond interface. To mimic the interfacial conditions in Cu-diamond composites, interface layers of different thickness and/or morphology were introduced between Cu thin film and diamond substrate. The resultant variations in h_c were determined with TDTR experiments and modeling, and compared with model calculations of h_c with the composite λ as an input parameter.

11:20am **TS1-1-11 Synthesizing MnO2/Graphene Composites by a Hydrothermal Method for use to Enhance the Performance of Supercapacitor**, ***P.R. So***, *J.M. Ting (jting@mail.ncku.edu.tw)*, *K.S. Rao*, National Cheng Kung University, Taiwan

In this study we have investgated the use of MnO2/graphene compositess as the electrode material in supercapacitor. A novel microwave-assisted hydrothermal method was used to synthesize MnO2 nanoparticles with and without the presence of reduced graphene. The reduced graphene was prepared by reducing graphene oxide fabricated using the Hummers method. The resulting reduced graphene, MnO2 nanoparticles, and MnO2/graphene samples were first characterized for the properties using X-ray diffraction, scanning electron microscopy, and transmission electron microscopy, and electron spectroscopy for chemical aalysis. The effect of hydrothermal conditions is presented and discussed. Electrodes made from selected reduced graphene, MnO2 nanoparticles, and MnO2/graphene composites were assembled into two-electrode capacitors. Cyclic voltammetry and galvanostatic charge/discharge techniques were then used to evaluate the electrochemical performance. The effect of the electrode material characteristics on the capacitor performance is presented and discussed.

Topical Symposia
Room: Royal Palm 1-3 - Session TS2-2

Advanced Characterization of Coatings and Thin Films

Moderator: S. Korte, University of Erlangen-Nürnberg, Germany, M. Sebastiani, University of Rome "Roma Tre", F. Giuliani, Imperial College London - South Kensington Campus, UK

8:00am **TS2-2-1 Correlation Between the Rockwell Indentation Test and the Progressive Load Scratch Test for Assessment of Coating Adhesion**, ***N. Randall*** *(nra@csm-instruments.com)*, CSM Instruments, Switzerland, *R. Bethke*, Fraunhofer IST, Germany, *G. Favaro*, CSM Instruments, Switzerland

In recent years it has become current practice to employ a wide range of test methods to assess the adhesive properties of thin films and coatings, ranging from the simple tape-peel test to the more advanced pull-off and 3-point bending tests. Many such methods have high operator subjectivity, high data variability and in many cases are unsuitable for industrial Quality Control (QC) use where assessment is done regularly and often by several operators. The Rockwell indentation test (ISO 26443 and VDI 3198) has become common for evaluating the adhesion of hard coatings deposited on various substrates, but the applied load (1472 N) is often too high causing the 200 µm radius diamond indenter to plunge too deeply into the substrate making it difficult to classify the resultant coating damage around the edges. The progressive load scratch test (ASTM C1624, ISO EN 1071-3, ISO 20502) is now widely used to characterize the adhesion of thin hard coatings with high repeatability. However, a direct correlation between these two methods has never been attempted.

It has been proposed that a smaller radius diamond indenter (possibly 50 µm radius) could be employed with the Rockwell indentation test, using a lower applied load, in order to concentrate the maximum stress nearer to the sample surface causing more focused failure of the coating-substrate interface. The objective of this study is to fabricate samples representative of the 6 failure categories of the standard Rockwell test, to then evaluate the same coatings with lower load and smaller indenter radius, and thirdly to test the same samples with the progressive load scratch test. It is hoped that this could lead to better correlation of data obtained with all such methods and aid industry in better QC control of their coatings.

