Technical Sessions
Key to Session/Paper Numbers

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 Biomedical Coatings

E Tribology and Mechanical Behavior of Coatings and Thin Films

F New Horizons in Coatings and Thin Films

G Applications, Manufacturing, and Equipment

PD Post Deadline Discoveries and Innovations

TS1 Computational and Experimental Studies of Inorganic, Organic, and Hybrid Thin Films: An Atomistic View

TS2 Coatings and Materials for Fuel Cells and Batteries

TS3 Surface Engineering for Thermal Transport, Storage, and Harvesting

TS4 Characterization: Linking Synthesis, Microstructure, and Properties

TS5 Energetic Materials and Micro-Structures for Nanomanufacturing

TS6 Coatings for Microelectronics and Active Devices

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 1 denotes the half day session in which the talk is being presented, morning or afternoon, and the paper number slot is -1). Sessions sponsored by two divisions are labeled with both acronyms (i.e., C2/E5, E5/C2).

SYMPOSIUM SCHEDULE POINTERS:

- All morning sessions begin at 8:00 am (except Monday, when the sessions begin at 10:00 am following the 8:00 am Plenary Session).
- All afternoon sessions begin at 1:30 pm, following the lunch break that starts at 12:10 pm.
- Invited speakers, (marked invited in the program) have 40 minutes; contributed speakers have a 20-minute limit.

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 they are compatible with the equipment being provided in the technical session rooms. The Presenter's Preview Room is the Terrace Salon 2. Please allow ample time for this test; preferably the day before you are scheduled to present – not immediately before your talk. The Preview Room's hours are Sunday, 3:30 - 6:30 pm and Monday – Thursday, 8:00 am - 5:30 pm.

IF YOU ARE MAKING A POSTER PRESENTATION:

Boards will be available for posting materials at ~Noon on Thursday, May 5. Prior to entering the Town & Country Room, Poster Presenters are to check-in at the table located in the doorway to the T & C room. Please show a photo ID as well as your registration badge; these must match the name of the ***presenting poster author*** in the ICMCTF program.
A sign listing the paper number, title, and presenting author will assist you in locating the correct board where your poster is to be displayed. The board size for your poster materials is ~ 4' x 4'. All poster materials MUST be posted prior to 5:00 pm. All Presenters are required to be at their presentation during the entire Poster Session, 5:00 - 7:00 pm; this is to encourage discussions with interested attendees during the poster session. Be forewarned, all poster materials will be discarded if not removed from the bulletin boards by 9:00 pm Thursday, evening.

Monday Morning, May 2, 2011

	Hard Coatings and Vapor Deposition Technology Room: Royal Palm 1-3 - Session B2-1 CVD Coatings and Technologies **Moderators:** S. Ruppi, Walter AG, F. Maury, CIRIMAT CNRS-INPT-UPS ENSIACET	Hard Coatings and Vapor Deposition Technology Room: Golden West - Session B4-1 Properties and Characterization of Hard Coatings and Surfaces **Moderators:** M. Fenker, FEM Research Institute, B. Zhao, Exxon Mobil
10:00 am	**B2-1-1 Invited** Mild Chemistry as a Strategy for the Preparation of Metal-Containing Films, **N. BAHLAWANE**, Bielefeld University, Germany & CRP-Gabriel Lippmann, Luxembourg	**B4-1-1** Comparative ab Initio and Experimental Study of Ti-Al-N, Zr-Al-N and Hf-Al-N, **P.H. MAYRHOFER**, D. HOLEC, R. RACHBAUER, Montanuniversität Leoben, Austria
10:20 am	Invited talk continued.	**B4-1-3** The Effect of Elastic Anisotropy on the Spinodal Decomposition in TiAlN: a Phase Field Study, **J.M. ULLBRAND**, Linköping University, Sweden, B. JANSSON, Seco Tools AB, Fagersta & Linköping University, Sweden, F. TASNÁDI, L. HULTMAN, M. ODÉN, Linköping University, Sweden
10:40 am	**B2-1-3** Deposition of Cobalt Oxide Thin Films by PECVD for Catalysis Application, **C. GUYON**, Chimie ParisTech, France, A. BARKALLAH, UPMC, France, F. ROUSSEAU, Chimie ParisTech, France, K. GIFFARD, UPMC, France, D. MORVAN, M. TATOULIAN, Chimie ParisTech, France	**B4-1-4** Effect of Internal Stress on Cutting Performance of Coated Carbide Tools, **S. IMAMURA**, A. SHIBATA, H. FUKUI, K. TANAKA, Sumitomo Electric Hardmetal Corp., Japan
11:00 am	**B2-1-4** Polymeric Barrier Coatings via Initiated Chemical Vapor Deposition, **T. PARKER**, J.D. DEMAREE, D. BAECHLE, U.S. Army Research Laboratory	**B4-1-5** In-Situ Measurement of Residual Stresses Developed During Triode Magnetron Sputtering Film Depositions with Step-Variation of Substrate Bias, **C.F. FERNANDES LAGATTA**, University of Sao Paulo, Brazil, A.A.C. RECCO, University of Santa Catarina, Brazil, A.P. TSCHIPTSCHIN, R.M. SOUZA, University of Sao Paulo, Brazil
11:20 am		**B4-1-6** Low-Temperature Plasma Nitriding of Ti-6Al-4V: Microstructural Characterization and Mechanical Properties, **K. FAROKHZADEH**, A. EDRISY, University of Windsor, Canada, G. PIGOTT, P.C. LIDSTER, Exactatherm Ltd., Canada
11:40 am		
12:00 pm		
	CETR FTS **Golden West Room – 12:15 - 1:15 pm**	**CETR FTS** **Golden West Room – 12:15 - 1:15 pm**

Monday Morning, May 2, 2011

	Fundamentals and Technology of Multifunctional Thin Films: Towards Optoelectronic Device Applications Room: Sunset - Session C1 Recent Advances in Optical Thin Films **Moderators:** K. Khajurivala, Janos Technology, Inc., R. Sczupak, Reynard Corporation	Biomedical Coatings Room: Royal Palm 4-6 - Session D1-1 Bioactive and Biocompatible Coatings and Surface Functionalization of Biomaterials **Moderators:** E. Saiz, Imperial College, S. Kumar, University of South Australia
10:00 am	**C1-1** Investigations of Diffusion Behaviour in Dielectric Coatings, **J. KULCZYK-MALECKA**, P. KELLY, G.T. WEST, Manchester Metropolitan University, UK, GCB. CLARKE, Pilkington Technology Management, UK, I. IORDANOVA, University of Sofia, Bulgaria, V. VISHNYAKOV, Manchester Metroplitan University, UK	**D1-1-1 Invited** Nanoscale Engineering of Biointerfaces via Parylene Coatings, **M. DEMIREL**, Pennsylvania State University
10:20 am	**C1-2** Electrochromic Performance of Hybrid Tungsten Oxide Films with Multiwalled-CNTs Additions, **C-.K. LIN**, S.-C. TSENG, C.-H. CHENG, C.-Y. CHEN, Feng Chia University, Taiwan, C.-C. CHEN, National United University, Taiwan	Invited talk continued.
10:40 am	**C1-3 Invited** Opto-Electronic Properties of Graphene Oxide Thin Films, **M. CHHOWALLA**, Rutgers University	**D1-1-3** Enhance Surface Reactivity of High Strength Biomedical Ceramics, **J.R. PIASCIK**, RTI International, S.D. WOLTER, Duke University, B.R. STONER, RTI International
11:00 am	Invited talk continued.	**D1-1-4** SiNWs-Stimulated Human Adipose Derived Stem Cell (hADSC) Growth Behavior, **H.-I. LIN**, National Tsing- Hua University, Taiwan, S.-W. KUO, K.-S. LEE, National Yang-Ming University, Taiwan, T.-J. YEN, National Tsing- Hua University, Taiwan
11:20 am	**C1-6** Effect of Crystallinity and Oxygen Vacancy on Photocatalytic Properties of TiO_2 Thin Films, **J.-H. HUANG**, M.-S. WONG, National Dong Hwa University, Taiwan	**D1-1-5** Vertically Aligned Carbon Nanotube Arrays and Their Application as Biological Scaffolds for Stem Cell Growth, **G. KUCUKAYAN**, V. BITIRIM, C. AKCALI, D. TUNCEL, E. BENGU, Bilkent University, Turkey
11:40 am	**C1-7** Structural and In-Depth Characterization of Variable Refractive Index Chromium-Silicon Mixed Oxides Produced by Reactive Ion Beam Mixing of the Cr/Si Interface, **R. ESCOBAR GALINDO**, L. VERGARA, O. SÁNCHEZ, Instituto de Ciencia de Materiales de Madrid, Spain, G. FUENTES, Asociación Industria Navarra (AIN), Spain, D. DUDAY, Centre de Recherche Public Gabriel Lippmann, Spain, N. BENITO, Universidad Autónoma de Madrid, Spain, N. VALLE, Centre de Recherche Public Gabriel Lippmann, Spain, V. JOCO, C. PALACIO, Universidad Autónoma de Madrid, Spain, J.R. RUBIO-ZUAZO, SpLine, European Synchrotron Radiation Facility, France	**D1-1-6** Controlling the Bioavailability of Silver Ions with a Nanocomposite Gradient Coating Produced in a Continuous Low-Pressure Plasma Process, **E. KÖRNER**, D. HEGEMANN, Empa, Switzerland
12:00 pm		
	CETR FTS **Golden West Room – 12:15 - 1:15 pm**	**CETR FTS** **Golden West Room – 12:15 - 1:15 pm**

Monday Morning, May 2, 2011

	Tribology and Mechanical Behavior of Coatings & Thin Films Room: California - Session E3-1 Tribology of Nanostructured and Amorphous Films **Moderators:** V. Fridrici, Ecole Centrale de Lyon - LTDS, O.L. Eryilmaz, Argonne National Laboratory	New Horizons in Coatings and Thin Films Room: Sunrise - Session F6 Coatings for Compliant Substrates **Moderators:** B. Beake, Micro Materials Ltd, R.M. Souza, University of Sao Paulo
10:00 am	**E3-1-1** Influence of Nanocrystalline Diamond Concentration on DLC Tribomechanical Characterizations, **V.J. TRAVA-AIROLDI**, F.R. MARCIANO, P.A. RADI, D.A. LIMA-OLIVEIRA, E.J. CORAT, Instituto Nacional de Pesquisas Espaciais - INPE, Brazil	**F6-1 Invited** Comparisons of the Mechanical and Tribological Properties of Ceramic Coatings on Glass and Polymeric Substrates, **P. KELLY**, Manchester Metropolitan University, UK, B. BEAKE, Micro Materials Ltd, UK, N. RENEVIER, University of Central Lancashire, UK
10:20 am	**E3-1-2** Effect of Diamond Nanoparticles Addition and Test Conditions on Tribological DLC Films Properties for Space Applications, **P.A. RADI**, F.R. MARCIANO, D.A. LIMA-OLIVEIRA, E.J. CORAT, V.J. TRAVA-AIROLDI, Instituto Nacional de Pesquisas Espaciais - INPE, Brazil, L.V. SANTOS, Technological Institute of Aeronautics, Brazil	Invited talk continued.
10:40 am	**E3-1-3** The Influence of Bilayer Period and Thickness Ratio on the Mechanical and Tribological Properties of CrSiN/TiAlN Multilayer Coatings, **M.-K. WU**, Tungnan University, Taiwan, J.-W. LEE, Mingchi University of Technology, Taiwan, J.-C. HUANG, Tungnan University, Taiwan, H.-W. CHEN, Y.-C. CHAN, J.-G. DUH, National Tsing Hua University, Taiwan	**F6-3** X-Ray Mechanical Properties of Metallic Thin Films Supported by Polyimide Substrates Studied under Controlled Biaxial Loading, **P.-O. RENAULT**, S. DJAZIRI, E. LE BOURHIS, P. GOUDEAU, University of Poitiers, France, D. THIAUDIÈRE, Synchrotron Soleil, France, D. FAURIE, CNRS, Lpmtm Upr9001, France, F. HILD, LMT Cachan, France
11:00 am	**E3-1-4** Microstructure, Scratch and Wear Behavior in Thick Ti-Si-C-N and Ti-Al-V-Si-C-N Nanocomposites, **Y.-C. CHAN**, H.-W. CHEN, National Tsing Hua University, Taiwan, R. WEI, Southwest Research Institute, J.-G. DUH, National Tsing Hua University, Taiwan, J.-W. LEE, Mingchi University of Technology, Taiwan	**F6-4** Film Compliance and Constrained Yielding Effects on Interfacial Failure in Polymer-Metal Thin Film Structures, **N.R. MOODY**, Sandia National Laboratories, M.D. ONG, Whitworth College, M.S. KENNEDY, Clemson University, E.D. REEDY, JR., E. CORONA, D.P. ADAMS, Sandia National Laboratories, D.F. BAHR, Washington State University
11:20 am	**E3-1-5 Invited** Design and Deposition of Amorphous Carbon Nanocomposite Coatings for Tribological Application, T. TAKENO, Tohoku University, Japan, J. FONTAINE, Ecole Centrale de Lyon - LTDS, France, **M. GOTO**, Ube National College of Technology, Japan, K. ITO, Nihon University, Japan, H. MIKI, K. ADACHI, Tohoku University, Japan, M. BELIN, Ecole Centrale de Lyon - LTDS, France, T. TAKAGI, Tohoku University, Japan	**F6-5** *In situ* Synchrotron X-Ray Strains Measurement in Film/Compliant Substrate Composites During Continuous Mechanical Tests, **D. FAURIE**, Université Paris, France, G. GEANDIER, P.-O. RENAULT, E. LE BOURHIS, P. GOUDEAU, University of Poitiers, France
11:40 am	Invited talk continued.	**F6-6** Paraffin Wax Passivation Layer Improvements in Electrical Characteristics of Bottom Gate Amorphous Indium-Gallium-Zinc Oxide Thin-Film Transistors, **G.-W. CHANG**, National Chiao Tung University, Taiwan
12:00 pm	**E3-1-7** Improvement in the Resistance to Corrosion and Tribo-Corrosion of 301 Stainless Steel and Ti-6Al-4V Substrates Induced by Silicon-Based Multilayer Coatings, **D. LI**, S. GURUVENKET, S. HASSANI, M. AZZI, Ecole Polytechnique de Montreal, Canada, J. SZPUNAR, McGill University, Canada, J. KLEMBERG-SAPIEHA, L. MARTINU, Ecole Polytechnique de Montreal, Canada	
12:20 pm	**CETR FTS** **Golden West Room – 12:15 - 1:15 pm**	**CETR FTS** **Golden West Room – 12:15 - 1:15 pm**

Characterization: Linking Synthesis, Microstructure, and Properties
Room: Tiki Pavilion - Session TS4-1
Moderators: C. Scheu, University of Munich, P. Schaaf, TU Ilmenau, Institut für Werkstofftechnik, F. Giuliani, Imperial College London

NOTES

10:00 am	**TS4-1-1 Invited** Strain Mapping in Nanostructures and Thin Films by Dark-Field Electron Holography, M. HŸTCH, **N. CHERKASHIN**, S. REBOH, E. JAVON, F. HOUDELLIER, E. SNOECK, CEMES-CNRS, Université de Toulouse, France
10:20 am	Invited talk continued.
10:40 am	**TS4-1-3** Electronic Structure Investigation of Amorphous CrC_x Films, **M. MAGNUSON**, Linköping University, Sweden, M. HANSON, Uppsala University, Sweden, J. LU, L. HULTMAN, Linköping University, Sweden, U. JANSSON, Uppsala University, Sweden
11:00 am	**TS4-1-4** Electrical and Structural Properties of Ultrathin Polycrystalline and Epitaxial TiN Films Grown by Reactive Magnetron Sputtering, F. MAGNUS, A.S. INGASON, S. OLAFSSON, University of Iceland, **JT. GUDMUNDSSON**, Shanghai Jiao Tong University, China
11:20 am	**TS4-1-5** On X-Ray Diffraction Study of Stresses and Preferred Grain Orientations in Thin Films - Specific Non-Routine Cases, **R.K. KUŽEL**, Charles University in Prague, Faculty of Mathematics and Physics, Czech Republic, Z. MATĚJ, L. NICHTOVÁ, Charles University in Prague, Faculty of Mathematics and Physics, J. BURŠÍK, Institute of Inorganic Chemistry of Academy of Sciences of the Czech Republic, D. ŠIMEK, Technical University Bergakademie Freiberg, Germany, J. MUSIL, University of West Bohemia, Czech Republic
11:40 am	**TS4-1-6** Information Depth of Mono-Atomic and Poly-Atomic Primary Ions in Secondary Ion Mass Spectrometry (SIMS): Fundamentals and Applications, F. KOLLMER, ION-TOF GmbH, Germany, D. BREITENSTEIN, Tascon GmbH, Germany, N. HAVERCROFT, ION-TOF USA, Inc., P. BRUENER, ION-TOF GmbH, Germany, M. FARTMANN, B. HAGENHOFF, Tascon GmbH, Germany, E. NIEHUIS, ION-TOF GmbH, Germany, **A. SCHNIEDERS**, ION-TOF USA, Inc.
12:00 pm	**TS4-1-7** XPS on Ar Atoms to Determine Local Structures of Thin Films Prepared by Magnetron Sputtering and PECVD, A. RASTGOO LAHROOD, **T. DE LOS ARCOS**, M. PRENZEL, J. WINTER, Ruhr-Universität Bochum, Germany

CETR FTS
Golden West Room – 12:15 - 1:15 pm

CETR FTS
Golden West Room – 12:15 - 1:15 pm

Monday Afternoon, May 2, 2011

	Hard Coatings and Vapor Deposition Technology Room: Royal Palm 1-3 - Session B2-2 CVD Coatings and Technologies **Moderators:** S. Ruppi, Walter AG, F. Maury, CIRIMAT CNRS-INPT-UPS ENSIACET	Hard Coatings and Vapor Deposition Technology Room: Golden West - Session B4-2 Properties and Characterization of Hard Coatings & Surfaces **Moderators:** M. Fenker, FEM Research Institute, B. Zhao, Exxon Mobil
1:30 pm	**B2-2-1 Invited** High-Speed Coating of α-Al_2O_3 Film by Laser Chemical Vapor Deposition on Cutting Tools, **T. GOTO**, Tohoku University, Japan	**B4-2-2** Al- and Cr-Doped TiSiCN Coatings with High Thermal Stability and Oxidation Resistance, **D.V. SHTANSKY**, K.A. KUPTSOV, P.V. KIRUYKHANTSEV-KORNEEV, A.N. SHEVEIKO, National University of Science and Technology "MISIS", Russia, A. FERNANDEZ, Instituto de Ciencia de Materiales de Sevilla, Spain
1:50 pm	Invited talk continued.	**B4-2-3 Invited** Transition Metal Oxynitride Coatings: Enhancing Performance by Adding Oxygen, **L. CASTALDI**, Oerlikon Balzers AG, Liechtenstein
2:10 pm	**B2-2-3** Protective Aluminum Oxide Coatings on Titanium Alloys from Al Metal-Organic Chemical Vapor Deposition, Y. BALCAEN, N. RADUTOIU, Université de Toulouse, INPT/ENIT, LGP, France, D. SAMELOR, Université de Toulouse, CIRIMAT/INPT/CNRS, France, **J. ALEXIS**, L. LACROIX, J.D. BEGUIN, Université de Toulouse, INPT/ENIT, LGP, France, A. GLEIZES, C. VALHAS, Université de Toulouse, CIRIMAT/INPT/CNRS, France	Invited talk continued.
2:30 pm	**B2-2-4** Thermal Stability and Cutting Performance of Ti or Zr-Doped κ-Al_2O_3 Coatings by CVD, **M. OKUDE**, K. TOMITA, E. NAKAMURA, A. OSADA, Mitsubishi Materials Corporation, Japan	**B4-2-5** Impact of Nb and Ta on the Phase Stability of Ti-Al-N Thin Films, **R. RACHBAUER**, D. HOLEC, P.H. MAYRHOFER, University of Leoben, Austria
2:50 pm	**B2-2-5** Microstructure and Wear Characteristics of Texture Controlled CVD a -Al_2O_3 and MT-CVD Ti(C,N) Layers during Steel Machining, R. M'SAOUBI, O. ALM, T. LARSSON, **M. JOHANSSON**, S. RUPPI, Seco Tools AB Fagersta, Sweden	**B4-2-6** Improved Thermal Stability of TiAlN Through Cr Additions, **R. FORSÉN**, H. LIND, Linköping University, Sweden, M. JOHANSSON, Seco Tools AB Fagersta, Sweden, F. TASNÁDI, I. ABRIKOSOV, N. GHAFOOR, M. ODÉN, Linköping University, Sweden
3:10 pm	**B2-2-6** Effect of the N/Al Ratio in the Gas Phase at Constant Supersaturation on AlN Epitaxy on Sapphire by HTCVD, N.E. BACCAR, Grenoble-INP, France, R. BOICHOIT, E. BLANQUET, **M. PONS**, SIMAP, France	**B4-2-7** Quantification of the Hydrogen Content of a-C and a-C:H-Coatings Produced at Various Bias Voltages and their Tribological Behavior under Different Humid Conditions, W. TILLMANN, **F. HOFFMANN**, S. MOMENI, Technische Universität Dortmund, Germany, R. HELLER, Forschungszentrum Dresden-Rossendorf (FDZ) e.V., Germany
3:30 pm	**B2-2-7** Doped CVD Coatings – Process, Properties and Machine Technology, **H. STRAKOV**, R. BONETTI, A. SCOTT, Ionbond AG, Switzerland	**B4-2-10** Bonding Structures and Mechanical Properties of Silicon Doped Carbon Nitride Films, **S.B. WEI**, T.M. SHAO, Tsinghua University, China **STUDENT AWARD FINALIST**
3:50 pm	**B2-2-8** CO Addition in Low-Pressure Chemical Vapor Deposition of Medium-Temperature TiCN Based Hard Coatings, **C. CZETTL**, Materials Center Leoben Forschung GmbH, Leoben, Austria, C. MITTERER, Montanuniversität Leoben, Austria, D. RAFAJA, U. MÜHLE, TU Bergakademie Freiberg, Germany, S. PUCHNER, TU Vienna, Austria, M. PENOY, C. MICHOTTE, CERATIZIT Luxembourg S. à. r. l. , Mamer, Luxembourg, M. KATHREIN, CERATIZIT Austria	
4:10 pm	**B2-2-10** Snthesis and Sensitivity by UV Light of SnO_2-ZnO Core-Shell Nanowires, **K.-Y. PAN**, H-C. SHIH, National Tsing Hua University, Taiwan, M.-H. CHAN, Instrument Technology Research Center, Taiwan	
4:30 pm	**B2-2-11** Optical and NO Gas Sensing Properties of GaN/Ga_2O_3 Zigzag Nanowires, **L.-W. CHANG**, J.-W. YEH, H-C. SHIH, National Tsing Hua University, Taiwan	
4:50 pm	**B2-2-12** Equilibrium Segregation of Graphene on Polycrystalline Ni Surfaces by Chemical Vapor Deposition, **C.-J. HSU**, P.-K. NAYAK, National Cheng Kung University, Taiwan, J.-C. SUNG, KINIK Company, Taiwan, S.-C. WANG, Southern Taiwan University, Taiwan, J.-L. HUANG, National Cheng Kung University, Taiwan	
	VAMAS 5:10 - 6:10 pm Golden West Room **Welcome Reception – Atlas Foyer 6:00 - 7:30 pm**	**VAMAS 5:10 - 6:10 pm Golden West Room** **Welcome Reception – Atlas Foyer 6:00 - 7:30 pm**