8:20am **TS2-2-2 How to Make Tribological Tests Physical**, ***N. Schwarzer*** *(n.schwarzer@siomec.de)*, Saxonian Institute of Surface Mechancis, Germany

Caused by the many effects taking place during a general tribological test it is a relatively ambiguous goal to create not just a tribo-model or simulation tool, but to make it fit for inversion and thus, analysis of such tribological tests. The talk features an approach where tribo parameters, like Archard's wear depth parameter kd, are extracted from effective interaction potentials [1], which themselves are built up and fed from more physical-oriented measurements like Nanoindentation and PHYSICAL scratch. By using such effective material potentials one can derive critical loading situations leading to failure (decomposition strength). A subsequent connection of these decomposition or failure states with the corresponding stress or strain distributions allows the development of rather comprehensive tribological parameter models applicable in wear and fatigue simulations as demonstrated in this work.

From this a new global increment wear model has been developed on the basis of the effective indenter concept [1, 2] by using the extended Hertzian approach [3]. The models do not only allow to analyze certain tribological experiments like the well known pin-on disk test or the more recently developed nano-fretting tests, but also to forward simulate such tests and even give hints for better component life-time predictions. Within the talk a few examples will be shown.

[1] N. Schwarzer, Short note on the effect of pressure induced increase of Young's modulus, Phil. Mag., submitted July 2011

[2] N. Schwarzer, G. M. Pharr: „On the evaluation of stresses during nanoindentation with sharp indenters", Thin Solid Films, Vol. 469-470C pp. 194-200

[3] N. Schwarzer, T. Chudoba, G. M. Pharr: „On the evaluation of stresses for coated materials during nanoindentation with sharp indenters", Surf. Coat. Technol, Vol 200/14-15 pp 4220-4226

[4] N. Schwarzer: "The extended Hertzian theory and its uses in analysing indentation experiments", Phil. Mag. 86(33-35) 21 Nov - 11 Dec 2006 5153 – 5767, Special Issue: "Instrumented Indentation Testing in Materials Research and Development"

8:40am **TS2-2-3 Depth Profiling >40-µm Anodized Coatings Using Glow Discharge Optical Emission Spectroscopy**, ***F. Li*** *(fuhe.li@balazs.com)*, *J. Laiduc*, *W. York*, *W. Rivello*, Air Liquide Electronics-Balazs NanoAnalysis, US

Radio Frequency (RF) glow discharge optical emission spectroscopy (GD-OES) has been developed in our laboratory to characterize various coatings and thin films. Thick dielectrics (insulators) such as anodized coatings, typically > 40 µm, are used in semiconductor, coating equipment, defense, aerospace, automotive, architectural, medical, marine, sporting goods, home appliances, and recreation. These thick coatings can be analyzed by RF GD-OES for elemental composition, spatial elemental distribution, and trace impurities. The use of RF plasma for material sputtering, excitation and ionization avoids many intrinsic limitations associated with traditional electron beam, ion beam or x-ray techniques. Deep depth profiling a > 40 µm anodized coating (e.g. Type III hard coatings) throughout its entire thickness down to its substrate at nm depth resolution can only be accomplished by RF GD-OES.

With simultaneous multi-element (40 or more including H, C, N, O, Na, Mg, Al, P, S, Cl, Fe…) profiling capability (real-time profiling), RF GD-OES has been successfully used to examine coating uniformity, interfacial contamination, and surface stoichiometry (<10 nm). The RF GD-OES results demonstrate the usefulness of this technique in optimizing anodization processes, facilitating base material (aluminum alloys) selection, controlling surface and interfacial contamination, and preventing premature failure of an anodized coating or subsequent layer. The signal intensity produced by RF GD-OES has a simple and well-defined mathematical (linear) relationship with elemental concentration in a material. A wide linear dynamic range (over six orders of magnitude) possessed by RF GD-OES coupled with various NIST traceable material standards developed in our laboratory have made accurate surface, interfacial and bulk analyses possible.