Monday Afternoon, May 2, 2011

	Fundamentals & Technology of Multifunctional Thin Films: Towards Optoelectronic Device Applications **Room: Sunset - Session C2/F4-1** **Thin Films for Photovoltaics and Active Devices** **Moderators:** T. Miyata, Kanazawa Institute of Technology, A.P. Ehiasarian, Sheffield Hallam University	**Biomedical Coatings** **Room: Royal Palm 4-6 - Session D1-2** **Bioactive and Biocompatible Coatings and Surface Functionalization of Biomaterials** **Moderators:** E. Saiz, Imperial College, S. Kumar, University of South Australia
1:30 pm	**C2/F4-1-1 Invited** Plasma Processing for Photovoltaics: Fundamentals and Applications, **R. VAN DE SANDEN**, Eindhoven University of Technology, Netherlands	**D1-2-1** Fabrication of Superhydrophilic and Superhydrophobic Surfaces on Titanium Substrates, **R. FLEMING**, M. ZOU, University of Arkansas
1:50 pm	Invited talk continued.	**D1-2-2** Strontium as a Bioactive Agent in Magnetron-Sputtered Titanium Coatings, **M. SILLASSEN**, O.Z. ANDERSEN, Aarhus University, Denmark, K.P. ALMTOFT, K. RECHENDORFF, L.P. NIELSEN, Danish Technological Institute, Tribology Centre, Denmark, M. FOSS, J. BØTTIGER, Aarhus University, Denmark
2:10 pm	**C2/F4-1-3** Glancing Angle Deposited Sculptured Titania Films for Light Scattering Enhancement in Solar Cells, **K.-H. HUNG**, Industrial Technology Research Institute, Taiwan, G.-D. CHIOU, M.-S. WONG, National Dong Hwa University, Taiwan, Y.C. WANG, W.-T. KUO, I-.S. CHUNG, C.-M. YEH, Industrial Technology Research Institute, Taiwan	**D1-2-3** Bioactivity and Corrosion Resistance of Surface Treated F138 Stainless Steel, **V.H. BAGGIO-SCHEID**, Institute of Advanced Studies, Brazil, L. MARCHINI, R.F. DA ROCHA, C.P. DE DECO, State University of São Paulo - UNESP, Brazil
2:30 pm	**C2/F4-1-4** Optical and Mechanical Characterisation of Nanostructured Antireflectance Coatings for Solar Cells, **J. MOGHAL**, University of Oxford, UK, J. BEST, M. GARDENER, Oxford Advanced Surfaces Group plc, UK, A.A.R. WATT, Univeristy of Oxford, UK, G. WAKEFIELD, Oxford Advanced Surfaces Group plc, UK	**D1-2-4** Mechanical, Tribological and Corrosion Behavior of Multilayer Coating of Ti/TiN/nc-TiN/a-Si_3N_4 Deposited by Sputtering on Stainless Steel M340 and Ti6Al4V Substrates for Biomedical Applications, **J. GARCIA**, Universidad Panamericana, Mexico, M. FLORES, Universidad de Guadalajara, Mexico, L. PAZOS, Instituto Nacional de Tecnologia Industrial, Argentina, O. JIMENEZ, Universidad de Guadalajara, Mexico
2:50 pm	**C2/F4-1-7 Invited** Polymeric Materials and Self-Assembled Interlayers for Printed Photovoltaic Cells, **A. FACCHETTI**, Polyera Corporation and Northwestern University	**D1-2-7** Development of Nanostructured Ternary Shape Memory Alloy Thin Films for Biomedical Applications, **N. KAUR**, N. CHOUDHARY, D. KAUR, Indian Institute of Technology Roorkee, India
3:10 pm	Invited talk continued.	
3:30 pm	**C2/F4-1-9** Fabrication of Large Area TiO_2 NT Dye-Sensitized Solar Cell on Stainless-Steel by Thermal Spraying and Anodizing Methods, **C.-C. CHEN**, National United University, Taiwan, C-.K. LIN, C.-J. CHANG, Feng Chia University, Taiwan, C.-H. HSU, Tatung University, Taiwan, W.-D. JHENG, National Chin-Yi University of Technology, Taiwan	
3:50 pm	**C2/F4-1-10** Effect of (poly)Phosphate Anion Structure on Characteristics of Pulsed DC PEO Coatings on Ti, for Dye Sensitised Solar Sell Applications, **P.-J. CHU**, A. YEROKHIN, University of Sheffield, UK, J.-L. HE, Feng Chai University, Taiwan, A. MATTHEWS, University of Sheffield, UK	
4:10 pm	**C2/F4-1-6** Effects of Additive in Cu Solution for Electrodeposition of $CuInSe_2$ Film, **T.-W. CHANG**, National Cheng Kung University, Taiwan, W-.H. LEE, National Cheng-Kung University, Taiwan, Y.-H. SU, F.-I. CHIH, National Cheng Kung University, Taiwan	
4:30 pm		
4:50 pm		
	VAMAS 5:10 - 6:10 pm Golden West Room **Welcome Reception – Atlas Foyer 6:00 - 7:30 pm**	**VAMAS 5:10 - 6:10 pm Golden West Room** **Welcome Reception – Atlas Foyer 6:00 - 7:30 pm**

Monday Afternoon, May 2, 2011

	Tribology & Mechanical Behavior of Coatings and Thin Films Room: California - Session E3-2 **Tribology of Nanostructured and Amorphous Films** **Moderators:** V. Fridrici, Ecole Centrale de Lyon - LTDS, O.L. Eryilmaz, Argonne National Laboratory	Characterization: Linking Synthesis, Microstructure, and Properties - Room: Tiki Pavilion - Session TS4-2 **Moderators:** C. Scheu, University of Munich, P. Schaaf, TU Ilmenau, Institut für Werkstofftechnik, F. Giuliani, Imperial College London
1:30 pm	**E3-2-1** Prediction of the Friction Behavior of Lubricated Tribological Systems Containing Amorphous Carbon Coatings using an Artificial Neural Network, **E. SCHULZ**, S. ROEHNER, S. TREMMEL, Friedrich-Alexander-University Erlangen-Nuremberg, Germany, Y. MUSAYEV, T. HOSENFELDT, Schaeffler Technologies GmbH & Co. KG, Germany, H. MEERKAMM, S. WARTZACK, Friedrich-Alexander-University Erlangen-Nuremberg, Germany	**TS4-2-3** Application of LEIS Static and Sputter Depth Profiling as a Novel Approach for Ultra-Thin Film Analysis, P. BRUENER, **T. GREHL**, R. MOELLERS, ION-TOF GmbH, Germany, N. HAVERCROFT, ION-TOF USA, Inc., H.H. BRONGERSMA, E. NIEHUIS, ION-TOF GmbH, Germany
1:50 pm	**E3-2-2** Fatigue Properties of a 21MnCr5 Steel Coated with an Amorphous Carbon Coating, **S. TREMMEL**, Friedrich-Alexander-University Erlangen-Nuremberg, Germany, B. VON GROßMANN, Georg Simon Ohm University of Applied Sciences Nuremberg, Germany, S. WARTZACK, Friedrich-Alexander-University Erlangen-Nuremberg, Germany	**TS4-2-4** Microstructure of Hot Dip Coated Fe-Si Steels, **I. INFANTE DANZO**, K. VERBEKEN, Y. HOUBAERT, Gent University, Belgium
2:10 pm	**E3-2-3** The Effect of Coating Properties on the Fracture Characteristics and Tribological Performance of a-C:H and ta-C Films, **H.A. RONKAINEN**, K. HOLMBERG, A. LAUKKANEN, T. ANDERSSON, VTT Technical Research Centre of Finland, M. KUMAGAI, M. KANO, T. HORIUCHI, Kanagawa Industrial Technology Center, Japan, T. SUZUKI, Keio University, Japan, M. TAKI, Onward Ceramic Coating Co, Ltd., Japan	**TS4-2-5** High Supercapacitive Stability of ZnO-Added Manganese Oxide Coatings, **C.-Y. CHEN**, H.-W. CHANG, Feng Chia University, Taiwan, S.-J. SHIH, National Taiwan University of Science and Technology, Taiwan, R.-B. YANG, C-.K. LIN, Feng Chia University, Taiwan
2:30 pm	**E3-2-4** Stress Reduction in Hard a-C:N DLC Coatings, **S. LOURING**, N.D. MADSEN, A.N. BERTHELSEN, Aarhus University, Denmark, B.H. CHRISTENSEN, K.P. ALMTOFT, L.P. NIELSEN, Danish Technological Institute, Tribology Centre, Denmark, J. BØTTIGER, Aarhus University, Denmark	**TS4-2-6 Invited** Spectroscopic Ellipsometry for Thin Film Characterization, **H. ARWIN**, Linköping University, Sweden
2:50 pm	**E3-2-5** 2.5 nm Thick TiSiN Protection Layer for HDD Magnetic Media, **F. ROSE**, D. POCKER, Q.-F. XIAO, B. MARCHON, Hitachi Global Storage Technologies Inc.	Invited talk continued.
3:10 pm	**E3-2-6** Tribology Behavior of Nanocrystallite Carbon Film Prepared by ECR Sputtering Method, **C. WANG**, D. DIAO, Xian Jiaotong University, China	**TS4-2-8** *In Situ*, Elevated Temperature Micro-Compression of Silicon, **J.M. WHEELER**, R. GHISLENI, J. MICHLER, Empa, Switzerland
3:30 pm	**E3-2-7** Tribological Behaviour of Aluminum Against Tungsten Doped DLC at Elevated Temperatures, **A. ABOU GHARAM**, University of Windsor, Canada, M.J. LUKITSCH, General Motors Research and Development Center, A.T. ALPAS, University of Windsor, Canada	**TS4-2-9** Synthesis and Characterization of Complex Alloy Thin Films, **A.M. PAGON**, E.D. DOYLE, D.G. MCCULLOCH, K. LATHAM, Royal Melbourne Institute of Technology University, Australia, J.E. BRADBY, Australian National University
3:50 pm	**E3-2-8** Identification of the Wear Mechanism on WC/C Nanostructured Coatings, S. EL MRABET, M.D. ABAD, **J.C. SANCHEZ-LOPEZ**, Instituto de Ciencia de Materiales de Sevilla, Spain	**TS4-2-11** Atomic-Scale Understanding of the Thermal Stability of 6H-SiC(0001): An *In Situ Scanning Tunneling Microscopy Study*, Y. MURATA, University of California at Los Angels, V. PETROVA, I. PETROV, University of Illinois at Urbana-Champaign, **S. KODAMBAKA**, University of California at Los Angels
4:10 pm	**E3-2-9 Invited** Advanced Applied Technology of DLC Coatings, **M. KANO**, Kanagawa Industrial Technology Center, Japan	**TS4-2-12** Swift Heavy Ion Induced Modifications of Nanostructured Ni-Mn-Sn Ferromagnetic Shape Memory Alloy Thin Films, **R. VISHNOI**, R. SINGHAL, **D. KAUR**, Indian Institute of Technology Roorkee, India
4:30 pm	Invited talk continued.	
4:50 pm	**E3-2-11** Superlow Friction of SiO_x-Doped DLC Coatings under Oxygen and Hydrogen Ambients, **J. FONTAINE**, Ecole Centrale de Lyon - LTDS, France, R.W. CARPICK, University of Pennsylvania, S.V. PRASAD, Sandia National Laboratories, T. LE MOGNE, S. BEC, Ecole Centrale de Lyon - LTDS, France	
5:10 pm	**E3-2-12** Mechanical and Tribological Properties of a-C:H Thin Films Prepared by an Unbalanced Magnetron Sputtering System, **B. FENG**, S.C. TAYLOR, L.V. DAVIES, Caterpillar Inc	**VAMAS 5:10 - 6:10 pm Golden West Room** **Welcome Reception – Atlas Foyer 6:00 - 7:30 pm**

Monday Afternoon, May 2, 2011

	Energetic Materials and Micro-Structures for Nanomanufacturing **Room: Sunrise - Session TS5** **Moderators:** C. Rebholz, University of Cyprus, C.C. Doumanidis, University of Massachusetts Lowell, T. Ando, Northeastern University	**NOTES**
1:30 pm	**TS5-1** Self-Propagating High Temperature Synthesis of B2-RuAl Thin Films, **K. WOLL**, F. MÜCKLICH, Saarland University, Germany	
1:50 pm	**TS5-2** Effects of Environment on the Self-Propagating Synthesis of Reactive Multilayers Fabricated by Sputter Deposition, **D.P. ADAMS**, J.P. MCDONALD, E.D. JONES, JR., M.A. RODRIGUEZ, Sandia National Laboratories	
2:10 pm	**TS5-3 Invited** Rapid Formation Reactions in Nanolayered Foils and Particles: Scientific Studies and Commercial Applications, **T.P. WEIHS**, Johns Hopkins University	
2:30 pm	Invited talk continued.	
2:50 pm	**TS5-5** The Effect of Interface Quality on Self Propagating Exothermic Reactions (SPER) in Ni-Al Multilayer Foils, **K. FADENBERGER**, I.E. GUNDUZ, University of Cyprus, F. NAHIF, RWTH Aachen University, K.P. GIANNAKOPOULOS, National Center for Scientific Research “Demokritos”, Greece, B. SCHMITT, Paul Scherrer Institut, Germany, J.M. SCHNEIDER, RWTH Aachen University, Germany, P.H. MAYRHOFER, University of Leoben, Austria, C.C. DOUMANIDIS, C. REBHOLZ, University of Cyprus **STUDENT AWARD FINALIST**	
3:10 pm	**TS5-6** Streak Spectrograph Temperature Analysis from Electrically Forced Multilayered Ni/Al Formation Reactions, **C.J. MORRIS**, U.S. Army Research Laboratory, P. WILKINS, C. MAY, Lawrence Livermore National Laboratory, E. ZAKAR, U.S. Army Research Laboratory, T.P. WEIHS, Johns Hopkins University	
3:30 pm	**TS5-8 Invited** Fully-Dense Reactive Nanocomposite Powders and their Reaction Mechanisms, **E.L. DREIZIN**, New Jersey Institute of Technology	
3:50 pm	Invited talk continued.	
4:10 pm	**TS5-10** Ignitable Al/Ni Compacts Produced by Mechanical Alloying: Structural, Chemical and Thermal Characterization, **A. HADJIAFXENTI**, I.E. GUNDUZ, University of Cyprus, S.M. AOUADI, Southern Illinois University, Carbondale, T. KYRATSI, C.C. DOUMANIDIS, C. REBHOLZ, University of Cyprus	
4:30 pm	**TS5-7** Large-Scale Simulations of Nanoscale Ni/Al Multilayer Foils, **I.E. GUNDUZ**, K. FADENBERGER, M. KOKONOU, C. REBHOLZ, C.C. DOUMANIDIS, University of Cyprus	
	VAMAS 5:10 - 6:10 pm Golden West Room **Welcome Reception – Atlas Foyer 6:00 - 7:30 pm**	**VAMAS 5:10 - 6:10 pm Golden West Room** **Welcome Reception – Atlas Foyer 6:00 - 7:30 pm**

Tuesday Morning, May 3, 2011

	Exhibitor Key Note Session Room: Tiki Pavilion	Hard Coatings and Vapor Deposition Technology Room: Royal Palm 1-3 - Session B1-1 PVD Coatings and Technologies **Moderators:** P. Eklund, Linköping University, J. Vetter, Sulzer Metaplas GmbH, J.-H. Huang, National Tsing Hua University
8:00 am	**EXHIBITORS KEYNOTE SESSION** **TIKI PAVILION – 9:40 AM** **Keynote speaker: Dr. William D. Sproul** **ABSTRACT** **Reactive Sputtering: Evolution, Development, and Latest Trends** **William D. Sproul** **Reactive Sputtering, Inc., San Marcos, CA** **and** **Jianliang Lin and John J. Moore** **Colorado School of Mines, CO** **Please View Abstract on Page xi**	**B1-1-1 Invited** Magnetron Sputtering, Past, Present and Future., **V. BELLIDO-GONZALEZ**, D. MONAGHAN, M. AUDRONIS, Gencoa Ltd, UK
8:20 am		Invited talk continued.
8:40 am		**B1-1-3** Capability of Gas Flow Sputtering to Coat Non Line of Sight Areas, **S. TANG**, U. SCHULZ, German Aerospace Center, Germany
9:00 am		**B1-1-4** Influence of Inert Gas Species on Plasma Characteristics and Film Growth in a Magnetron Discharge, **G.T. WEST**, P. KELLY, Manchester Metropolitan University, UK
9:20 am		**B1-1-5 Invited** Large Area EB-PVD and Plasma Activated EB Evaporation - Status and Prospects, **E. REINHOLD**, J. FABER, VON ARDENNE Anlagentechnik GmbH, Germany
9:40 am		Invited talk continued.
10:00 am		**B1-1-7** High Power Discharge-Based EB Sources for PVD and Vacuum Metallurgy – PIC Simulation and Experimental Results, **P. FEINAEUGLE**, G. MATTAUSCH, F.-H. ROEGNER, Fraunhofer-Institut fur Elektronenstrahl- und Plasmatechnik (FEP), Germany
10:20 am		**B1-1-10** Modification of PVD TiN Coatings by Interrupting Film Growth, **T. SINKOVITS**, Y. ZHAO, D. SAINI, University of Wollongong, Australia, S.J. DOWEY, Surface Technology Coatings Pty, Australia
10:40 am		**B1-1-11** Thick Nanocrystalline AlCr(Si)N/TiN Hardcoatings Deposited by DC Arc Evaporation, **F. KAULFUSS**, Fraunhofer IWS, Germany, C. ENDTER, P. BOGUTZKI, W. SIEBERT, Dresden University of Technology, Germany, O. ZIMMER, Fraunhofer-Institut für Werkstoff- und Strahltechnik IWS Dresden, Germany
11:00 am		**B1-1-12** Study of CrN and NbC Interlayers for HFCVD Diamond Deposition onto WC-Co Substrates, **M. FENKER**, K. PETRIKOWSKI, FEM Research Institute, Germany, J. GÄBLER, S. PLEGER, L. SCHÄFER, Fraunhofer IST, Braunschweig, Germany
11:20 am		**B1-1-9** Microstructure and Mechanical Properties of Hard Ceramic Coatings Deposited by Arc Plasma Acceleration Process, **V.N. KHOMINICH**, D.C. BELL, Phygen Coatings Inc, N. SCHWARZER, Saxonian Institute of Surface Mechanics, Germany, G. FAVARO, CSM Instruments, Switzerland
11:40 am		
	Exhibition Open Today **11:00 am - 7:00 pm** **Town and Country/San Diego Room**	**Exhibition Open Today** **11:00 am - 7:00 pm** **Town and Country/San Diego Room**

Tuesday Morning, May 3, 2011

	Hard Coatings and Vapor Deposition Technology Room: Golden West - Session B4-3 Properties and Characterization of Hard Coatings and Surfaces **Moderators:** M. Fenker, FEM Research Institute, B. Zhao, Exxon Mobil	Fundamentals and Technology of Multifunctional Thin Films: Towards Optoelectronic Device Applications Room: Sunset - Session C2/F4-2 Thin Films for Photovoltaics and Active Devices **Moderators:** T. Miyata, Kanazawa Institute of Technology, A.P. Ehiasarian, Sheffield Hallam University
8:00 am	**B4-3-2** Layer Structure and Interface Effects on Corrosion Behavior of Multilayer CrN/NiP Composite Coatings, **Y.-Y. LI**, F.-B. WU, National United University, Taiwan	**C2/F4-2-1** Influence of Sputtering Powers on the Characteristics of ZnO:B Thin Films, L.-H. WONG, **Y.-S. LAI**, National United University, Taiwan, D.-S. WUU, National Chung Hsing University, Taiwan, J.-L. WANG, Ming Chi University of Technology, Taiwan
8:20 am	**B4-3-3 Invited** In Situ Structural Characterization of TM-Si-N and TM-B-N Coatings During Air Oxidation, **J.-F. PIERSON**, A. MÈGE-REVIL, D. PILLOUD, Ecole des Mines de Nancy, France	**C2/F4-2-2** High Mobility Transparent Conducting Oxides: A Modulation Doping Approach, **S.H.N. LIM**, R.J. MENDELSBERG, A. ANDERS, K.M. YU, Lawrence Berkeley National Laboratory
8:40 am	Invited talk continued.	**C2/F4-2-3** Dominant Factors Determining Moisture Resistance of Highly Transparent Conductive Ga-Doped ZnO Films, **Y. SATO**, T. YAMADA, H. MAKINO, N. YAMAMOTO, T. YAMAMOTO, Kochi University of Technology, Japan
9:00 am	**B4-3-5** Monitoring of Pitting Formation and Growth in TiN Film Deposited by Arc PVD Method as a Function of Time with Polarization Resistance and EIS, **I.K. KÜÇÜK**, Cumhuriyet University, Turkey, C.S. SARIOGLU, Marmara University, Turkey	**C2/F4-2-4** Changes in Electrical and Optical Properties of Polycrystalline Ga-Doped ZnO Thin Films Due to Thermal Desorption of Zinc, **H. MAKINO**, Y. SATO, N. YAMAMOTO, T. YAMAMOTO, Kochi University of Technology, Japan
9:20 am	**B4-3-6** Microstructure and Mechanical Properties Evaluation of Pulsed DC Magnetron Sputtered Cr-B and Cr-B-N Films, C.-H. CHENG, Tungnan University, Taiwan, J.-W. LEE, Mingchi University of Technology, Taiwan, J.-C. HUANG, Tungnan University, Taiwan, H.-W. CHEN, Y.-C. CHAN, **J.-G. DUH**, National Tsing Hua University, Taiwan	**C2/F4-2-6** Bending Properties of Transparent Conductive Ga-doped ZnO Films, **K. NAGAMOTO**, K. KATO, S. NAGANAWA, T. KONDO, LINTEC Corporation, Japan, Y. SATO, H. MAKINO, N. YAMAMOTO, T. YAMAMOTO, Kochi University of Technology, Japan
9:40 am	**B4-3-8** Atomic and Electronic Structural Studies of Metal Nitrides (VN, CrN)/ MgO Interface by C_S-Corrected TEM, **Z. ZHANG**, B. RASHKOVA, Austrian Academy of Sciences, Austria, G. DEHM, Montanuniversität Leoben, Austria, P. LAZAR, J. REDINGER, Vienna University of Technology, Austria, R. PODLOUCKY, University of Vienna, Austria	**C2/F4-2-7** H-Bonded Effects and Properties of Novel Supramolecular Nanocomposites Containing Aryl-Imidazo-Phenanthroline -Based Metallo- Polymer H-Donors and Surface-Modified ZnO Nanoparticle H-Acceptors, **H.-P. FANG**, H.-C. LIN, National Chiao Tung University, Taiwan
10:00 am	**B4-3-11** The Mechanical Properties of Ti-Si-N Nanocomposite Films Deposited by Magnetron Sputtering, W.-R. CHEN, **G.-P. YU**, J.-H. HUANG, National Tsing Hua University, Taiwan	**C2/F4-2-8** Non-vacuum Process of ZnO Thin Films Grown by Spray Pyrolysis Technique, **K. YOSHINO**, University of Miyazaki, Japan, Y. TAKEMOTO, M. SHINMIYA, M. OSHIMA, University fof Miyazaki, Japan, K. TOYODA, K. INABA, K. HAGA, K. TOKUDOME, Tosoh-finechem Co. Ltd., Japan
10:20 am	**B4-3-12** Mechanical Properties of TaN-Cu Nanocomposite Thin Films After Multiple Annealing, **J.-H. HSIEH**, Y.-J. LIN, Ming Chi University of Technology, Taiwan, S.I. CHANG, National Chung Hsing University, Taiwan	**C2/F4-2-9** Electrical Conductivity Enhancement of Nb-Doped TiO_2 Sputtered Thin Films by a Post Hot-Wire Annealing in a H_2 Atmosphere, **C.J. TAVARES**, M.V. CASTRO, P. ALPUIM, E.S. MARINS, A.S. SAMANTILLEKE, S. FERDOV, M. BENELMEKKI, University of Minho, Portugal, E. XURIGUERA, Universitat de Barcelona, Spain
10:40 am	**B4-3-9** Investigation of Fundamental Deformation Parameters of Magnetron Sputtered TiAlN Films using High Temperature Nanoindentation from 300 K to 623 K, **M. WERCHOTA**, Montanuniversität Leoben, Austria, P.H. MAYRHOFER, University of Leoben, Austria	**C2/F4-2-10** Structural and Electrical Properties of Sol-Gel Derived Yttrium Oxide Dielectric Films, **C.-Y. TSAY**, C.-H. CHENG, Feng Chia University, Taiwan, Y.-W. WANG, National Changhua University of Education, Taiwan, C.-J. CHANG, C.-K. LIN, Feng Chia University, Taiwan
11:00 am		**C2/F4-2-11** Preparation, Synthesis Techniques and Some Properties on CdMnS Diluted Magnetic Semiconductor Thin Films, **J. DARGAD**, Dayanand Science College, India
11:20 am		**C2/F4-2-12** Structural, Electrical and Optical Properties of $AgInTe_2$ Films Grown by a Hot Wall Technique, **A. SINGH**, R.K. BEDI, Guru Nanak dev University, Amritsar, India
11:40 am		
	Exhibition Open Today 11:00 am - 7:00 pm Town and Country/San Diego Room	**Exhibition Open Today 11:00 am - 7:00 pm Town and Country/San Diego Room**