9:00am **TS2-2-4 Mechanical Properties of Nanocrystalline Coatings Revealed by Bending Tests on Fabrication-Unaffected Micro-Cantilevers**, ***A. Riedl*** *(angelika.riedl@mcl.at)*, Materials Center Leoben Forschung GmbH, Austria, *R. Daniel*, Montanuniversität Leoben, Austria, *M. Stefenelli*, Materials Center Leoben Forschung GmbH, Austria, *T. Schöberl, O. Kolednik, C. Mitterer, J. Keckes*, Montanuniversität Leoben, Austria

Thin nanocrystalline coatings featuring outstanding mechanical properties have gained much interest in recent years. The application of deposition techniques operating far from the thermodynamic equilibrium results in the formation of pronounced depth inhomogeneities in microstructure and strain over coating thickness compared to their bulk counterparts. Thus, instead of surface sensitive parameters obtained using indentation techniques, knowledge about their mechanical behaviour is required in order to assess the relationship between process conditions, thickness-dependent coating properties and functional behaviour. The presented approach is a step forward in the characterization of thickness-averaged mechanical properties of crystalline coatings at the micrometer scale. It consists of an etching step of the substrate to isolate the coating without affecting its interface to surface inhomogeneity, thus preserving its nucleation zone. Afterwards, a rectangular cantilever is fabricated by cutting the free-standing coating with a focused gallium ion beam. The cantilever beam is loaded by an indenter, where load-displacement curves are recorded until fracture. Then, the fracture surfaces are evaluated by scanning electron microscopy. Using this approach, the fracture mechanism can be identified and linked to coating microstructure and residual stress state. The influence of deposition parameters, annealing treatments and coating architectures on the fracture properties of representative CrN and TiAlN coatings will be demonstrated. The approach allows the identification of mechanisms, which are responsible for the deterioration of the coating performance and which are often not well understood or remain unrevealed by other characterization techniques.

9:20am **TS2-2-5 Cyclic and Monotonic Mechanical Properties of Micro Samples Acquired with Custom Built Setups Working up to 1000 Hz – CuAl10Ni5Fe4, 3Y-PZT**, ***T. Kennerknecht*** *(tobias.kennerknecht@iwm.fraunhofer.de)*, Fraunhofer Institute for Mechanics of Materials, IWM, Germany, *S. Pelletier, T. Straub*, Karlsruhe Institute of Technology, Germany, *C. Eberl*, Fraunhofer Institute for Mechanics of Materials, IWM, Germany

Testing micro samples, thin films or coatings requires novel techniques and special equipment with a maximum flexibility to adjust for the samples. Thus, several piezo driven custom built setups were developed in our group, in order to investigate micro samples and thin films loaded in uniaxial tension, compression, bending or subjected to a multiaxial stress state. Most of these setups are designed for cyclic experiments and work in resonance, allowing for fatigue tests at frequencies up to 1000 Hz. Thus, very high cycle fatigue experiments (more than 1E8 cycles) can be performed in a reasonable amount of time. Furthermore, monotonic tests are available, using a setup, which can realize frequencies from 0 to 100 Hz. The present paper will give an overview on experiments conducted with the latter setup (low frequency setup, LFS) as well as with a resonant uniaxial tension-compression-setup (resonant setup, RS) working at frequencies up to 2 kHz. In addition, damage- and microstructural analyses will be addressed, which were established using electron microscopy and a focused ion beam, in order to reveal failure mechanisms. The investigated materials treated in this paper are aluminum bronze (CuAl10Ni5Fe, cross section 260 µm x 130 µm) and 3Y-TZP (Yttria stabilized zirconia, dimensions: 200 x 200 x 1200 μm^3), which were manufactured using specially developed micro casting processes (KIT, Karlsruhe), and which are comparable to free standing thin films. Both setups are excited by means of a piezo. Data is acquired by means of a field programmable gate array, which enables parallel acquisition of 8 analog channels at sample rates up to 200 kHz and partial on board treatment of the data. In the LFS, a camera with microscope is used for optical strain measurement performed with digital image correlation. Load is measured using a dynamic load cell. The travel range of the piezo is enlarged by means of a linear stage. The setup can be adapted for flat dog bone tensile samples as well as for three point bending tests. In the RS, the piezo actuator carrying the sample is aligned in direction of gravity. A mass is attached at the free end of the sample, and the system is excited sinusoidally at its natural push-pull frequency. The displacement of the freely hanging mass is measured using a capacitive sensor. Thus, the inertial load of the mass acting as the applied cyclic load on the sample can be determined. The results will help understanding the active fatigue mechanisms and damage formation of micro molded aluminum bronze and of 3Y-TZP. We greatly acknowledge the German Science Foundation (DFG) for sponsoring this work.