Tuesday Morning, May 3, 2011

	Biomedical Coatings Room: Royal Palm 4-6 - Session D2 Coatings for Biomedical Implants **Moderators:** R. Hauert, Empa, J.R. Piascik, RTI International	Tribology and Mechanical Behavior of Coatings &Thin Films Room: California - Session E1-1 - Friction and Wear of Coatings: Lubrication, Surface Effects, and Modeling **Moderators:** J.C. Sanchez-Lopez, Instituto de Ciencia de Materiales de Sevilla (CSIC-US), R.D. Evans, The Timken Company, S.M. Aouadi, Southern Illinois University, Carbondale
8:00 am	**D2-1** Tribological Behavior of DLC Coated CoCrMo Alloys for Medical Joint Applications, **R. HAUERT**, U. MÜLLER, Empa, Switzerland, G. THORWARTH, Synthes GmbH, Switzerland, K. THORWARTH, M. PARLINSKA-WOJTAN, C.V. FALUB, Empa, Switzerland, C. VOISARD, Synthes GmbH, Switzerland, M. STIEFEL, Empa, Switzerland	**E1-1-1 Invited** Transition Metal Nitride Based Hard Coatings with Self-Lubricious Properties at Elevated Temperatures, **C. MITTERER**, Montanuniversität Leoben, Austria
8:20 am	**D2-2** *In Situ* Fabrication of TiN layer on the Nanostructured Surface of Orthopedic NiTi Alloy, **T. HU**, S.L. WU, J. JIANG, City University of Hong Kong, Y. ZHAO, The University of Hong Kong, C.L. CHU, Southeast University, China, P.K. CHU, K.W.K. YEUNG, City University of Hong Kong	Invited talk continued.
8:40 am	**D2-3 Invited** From DLC to Nanocrystalline Carbon Coating for Biomedical Applications, **S. MITURA**, K. MITURA, Koszalin University of Technology, Poland, P. NIEDZIELSKI, J. GRABARCZYK, Lodz University of Technology, Poland	**E1-1-3** Next Generation Temperature Adaptive Nanocomposite Coatings, **D. STONE**, Southern Illinois University, Carbondale, T. SMITH, C. MURATORE, A.A. VOEVODIN, Air Force Research Laboratory, S.M. AOUADI, Southern Illinois University, Carbondale
9:00 am	Invited talk continued.	**E1-1-4** Effect of Temperature on the Tribological Behavior of a MoS_2 Based Solid Lubricant Coating, **M. BERNARD**, V. FRIDRICI, PH. KAPSA, Ecole Centrale de Lyon - LTDS, France
9:20 am	**D2-5** Characterization of Drug Distribution in Model Polymer Films using XPS Sputter Depth Profiling, **D. SURMAN**, Kratos Analytical Inc., S. HUTTON, Kratos Analytical Ltd., UK, M. ALEXANDER, A. RAFATI, University of Nottingham, UK	**E1-1-5** A Study of Mechanical and Tribological Properties of Self-Lubricating TiAlVN Coatings at Elevated Temperatures, W. TILLMANN, **S. MOMENI**, F. HOFFMANN, Technische Universität Dortmund, Germany
9:40 am	**D2-6** Strength and Fracture Behavior of Hydroxyapatite Coatings, **H.S.T. AHMED**, A.F. JANKOWSKI, Texas Tech University	**E1-1-6** CrN-Ag and $Cr_{0.65}Al_{0.35}N$-Ag Nanocomposite Coatings for High-Temperature Adaptive Lubrication, **C.P. MULLIGAN**, Benet Laboratories, US Army ARDEC, R. DENG, T.A. BLANCHET, D. GALL, Rensselaer Polytechnic Institute
10:00 am	**D2-7** Nanomechanical Characterization of Atomic Layer Deposition Coatings for Biomedical Applications, **N. BAUER**, Oregon State University, M. WANG, Oregon Health and Science University, S. SMITH, Oregon State University, J. MITCHELL, Oregon Health and Science University, J. CONLEY, JR., Oregon State University	**E1-1-7** Innovative High Temperature Nanotribology – to 800C, **B. BEAKE**, J.F. SMITH, Micro Materials Ltd, UK
10:20 am	**D2-8** Ellipsometric Study of Protein Adsorption onto Biocompatible Coatings, **P. SILVA-BERMUDEZ**, S.E. RODIL, Universidad Nacional Autonoma de Mexico	**E1-1-8 Invited** Tribology of Nanocrystalline Oxides and Adaptive Nanocomposite Coatings: Achieving Low Friction and Wear by Shear Accommodation, **T.W. SCHARF**, The University of North Texas
10:40 am	**D2-9** Large-Scale Synthesis of Hierarchical Titanate Spheres as Cell Interface on Titanium Alloys for Bone Tissue Regeneration, S.L. WU, City Univ of Hong Kong, X.M. LIU, Hubei Univ, China, **K.W.K. YEUNG**, City Univ of Hong Kong, Z.F. DI, Chinese Academy of Sciences (CAS), China, T. HU, City Univ of Hong Kong, Z.S. XU, Hubei Univ, China, J.C.Y. CHUNG, P.K. CHU, City Univ of Hong Kong	Invited talk continued.
11:00 am		**E1-1-10** Simulations of Tribology in Nanocrystalline Metallic Films, **M. CHANDROSS**, S. CHENG, Sandia National Laboratories
11:20 am		**E1-1-11** Methodology of Selection of Coatings for Tribological Applications: Database Approach, **V. FRIDRICI**, Ecole Centrale de Lyon - LTDS, France, D.B. LUO, Southwest Jiaotong University, China, PH. KAPSA, Ecole Centrale de Lyon - LTDS, France
11:40 am		**E1-1-12** Analysis of Friction and Wear Mechanisms on Hard Coatings Deposited byReactive Magnetron Sputtering, **J.S. RESTREPO**, Universidad Nacional Autonoma de Mexico, M.F. CANO, F. SEQUEDA, J.M. GONZALEZ, A. RUDEN, Universidad del valle, Colombia, S.M. SAUNDERS, Universidad Nacional Autonoma de Mexico
	Exhibition Open Today **11:00 am - 7:00 pm** **Town and Country/San Diego Room**	**Exhibition Open Today** **11:00 am - 7:00 pm** **Town and Country/San Diego Room**

Tuesday Morning, May 3, 2011

Computational and Experimental Studies of Inorganic, Organic, and Hybrid Thin Films: An Atomistic View
Room: Sunrise - Session TS1

Moderators: A. Amassian, KAUST, J. Rosén, Linköping University

Time	Session	NOTES
8:00 am	**TS1-1 Invited** Semiconductor Nanostructures Direct-Write with an Atomic Force Microscope, **M. ROLANDI**, University of Washington	
8:20 am	Invited talk continued.	
8:40 am	**TS1-3 Invited** A Predictive Modeling Framework for Morphology Evolution in Thin Film Organic Photovoltaic Cells, **B. GANAPATHYSUBRAMANIAN**, Iowa State University	
9:00 am	Invited talk continued.	
9:20 am	**TS1-5 Invited** Real-Time Observation of Thin Film Growth, **F. SCHREIBER**, Universitaet Tuebingen, Germany	
9:40 am	Invited talk continued.	
10:00 am	**TS1-8** Computational Study of Complex Oxide Thin Film Growth with Emphasis on Surface Diffusion During the Growth Process, **V. GEORGIEVA**, University of Antwerp, Belgium, M. SARAIVA, Ghent University, Belgium, N. JEHANATHAN, G. VAN TENDELOO, University of Antwerp, Belgium, D. DEPLA, Ghent University, Belgium, A. BOGAERTS, University of Antwerp, Belgium	
10:20 am	**TS1-9** Influence of Grain Boundary Chemistry in Mix-Mobility Thin Film Growth, B. FU, W. AN, C.H. TURNER, **G.B. THOMPSON**, University of Alabama	
10:40 am		
11:00 am		
11:20 am		
11:40 am		
	Exhibition Open Today 11:00 am - 7:00 pm Town and Country/San Diego Room	**Exhibition Open Today 11:00 am - 7:00 pm Town and Country/San Diego Room**

Tuesday Afternoon, May 3, 2011

	Hard Coatings and Vapor Deposition Technology Room: Royal Palm 1-3 - Session B1-2 PVD Coatings and Technologies **Moderators:** P. Eklund, Linköping University, J. Vetter, Sulzer Metaplas GmbH, J.-H. Huang, National Tsing Hua University	Hard Coatings and Vapor Deposition Technology Room: Golden West - Session B3 Laser and Ion Beam Assisted Coatings and Technologies **Moderators:** K. Sarakinos, Linköping University, S.B. Fairchild, Air Force Research Laboratory
1:30 pm	**B1-2-1** Growth Morphology and Corrosion Resistance of Magnetron Sputtered Cr Films, **K.-T. CHIANG**, R. WEI, Southwest Research Institute	**B3-1** Growth of $Bi_5Fe_{0.5}Co_{0.5}Ti_3O_{15}$ Thin Films by Pulsed Laser Deposition, **Y. LU**, U.S. Air Force Academy, G.J. BROWN, Air Force Research Laboratory, G. KOZLOWSKI, Air Force Research Laboratory/Wright State University, K. EYINK, Air Force Research Laboratory, L. GRAZULIS, Air Force Research Laboratory/UDRI, K. MAHALINGAM, Air Force Research Laboratory
1:50 pm	**B1-2-2** Fundamental Studies on the Deposition of Nanocrystalline Diamond (n-D) Films by Means of Pulsed Laser Deposition, **H. GRÜTTNER**, Hochschule Mittweida - University of Applied Sciences, Germany	**B3-3-** Nanoparticle Fabrication by Through Thin Film Ablation, **P.T. MURRAY**, E. SHIN, L. PETRY, University of Dayton
2:10 pm	**B1-2-3 Invited** Oxidation and Degradation of Nitride Thin Films at High Temperature under Controlled Atmosphere, **F.-H. LU**, National Chung Hsing University, Taiwan	**B3-4** Laser-Deposition and Characterization of Amorphous Thermoelectric Films, **G. WILKS**, Air Force Research Laboratory, P.T. MURRAY, University of Dayton, S.B. FAIRCHILD, N. GOTHARD, J.E. SPOWART, Air Force Research Laboratory
2:30 pm	Invited talk continued.	**B3-5 Invited** Multi-Beam, Multi-Target Pulsed Laser Deposition: Beyond Single Film Deposition, **R. EASON**, University of Southampton, UK
2:50 pm	**B1-2-5** Effects of Pulsed Laser Irradiation of As-Deposited c-BN-Films using Photons of 157 nm Wavelength, **R. BERTRAM**, Hochschule Mittweida - University of Applied Sciences, Germany	Invited talk continued.
3:10 pm	**B1-2-6** High Power Impulse Magnetron Sputtering of Niobium in Non-Reactive and Reactive Gas Environments, **R.J. MENDELSBERG**, S.H.N. LIM, K.M. YU, A. ANDERS, Lawrence Berkeley National Laboratory	**B3-7** Capacitive Properties of x $BaTiO_3$-(1-x) $BiScO_3$ Thin Films Fabricated by Pulsed Laser Deposition, **C.E. STUTZ**, Air Force Research Laboratory, G. KOZLOWSKI, Wright State Univ, S. SMITH, AFRL/UDRI, A. BAKER, C. RANDALL, S. TROLIER-MCKINSTRY, Pennsylvania State University, G. LANDIS, AFRL/UDRI, J.G. JONES, AFRL, T.C. BACK, AFRL/UTC
3:30 pm	**B1-2-7** Barrier Capability of Reactively Sputtered $Ta_xZr_{1-x}N$ Films with Slight Ta Addition Against Copper Diffusion, **J.-L. RUAN**, J.-L. HUANG, National Cheng Kung University, Taiwan, H.-H. LU, National Chin-Yi University of Technology, Taiwan, J.-S. CHEN, National Cheng Kung University, Taiwan, D.-F. LII, Cheng Shiu University, Taiwan	**B3-8** Attempt to Synthesize a Ti_3SiC_2 Coating by Pulsed Laser Deposition of a Ti-Si-C Multilayer Structure, M. HOPFELD, T. KUPS, E. REMDT, M. WILKE, **P. SCHAAF**, TU Ilmenau, Institut für Werkstofftechnik, Germany
3:50 pm	**B1-2-8** The Influence of Substrate Biasing on the Crystal Orientation of γ-Al_2O_3 Films, **M. PRENZEL**, T. BALONIAK, A. KORTMANN, T. DE LOS ARCOS, A. VON KEUDELL, Ruhr-Universität Bochum, Germany	**B3-9** Pusled Laser Deposition of CsI, TiC, and HfC Coatings for Field Emission Cathodes, **T.C. BACK**, Air Force Research Laboratory/UTC, M. CAHAY, University of Cincinnati, P.T. MURRAY, University of Dayton, S.B. FAIRCHILD, J. BOECKL, Air Force Research Laboratory
4:10 pm	**B1-2-9** Target Erosion Effects in Reactive Pulsed DC Magnetron Sputtering of Amorphous and Crystalline Alumina, **N.D. MADSEN**, S. LOURING, A.N. BERTHELSEN, Aarhus University, Denmark, B.H. CHRISTENSEN, K.P. ALMTOFT, L.P. NIELSEN, Danish Technological Institute, Tribology Centre, Denmark, J. BØTTIGER, Aarhus University, Denmark	**B3-10** Growth and Characterization of SBN60:Ce Thin Films, **H. BULLER**, D. EVANS, Air Force Research Laboratory, G. COOK, Air Force Research Laboratory/Azimuth, S. BASUN, Air Force Research Laboratory/UTC, G. KOZLOWSKI, Air Force Research Laboratory/Wright State University
4:30 pm	**B1-2-10** Thermal Stability of Magnetron Sputtered Alumina Coatings with Crystalline Metastable Structure, **P. ZEMAN**, S. PROKSOVA, J. BLAZEK, R. CERSTVY, J. MUSIL, University of West Bohemia, Czech Republic	**B3-11** Structural and Compositional Control of BCN Films in PLD-Based Deposition Processes, **M.A. LANGE**, AFRL/RXBT and UTC, A. REED, C. MURATORE, Air Force Research Laboratory, J. HU, Air Force Research Laboratory/UDRI, J.J. GENGLER, Air Force Research Laboratory/Spectral Energies, J.E. BULTMAN, Air Force Research Laboratory/UDRI, J.G. JONES, A.A. VOEVODIN, Air Force Research Laboratory
4:50 pm	**B1-2-11** Effect of Seed Layer Composition on the Structure of Arc-Evaporated High Al_2O_3 Containing $(Al,Cr)_2O_3$ Hard Coatings, **M. POHLER**, R. FRANZ, Montanuniversität Leoben, Austria, J. RAMM, OC Oerlikon Balzers AG, Liechtenstein, C. POLZER, PLANSEE Composite Materials GmbH, Germany, C. MITTERER, Montanuniversität Leoben, Austria	**B3-12** Bonding Structures, Mechanical Properties and Biological Behaviors of CN_x Films Prepared by Ion Beam Assisted Deposition and Laser Induced Arc Deposition, **T.M. SHAO**, S.B. WEI, L. YIN, The State Key Lab. of Tribology at Tsinghua University, China
5:10 pm	**B1-2-12** Face-Centered Cubic $(Al_{1-x}Cr_x)_2O_3$ Thin Films: Deposition, Characterization, and Heat Treatment Studies, **A. KHATIBI**, J. PALISAITIS, P.O.Å. PERSSON, J. JENSEN, J. BIRCH, P. EKLUND, L. HULTMAN, Linköping University, Sweden	
5:30 pm	**B1-2-13** Synthesis of Free Standing Al-Cu Intermetallics by Cathodic Arc Plasma Treatment, **E.A. ARPAT**, M. URGEN, Istanbul Technical University, Turkey	**Exhibits Reception** **5:30 - 7:00 pm** **Exhibition Hall**

Tuesday Afternoon, May 3, 2011

	Fundamentals and Technology of Multifunctional Thin Films: Towards Optoelectronic Device Applications **Room: Sunset - Session C2/F4-3** **Thin Films for Photovoltaics and Active Devices** **Moderators:** T. Miyata, Kanazawa Institute of Technology, A.P. Ehiasarian, Sheffield Hallam University	**Biomedical Coatings** **Room: Royal Palm 4-6 - Session D3** **Coatings for Mitigating Bio-Corrosion, Tribo-Corrosion and Bio-Fouling** **Moderators:** M.M. Stack, University of Strathclyde, M.T. Mathew, Rush University Medical Center
1:30 pm	**C2/F4-3-1** Ultrathin Metals – a New Approach for Transparent Conductive Films, **O. ZIMMER**, M. SCHWACH, Fraunhofer-Institut für Werkstoff- und Strahltechnik IWS Dresden, Germany, S. SCHÄDLICH, IWS Dresden, Fraunhofer Institute for Material and Beam Technology, Germany	**D3-1 Invited** Metal Oxide Coatings for Dental Implants: What is Important?, P.N. ROJAS, G. RAMÍREZ, A. ALMAGUER, Universidad Nacional Autonoma de Mexico, R. OLIVARES-NAVARRETE, Georgia Institute of Technology, P. SILVA-BERMUDEZ, S. MUHL, **S.E. RODIL**, Universidad Nacional Autonoma de Mexico
1:50 pm	**C2/F4-3-2** Energy Band Lineup of Transparent Conducting Materials and High Efficient Electrodes for Organic Semiconductors, **H. YANAGI**, University of Yamanashi, Japan, T. KAMIYA, H. HOSONO, Tokyo Institute of Technology, Japan	Invited talk continued.
2:10 pm	**C2/F4-3-3** Quality Improvement of Organic Thin Films Deposited on Vibrating Substrates, Y. ANGULO, P.G. CALDAS, **M. CREMONA**, R. PRIOLI, PUC-Rio, Brazil	**D3-3** Synthesis, Characterization and Performance of Silver Nanoparticle Coatings on Bioimplants, **C.G. TAKOUDIS**, University of Illinois at Chicago
2:30 pm	**C2/F4-3-5** Investigation of the Gate-Bias Induced Instability for InGaZnO TFTs Under Dark and Light Illumination, **T.-C. CHEN**, Y.-K. YANG, National Sun Yat-sen University, Taiwan	**D3-5** Tribo-Corrosion Mechanisms of Ti Based PVD Coatings on Y-TZP Dental Implants, **M.M. STACK**, University of Strathclyde, UK, W.-L. LI, National Cheng Kung University, Taiwan
2:50 pm	**C2/F4-3-6** Effect of N_2O Plasma Treatment on the Improvement of Instability Under Light Illumination for InGaZnO Thin-Film Transistors, **T.-Y. HSIEH**, National Sun Yat-Sen University, Taiwan	**D3-7 Invited** Biotribolayer Formation in Metal-on-Metal Hip Prostheses- a Beneficial Coating Process?, **M.A. WIMMER**, M.T. MATHEW, M.P. LAURENT, Rush University Medical Center, A. FISCHER, University of Duisburg-Essen, J. JACOBS, Rush University Medical Center
3:10 pm	**C2/F4-3-7** Surface States Related the Bias Stability of Amorphous In-Ga-Zn-O Thin Film Transistors Under Different Ambient Gas, **Y.-C. CHEN**, National Sun Yat-Sen University, Taiwan	Invited talk continued.
3:30 pm	**C2/F4-3-8** Hot Carrier Effect on Gate-Induced Drain Leakage Current in n-MOSFETs with HfO2/Ti_xN_{1-x} Gate Stacks, **C.-H. DAI**, National Sun Yat-Sen University, Taiwan	**D3-10** Fabrication of Superhydrophobic Surfaces on Stainless Steel Substrates for Potential Biomedical Applications, S. BECKFORD, **M. ZOU**, University of Arkansas
3:50 pm	**C2/F4-3-10** Pulse Laser Deposition and Characterization of V_2O_5/Mn_3O_4 Composites Thin Films for Supercapacitor Application, C.-C. CHANG, **C.-H. HSU**, K.-W. YEH, T.-W. HUANG, M.-K. WU, Institute of Physics, Academia Sinica Taiwan, Taiwan, Republic of China	**D3-11** What is the Role of Lipopolysaccharide (LPS) on the Tribocorrosive Behavior of Titanium in Dentistry?, **V.A.R. BARAO**, Univ Estadual Paulista, Brazil, M.T. MATHEW, Rush University Medical Center, J.C. YUAN, University of Illinois at Chicago, W.G. ASSUNCAO, Univ Estadual Paulista, Brazil, M.A. WIMMER, Rush University Medical Center, C. SUKOTJO, University of Illinois at Chicago **STUDENT AWARD FINALIST**
4:10 pm	**C2/F4-3-9** Chemiresistive Chlorine Gas Sensor Based on Spin Coated Copper(II) 1,4,8,11,15,18,22,25-Octabutoxy-29H,31H-Phthalocyanine Films, **R. SAINI**, A. MAHAJAN, R.K. BEDI, Guru nanak dev University, Amritsar, India	**D3-9** Bio-Tribological Properties of UHMWPE Against Surface Modified Titanium Alloy, **D. XIONG**, L. XIONG, Nanjing University of Science and Technology, China
4:30 pm		
4:50 pm		
5:10 pm		
	Exhibits Reception **5:30 - 7:00 pm** **Exhibition Hall**	**Exhibits Reception** **5:30 - 7:00 pm** **Exhibition Hall**