9:40am **TS2-2-6 High Cycle Fatigue of Al and Cu Thin Films by a Novel High-Throughput Method**, *S. Burger*, ***C. Eberl*** *(chris.eberl@kit.edu)*, Karlsruhe Institute of Technology, Germany, *A. Siegel, A. Ludwig*, Ruhr University of Bochum, Germany, *O. Kraft*, Karlsruhe Institute of Technology, Germany

Mechanical properties and fatigue lifetime of thin films differ significantly from those of bulk materials. With decreasing film thickness the fatigue failure changes from a dislocation based mechanism to pore formation and grain boundary cracking. To obtain a better understanding of the governing mechanisms, a new fatigue setup for micro cantilever bending was developed. A micro-machined Si cantilever coated with Al or Cu thin films is excited at its resonance frequency by a piezo actuator. The thin film undergoes cycles of different strain amplitudes along the cantilever from a maximum near the shoulder to zero at the free end. With a reflected laser beam from the surface the bending amplitude as well as the reflectivity is detected. Thus, by observing the damage front on the thin film after a certain number of cycles, it is possible to compile a fatigue lifetime diagram from one cantilever. Experimental results of cycled thin films of sputter deposited Al, Cu, and Cu with a Ti seed layer will be presented. The micro- and damage structure of these samples was qualitatively and quantitatively analyzed by a SEM/FIB Dual Beam. The results will be discussed in the light of current models for fatigue in thin films. Furthermore, a growth law based description for damage formation induced by fatigue will be presented.

10:00am **TS2-2-7 Structural, Morphological and Mechanical Characterization of Mo Sputtered Coatings**, ***S.M. Deambrosis*** *(silvia.deambrosis@ieni.cnr.it)*, *E. Miorin, M. Fabrizio*, CNR, Italy, *M. Sebastiani, E. Bemporad*, University "Roma Tre" Rome, Italy

The use of Molybdenum is of interest in various technological areas. Because of its remarkable properties (high melting point (2610°C), high conductivity, good chemical stability and high hardness), Mo coatings have been used in microelectronics (gates for MOS integrated circuits, interconnections, and diffusion barriers), as back contacts for solar cells and they are suitable candidates to fabricate superconducting microcalorimeters for high-performance radiation detectors. Moreover Molybdenum films are used in nuclear energy applications and for missile and aircraft parts. As a consequence of their appeal, a variety of deposition techniques and conditions has been employed to obtain Mo coatings.Nonetheless, a detailed study of the process-structure-properties for Mo-based coatings is still lacking in the literature.In this work, we present an investigation, based on the use of high resolution characterization methodologies, on the properties of Mo deposited by sputtering on titanium substrates. Different films have been grown under different sputtering conditions to find a correlation between a variety of deposition parameters and the intrinsic properties of the films. The working gas has been also changed (Ar, Xe, etc.) to evaluate its influence on the growing layer. Microstructural characterization activities consisted of scanning electron microscopy (SEM), X-ray diffraction (XRD) and focused ion beam (FIB) cross section analysis. The residual stress distribution was investigated by using an innovative high resolution focused ion beam micro-ring-core method. The nano-mechanical properties of the films (hardness and modulus) were analyzed by nanoindentation testing. Wear resistance and adhesion were finally analyzed by means of scratch and tribological tests, using a fully-computerized UMT tester. Results showed a significant modification of coatings' microstructure, depending on the adopted working gas and process parameters. In particular, a transition from a micro-crystalline columnar microstructure to a nano-porous microstructure was observed by using different kind of working gas. Modifications of the residual stress field and mechanical properties were also observed, as a function of the process parameters, and a correlation with observed adhesion and wear resistance is proposed.

10:20am **TS2-2-8 Effect of AlN Layer on the Growth and on the Structure of Reactive Sputtered TiAlN Thin Films and Multilayers**, ***A. Rizzo*** *(antonella.rizzo@enea.it), D. Valerini, L. Mirenghi, R. Terzi, L. Tapfer*, ENEA, Italy, *R. Giannoccaro, U. Galietti*, Politecnico di Bari, DIMEG, Italy

Machining of aerospace materials is one of the major challenges of modern manufacturing. It has been assessed that nano-multilayered PVD coatings applied at tooling of cemented carbide are useful for a significant tool life improvement in hard conditions of the cutting machine such as in the case of superalloys nichel-based (Incone l 718) and of the alloys titanium-based (TiAl6V4). In particular, TiAlN/AlN multilayers are attracting great interest for the possibility to modulate their mechanical and tribological properties through the multilayer design. In this work TiAlN single layer, TiAlN/AlN gradient structure and TiAlN/AlN nano-multilayers were prepared using a reactive magnetron sputtering system equipped with TiAl and Al targets. The aim of this work is to investigate how the multilayer design affects the thermal and tribological properties of the coatings. The chemical composition has been carried out by XPS analyses. The thermal stability has been characterized by X-ray diffraction, calorimetry and thermogravity while the mechanical properties have been investigated by wear tests.In the as deposited sample the main peak has been deconvoluted into two components c-AlN and c-TiAlN, confirming the template function of the cubic phase of AlN film. c-AlN reflection increases as expected up to 700 °C, disappears at 1000 °C to arise in hexagonal phase. c-TiN reflection comes out at 700 °C to increase at increasing annealing temperature. c-TiAlN reflection at 700 °C is narrower (indicating a higher structural order due to a recovery process) and also shifted on the left (indicating the presence of structural stress due to the decomposition process highlighted by c-TiN presence). The sliding tests carried out at 30 °C indicated a wear rate of about $5x10^5$ $mm^3/N/m$ for all coatings which have been observed. At 400 °C the single-layer coating presents a wear rate of the same order of magnitude as those tested at room temperature. The TiAlN/AlN coating with a gradient structure has a chemical composition of Ti 19 %, Al 36 %, N 43 %. The multilayered coated samples decreased their wear rate by one order of magnitude reaching their optimum in the sample of TiAlN/AlN nano-structured with a chemical composition of Ti 23 Al 40 %, N 37 %. A ll multilayered coatings exhibit an onset of the pronounced exothermic peak due to oxidation at ≥900 °C, hence, at least ~400 °C above that for c-TiN.

10:40am **TS2-2-9 Structural Characterization of Amorphous GdTM2 (TM=Fe, Ni and Co) from First-principles**, ***R. Lizarraga*** *(raquel.lizarraga@gmail.com), E. Holmstrom*, Universidad Austral de Chile, Chile

We performed a structural characterization of amorphous GdTM2 (TM=Fe, Ni, and Co) metallic glasses. An efficient and computationally inexpensive method based on Density Functional theory is used to obtain amorphous structures of the glasses. In our analysis we calculate radial distribution functions, angle distribution functions as well as bond lengths and average coordination numbers. The coordination number for the Gd-Gd pairs increases in the series a-GdNi2, a-GdCo2 and a-GdFe2, whereas the TM-Gd pair coordination number decreases is that order. This is in excellent agreement with the experimental data from the anomalous x-ray scattering method.