Tuesday Afternoon, May 3, 2011

	Tribology and Mechanical Behavior of Coatings & Thin Films Room: California - Session E1-2 - Friction and Wear of Coatings: Lubrication, Surface Effects, and Modeling **Moderators:** J.C. Sanchez-Lopez, Instituto de Ciencia de Materiales de Sevilla (CSIC-US), H. Evans, University of Birmingham, S.M. Aouadi, Southern Illinois University, Carbondale	Coatings and Materials for Fuel Cells and Batteries Room: Sunrise - Session TS2 **Moderators:** E. Yu, Newcastle University, G.V. Dadheech, General Motors
1:30 pm	**E1-2-1** Developing Coatings for Increased Operational Life in Gears, **S.J. BULL**, A. OILA, Newcastle University, UK	**TS2-3** Development of Li-Mn-O Thin Film Cathodes for Lithium-Ion Batteries by Magnetron Sputtering and Laser-Assisted Structuring and Annealing, C. ZIEBERT, J. FISCHER, N. THIEL, J. PROELL, R. KOHLER, M. RINKE, W. PFLEGING, **S. ULRICH**, Karlsruhe Institute of Technology, Germany
1:50 pm	**E1-2-2** Understanding Lubrication Mechanism of Novel Boron-Based Lubricant Tested on ta-C Coating for Automotive Applications, **K. MISTRY**, J.-H. KIM, E. BRIGGS, O.L. ERYILMAZ, A. ERDEMIR, Argonne National Laboratory	**TS2-4** Lithium Insertion into Vertically-Aligned Carbon Nanotubes During Growth, K. RANA, G. KUCUKAYAN, **E. BNEGU**, Bilkent University, Turkey
2:10 pm	**E1-2-3** Influence of the Lubricant on the Frictional Behaviour of Amorphous Carbon Coatings Sliding Against Steel, **C. HEAU**, P. MAURIN-PERRIER, L. MOURIER, HEF R&D, France	**TS2-5** Influence of a Coating on the Oxidation Resistance and Resistivity of Several Chromia Former Alloys for High Temperature Vapor Electrolysis Application, **S. GUILLOU**, C. DESGRANGES, CEA, France, S. CHEVALIER, University of Bourgogne, France
2:30 pm	**E1-2-4** Nanocomposite Ti-Ni-C Coatings for Electrical Contact Brush Applications, **M. MALMROS**, U. WIKLUND, Uppsala University, Sweden	**TS2-6** Deposition and Post-Annealing of Ceria Films Deposited by Pulsed Unbalanced Mangetron Sputtering, **I.-W. PARK**, J.J. MOORE, J. LIN, Colorado School of Mines, M. MANUEL, Univ of Florida, A. EL-AZAB, Florida State Univ, T. ALLEN, P. XU, Univ of Wisconsin, D. HURLEY, M. KHAFIZOV, Idaho National Laboratory
2:50 pm	**E1-2-5 Invited** Space Tribometers: Experiments on Orbit, B.A. KRICK, **G.W. SAWYER**, University of Florida	**TS2-7** Sputtered Lanthanum Silicate Electrolytes for SOFCs, **J.C. OLIVEIRA**, University of Coimbra, Portugal, M.M. VIEIRA, Polytechnic Institute of Leiria, Portugal, A.L. SHAULA, A. CAVALEIRO, University of Coimbra, Portugal
3:10 pm	Invited talk continued.	**TS2-9** Electrolytic Co-Deposition for Synthesis of $(Mn,Co)_3O_4$ Spinel Coatings to Protect SOFC Interconnect Alloys, **J.H. ZHU**, M.J. LEWIS, Tennessee Technological University
3:30 pm	**E1-2-7** Ultra-Low Carbon (ULC) Steel Modified by Triode Plasma Nitriding and PVD Coating: Effects on the Micro-Abrasive Wear Behavior, **C.A. LLANES LEYVA**, C. GODOY, Univ Federal de Minas Gerais, Brazil, A.C. BOZZI, Univ Federal do Espírito Santo, Brazil, J.C. AVELAR-BATISTA WILSON, Tecvac Ltd, UK	**TS2-10** Development of Low Cost Protection Coatings for SOFC Interconnect Applications, **G. XIA**, X.H. LI, J.D. TEMPLETON, R.C. SCOTT, J.W. STEVENSON, Pacific Northwest National Laboratory
3:50 pm	**E1-2-9** Application of the Friction Energy Density Approach to Quantify the Fretting Wear Endurance of MoS_2 Solid Lubricant Films: Influence of Temperature and Frequency, **S. FOUVRY**, H. GALLIEN, Ecole Centrale de Lyon - LTDS, France	**TS2-8** Nanostructured Titania Materials for PEM Fuel Cell Water Management, M.A. ELHAMID, **G.V. DADHEECH**, General Motors
4:10 pm	**E1-2-12** The Onset of Plastic Yielding in Coated Spherical Contact, R. GOLTSBERG, G. DAVIDI, **I. ETSION**, Technion, Israel	
4:30 pm	**E1-2-10** Tribological Properties of Laser Surface Texturing and Molybdenizing Duplex-Treated Steel, **J.L. LI**, D. XIONG, Nanjing University of Science and Technology, China	
4:50 pm		
5:10 pm		
	Exhibits Reception 5:30 - 7:00 pm Exhibition Hall	**Exhibits Reception 5:30 - 7:00 pm Exhibition Hall**

Wednesday Morning, May 4, 2011

	Coatings for Use at High Temperature Room: Sunrise - Session A1-1 - Coatings to Resist High Temperature Oxidation, Corrosion and Fouling **Moderators:** Y. Zhang, Tennessee Technological University, J.R. Nicholls, Cranfield University, L.G. Johansson, Chalmers University of Technology, D. Naumenko, Forschungszentrum Julich	Hard Coatings and Vapor Deposition Technology Room: Royal Palm 1-3 - Session B1-3 PVD Coatings and Technologies **Moderators:** P. Eklund, Linköping University, J. Vetter, Sulzer Metaplas GmbH, J.-H. Huang, National Tsing Hua University
8:00 am	**A1-1-1 Invited** Oxidation Failure of TBC Systems: An Assessment of Mechanisms, **H. EVANS**, University of Birmingham, UK	**B1-3-1** Cylindrical Magnetrons Sputter Deposition of Ti-Si-C-N Nanocomposite Coatings on Inner Surface of Cylinders, **R. WEI**, Southwest Research Institute
8:20 am	Invited talk continued.	**B1-3-2** Arc Deposited Ti-Si-C-N Hard Coatings from Ternary Ti_3SiC_2 Cathodes, **A. ERIKSSON**, J.Q. ZHU, N. GHAFOOR, Linköping University, Sweden, M. JOHANSSON, Seco Tools AB Fagersta, Sweden, J. SJÖLÉN, Seco Tools AB, Sweden, J. JENSEN, G. GRECZYNSKI, M. ODÉN, L. HULTMAN, J. ROSÉN, Linköping University, Sweden
8:40 am	**A1-1-4** The Effects of Ni:Co Ratio on the Phase Stability and High-Temperature Corrosion Resistance of (Ni, Co)CrAlY Alloys and Coatings, **Z. TANG**, Iowa State University, F. ZHANG, CompuTherm, LLC, B. GLEESON, University of Pittsburgh	**B1-3-3 Invited** Atomic Scale Studies of Nanocomposite Coatings with Atom Probe Tomography, **J.M. CAIRNEY**, University of Sydney, Australia, F. TANG, The University of New South Wales, Australia, P.J. FELFER, The University of Sydney, Australia, A. BENDAVID, P. MARTIN, CSIRO, Australia
9:00 am	**A1-1-5** The Development of New Bond Coat Compositions for Thermal Barrier Coating Systems Operating in Industrial Gas Turbine Conditions, **M. SERAFFON**, N.J. SIMMS, J. SUMNER, J.R. NICHOLLS, Cranfield University, UK	Invited talk continued.
9:20 am	**A1-1-6** The Effect of Composition on the Durability of β-phase Bond Coats, **R.W. JACKSON**, University of California, Santa Barbara, R. ADHARAPURAPU, GE Global Research, B.T. HAZEL, GE Aviation, D.M. LIPKIN, GE Global Research, C.G. LEVI, T.M. POLLOCK, University of California, Santa Barbara	**B1-3-5** Structural and Mechanical Property of (TiCrAlSi)N Coating with Different Si Contents, **H. ITO**, K. YAMAMOTO, T. OKUDE, Kobe Steel Ltd., Japan
9:40 am	**A1-1-7** Structure and Cyclic Oxidation Resistance of Pt, Pd and Pt/Pd Modified Aluminide Coatings on CMSX-4 Superalloy, **R. SWADŹBA**, B. WITALA, Silesian University of Technology, Poland	**B1-3-6** Seed Layer Influence on the Texture, Orientation and Piezoelectric Properties of Pulsed-DC Sputtered AlN Thin Films, **M. HASHEMINIASARI**, J. SCALES, J. LIN, J.J. MOORE, Colorado School of Mines
10:00 am	**A1-1-8** Compositional Effects on the Hot Corrosion of β -NiAl Alloys, **M.N. TASK**, F.S. PETTIT, B. GLEESON, G.H. MEIER, University of Pittsburgh	**B1-3-7 Invited**Industrial-Scale Sputter Deposition of Photocatalytic Active Titania (TiO_2) and Thin Film (YSZ/CGO) for Solid Oxide Fuel Cells, **L.P. NIELSEN**, K.P. ALMTOFT, I.H. ANDERSEN, B.H. CHRISTENSEN, Danish Tech Inst, Tribology Cntr, Denmark, M.B. SØRENSEN, Danish Tech Inst, Plastic Tech, A.J. NIELSEN, C. VAHLSTRUP, J. BØTTIGER, Aarhus Univ, S. SØNDERBY, Linköping Univ, Sweden
10:20 am	**A1-1-9** Thermal Cycling Behavior of TBC Systems with Doped Pt-rich γ-γ' Bond Coatings Made by Spark Plasma Sintering (SPS), **S.D. SELEZNEFF**, M. BOIDOT, D. OQUAB, Inst Carnot CIRIMAT ENSIACET, France, C. ESTOURNÈS, CIRIMAT & PNF2/CNRS, France, D. MONCEAU, Inst Carnot CIRIMAT ENSIACET, France	Invited talk continued.
10:40 am	**A1-1-10** Coating Performance on Low Re Superalloy, B.A. PINT, J.A. HAYNES, Oak Ridge National Laboratory, Y. ZHANG, Tennessee Technological University, **A. VANDEPUT**, CIRIMAT - ENSIACET Toulouse	**B1-3-9** Antibacterial Activity of TiO_2 Coatings Deposited by CAE-PVD, **J. ESPARZA**, A. I. N., Spain
11:00 am	**A1-1-12** Type I Hot Corrosion of PGM-Modified NiAl Bond Coat, **V.S. DHEERADHADA**, D.M. LIPKIN, General Electric, T.M. POLLOCK, University of California, Santa Barbara, B.T. HAZEL, GE Aviation, A. VAN DER VEN, R. ADHARAPURAPY, University of Michigan	**B1-3-10** Preparation of $BiFeO_3$/$LaNiO_3$ Multiferroic Oxide Superlattice Structure Prepared by RF Sputtering, **Y.-T. LIU**, National Chiao Tung University, Taiwan, S.-J. CHIU, National Tsing Hua University, Taiwan, H.-Y. LEE, National Synchrotron Radiation Research Center, Taiwan, S.-Y. CHEN, National Chiao Tung University, Taiwan
11:20 am		**B1-3-11** Evolution of the Structure and Optoelectrical Performance of ZnO Thin Films Deposited by DC Magnetron Sputtering after Post Deposition Annealing Treatments, **M. YUSTE**, R. ESCOBAR GALINDO, I. CARETTI, O. SÁNCHEZ, Instituto de Ciencia de Materiales de Madrid, Spain
11:40 am		**B1-3-12** Characterization and Piezoelectric Properties of Reactively Sputtered (Sc, Al) N Thin Films on Diamond Structure, **M.-Y. WU**, J.-L. HUANG, J.-H. SONG, National Cheng Kung University, Taiwan, J.-C. SUNG, KINIK Company, Taiwan, Y.-C. CHEN, National Cheng Kung University, Taiwan, S. WU, Tung Fang Design University, Taiwan, D.-F. LII, Cheng Shiu University, Taiwan
	Exhibition Closes Today at 2:00 pm **CSM FTS at 12:15 - 1:15 pm California Room**	**Exhibition Closes Today at 2:00 pm** **CSM FTS at 12:15 - 1:15 pm California Room**