11:00am **TS2-2-10 Influence of Stoichiometry and Architecture on Mechanical Properties of Cathodic Arc Deposited Ti-Al-Cr-N Coatings**, ***S. Pemmasani*** *(saipramod@gmail.com)*, International Advanced Research Centre for Powder Metallurgy and New Materials (ARCI), India, *R. Gundakaram*, International Advanced Research Centre for Powder Metallurgy and New Materials(ARCI), India, *K. Rajulapati*, University of Hyderabad, India, *R. Mantripragada, S. Koppoju, K. Valleti, S. Joshi*, International Advanced Research Centre for Powder Metallurgy and New Materials(ARCI), India

Titanium and Chromium based nitrides find widespread applications as wear resistant coatings on cutting and forming tools. There have been continuous efforts to enhance their performance through various means, including designing their architecture in the form of nanocrystalline, nanocomposite or multilayer coatings. The mechanical properties of these coatings are significantly influenced by the crystal structure, microstructure and composition of the coating. Consequently, there exists an opportunity to control the coating performance by either tailoring the composition, through addition of alloying elements to achieve different stoichiometry, or the microstructure, through introduction of multilayers and nanosized grains. In the case of multilayer coatings, deposition of alternate layers with varying modulus is known to enhance crack resistance and, in turn, the toughness of the coating.

In the present study, Ti-Al-Cr-N based coatings were deposited by cathodic arc evaporation in monolayer and multilayer configurations on tool material substrates. The Al and Cr percentage in the coatings was varied in the range 0-65% by suitably manipulating the process parameters and four different compositions were comprehensively investigated. XRD analysis was carried out to ascertain the crystal structure while microstructural characterization was carried out by FIB-SEM and TEM to observe the variation in grain structure on the surface and cross section of the coatings. Stresses were measured employing an X-ray residual stress analyzer. Mechanical characterization was done using nanoindentation to determine the hardness and modulus, and scratch testing to assess adhesion. *In situ* scanning probe microscopy was also used to map the mechanical properties of the multilayer coatings. The hardness and modulus of the coatings were found to vary with Al and Cr percentage and correlated with the plasticity, toughness and residual stresses present in the coatings. Results suggest that there exists a critical Al content at which a maximum in hardness is obtained. Furthermore, the variation in sub-surface deformation during scratch testing and toughness with changing composition, and due to the multilayer configuration in the coating, was studied. Mapping of modulus variation between different layers of the multilayer coatings revealed that a substantial modulus mismatch existed between alternate layers that could lead to enhanced toughness. The implications of this study in enabling identification of a suitable coating composition and architecture to yield properties desirable for industrial applications will also be discussed.

11:20am **TS2-2-11 Fabrication and Characterization of Polymethylmethacrylate (PMMA) Thin Film by Plasma Polymerization**, *C. Li (cli10@yahoo.com)*, National Central University, Taiwan, Republic of China, *J.H. Hsieh*, Ming Chi University of Technology, Taiwan, Republic of China, ***Y.H. Lin***, National Central University, Taiwan

Poly×methyl×methacrylate (PMMA), also called acrylic glass, is transparent, chemically stable, thermoplastic and inexpensive, making it suitable for many biochemical applications. Among different fabrication processes of PMMA such as gelation, injection and casting, plasma polymerization is the one capable of depositing nano scale films on almost any substrate uniformly and rapidly. In this study, we investigated the structure, composition, surface and mechanical properties of deposited PMMA films on glass by RF power plasma inside a vacuum chamber. The deposition was carried out under different RF power, working pressure and deposition time, from which an optimal fabrication condition was explored. On the characterization part, following tests were carefully conducted: the thickness (around 20 to 160nm) was estimated by surface profiler; microstructures was determined by Fourier transform infrared spectroscopy (FT-IR); surface chemical compositions were examined by X-ray photoelectron spectroscopy (XPS); surface morphology, roughness and mechanical stiffness were measured by atomic force microscopy (AFM) and the wettability by water contact angle. Primary results showed that deposited films are physically and chemically stable for more than a week, which are readily available for cell culture, anti-microbial tests, drugs or proteins release and other bioengineering applications.

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