Wednesday Morning, May 4, 2011

	Hard Coatings and Vapor Deposition Technology **Room: Golden West - Session B6-1** **Application-Oriented Coating Design and Architectures** **Moderators:** C. Mitterer, Montanuniversität Leoben, M. Stueber, Karlsruhe Institute of Technology	**Fundamentals and Technology of Multifunctional Thin Films: Towards Optoelectronic Device Applications** **Room: Sunset - Session C3** **Optical Characterization of Thin Films, Surfaces, and Devices** **Moderators:** U. Beck, BAM, E. Schubert, University of Nebraska-Lincoln
8:00 am	**B6-1-1** Phase Diagram Based Design of a Spinel-Corundum Coating, **J. RAMM**, OC Oerlikon Balzers AG, Liechtenstein, M. DÖBELI, ETH Zürich, Switzerland, D. KURAPOV, H. RUDIGIER, M. SOBIECH, OC Oerlikon Balzers AG, Germany, J. THOMAS, IFW Dresden, Germany, B. WIDRIG, OC Oerlikon Balzers AG, Germany	**C3-1 Invited** Analysing Solid Surfaces by FT-IR Imaging ANR AFM-Raman-Spectroscopy, J. SAWATZKI, **BOESE**, Bruker Optik GmbH, Germany
8:20 am	**B6-1-3** Controlled Phase Transformation for Local Property Design in MAX Phase Coatings, **O. SCHROETER**, C. LEYENS, R. BASU, Technische Universität Dresden, Germany	Invited talk continued.
8:40 am	**B6-1-4 Invited** Quantum Design of Hard Boron-Rich coatings, **D. MUSIC**, J.M. SCHNEIDER, RWTH Aachen University, Germany	**C3-3** X-Ray Fluorescence as a Powerful Tool for the Study of Chemistry of Thin Films, A. SIOZIOS, D.F. ANAGNOSTOPOULOS, M.A. KARAKASSIDES, **P. PATSALAS**, University of Ioannina, Greece
9:00 am	Invited talk continued.	**C3-4** Electrochromic Properties of Nanocrystalline MoO_3/V_2O_5 Composite Thin Films, **C.-C. CHANG**, C.-H. HSU, K.-W. YEH, Academia Sinica, Taiwan, C.-S. HSU, C.-C. CHAN, C-.K. LIN, Feng Chia University, Taiwan, M.-K. WU, Academia Sinica, Taiwan
9:20 am	**B6-1-6** DFT Combinatorics by Extending the Rule of Mixture to Sub Unit-Cell Level, **M. TO BABEN**, D. MUSIC, J. EMMERLICH, J.M. SCHNEIDER, RWTH Aachen University, Germany	**C3-5** Nitrogen-Doping Induced Changes in the Microstructure and Optical Properties of Nanocrystalline WO_3 Thin Films, **R.S. VEMURI**, S.K. GULLAPALLI, C.V. RAMANA, University of Texas at El Paso
9:40 am	**B6-1-7** Growth and Characterization of Single-Crystal $V_xW_{1-x}N(001)$ Thin Films, **H. KINDLUND**, J. BIRCH, L. HULTMAN, Linköping University, Sweden	**C3-6** Effect of Growth Temperature on the Structure, Electrical and Optical Characteristics of Sputter-Deposited Y_2O_3 Thin Films, **V.H. MUDAVAKKAT**, K. BHARATHI, Univ of Texas at El Paso, V.N. KRUCHININ, L.D. POKROVSKY, V.V. ATUCHIN, Inst of Semiconductor Physics, Russia, C.V. RAMANA, Univ of Texas at El Paso
10:00 am	**B6-1-8** Ductility Enhancement in Transition Metal Nitrides by Alloying and Valence Electron Concentration Tuning, **D.G. SANGIOVANNI**, V. CHIRITA, L. HULTMAN, Linköping University, Sweden	**C3-7 Invited** Characterization of Nanometer Films by X-Ray and EUV Reflectometry, **S. BRAUN**, M. MENZEL, S. SCHÄDLICH, A. LESON, IWS Dresden, Fraunhofer Institute for Material and Beam Technology, Germany
10:20 am	**B6-1-9** Microstructural Study and Mechanical Properties of TiC/C Composite Coatings Deposited by Hybrid PVD/PECVD Process, **A.-A. EL MEL**, E. GAUTRON, B. ANGLERAUD, A. GRANIER, Univ de Nantes, France, V. BURŠÍKOVÁ, P. VAŠINA, P. SOUČEK, Masaryk Univ Czech Rep, P.-Y. TESSIER, Univ de Nantes, France	Invited talk continued.
10:40 am	**B6-1-10** In-Situ XRD Investigations of Interface Reactions in Nanoscale Cr/ta-C Multilayers, **U. RATAYSKI**, D. RAFAJA, U. MÜHLE, TU Bergakademie Freiberg, Germany, C. BAEHTZ, Forschungszentrum Dresden-Rossendorf, H.-J. SCHEIBE, M. LEONHARDT, Fraunhofer-Institut für Werkstoff- und Strahltechnik IWS Dresden	**C3-10** Morphological Evolution and Optical Characterization of ZnO Thin Films on PET and Glass Substrates by RF-Sputtering Technique, **J.R. BORTOLETO**, State Univ of São Paulo - UNESP, Brazil, E.P. DA SILVA, E. AMORIM, E. MARTINS, UNESP - Univ Estadual Paulista, Brazil, S.F. DURRANT, State Univ of São Paulo - UNESP, Brazil, P.N. LISBOA-FILHO, UNESP – Univ Estadual Paulista, Brazil
11:00 am	**B6-1-11** Fabry-Perot Based Layer Systems with Embedded Public, Hidden and Forensic Information for Anti-Counterfeiting Applications, **U. BECK**, R. STEPHANOWITZ, A. HERTWIG, BAM, Germany, R. DOMNICK, M. BELZNER, ARA Coatings, Germany, D. HÖNIG, S. SCHNEIDER, ACCURION, Germany	**C3-11** Enhanced Photoluminescence from $Zn_{0.55}Cd_{0.45}S$:Mn/ZnS Core Shell Nanostructures, S. SINGHAL, **A.K. CHAWLA**, H.O. GUPTA, R. CHANDRA, Indian Institute of Technology Roorkee, India
11:20 am	**B6-1-12** Simulation of a Variety of Applications for Complex Coating Structures, **N. BIERWISCH**, N. SCHWARZER, Saxonian Institute of Surface Mechanics, Germany	**C3-12** Environment Sensitivity and Film Stability of InGaZnO TFT with Annealing Temperature Dependence, **Z.-X. FU**, National Chiao Tung University, Taiwan, Z.-Z. LI, Minghsin Univ of Science and Technology, Taiwan, Y.-T. CHOU, P.-T. LIU, National Chiao Tung Univ, Taiwan, B.-M.. CHEN, Minghsin Univ of Sci & Tech, Taiwan
11:40 am		**C3-13** Structural and Optical Properties of Chlorinated Plasma Polymers, R. TURRI, State University of São Paulo - UNESP, Brazil, C.U. DAVANZO, UNICAMP, Brazil, W.H. SCHREINER, State University of Paraná, Brazil, J.H. DIAS DA SILVA, M.B. APPOLINARIO, **S.F. DURRANT**, State University of São Paulo - UNESP, Brazil
	Exhibition Closes Today at 2:00 pm **CSM FTS at 12:15 - 1:15 pm California Room**	**Exhibition Closes Today at 2:00 pm** **CSM FTS at 12:15 - 1:15 pm California Room**

Wednesday Morning, May 4, 2011

	Applications, Manufacturing, and Equipment Room: Royal Palm 4-6 - Session G3 **Atmospheric and Hybrid Plasma Technologies** **Moderators:** H. Barankova, Uppsala University, S. Dixit, Plasma Technologies, Ltd.	Applications, Manufacturing, and Equipment Room: California - Session G4/E4 **Coatings for Machining Advanced Materials and Advanced Manufacturing Methods** **Moderators:** M. Arndt, OC Oerlikon Balzers AG, X. Nie, University of Windsor
8:00 am	**G3-1** Atmospheric Pressure Plasma Treatment of Polymers for Ink-Jet Deposition of Flexible Solar Cell Platforms, **D.D. PAPPAS**, V. RODRIGUEZ-SANTIAGO, M.S. FLEISCHMAN, A.A. BUJANDA, U.S. Army Research Laboratory, V. CHHASATIA, B. LEE, Y. SUN, Drexel University	**G4/E4-1** Nanocomposite (Ti,Cr,Al,Si)N Coatings for Hard Machining of PM High Speed Steel, K. BOBZIN, F. KLOCKE, RWTH Aachen University, Germany, K. ARNTZ, Fraunhofer-Inst für Produktionstechnologie IPT, Germany, N. BAGCIVAN, RWTH Aachen Univ, Germany, M. STOLORZ, Fraunhofer-Inst für Produktionstechnologie IPT, Germany, **M. EWERING**, L. STALPERS, RWTH Aachen Univ, Germany
8:20 am	**G3-2** Investigation on the Discharge Formation Mechanisms and Surface Analysis of SiO_2-Like Layers on Polymers Synthesized Using High Current Dielectric Barrier Discharge at Atmospheric Pressure, **M.C.M. VAN DE SANDEN**, A. PREMKUMAR PETER, Eindhoven Univ of Tech, Netherlands, S.A. STAROSTIN, H.W.D. DE VRIES, FUJIFILM, Netherlands, M. CREATORE, Eindhoven University of Technology, Netherlands	**G4/E4-2** Substrate Surface Etching Effects on Machining Performance of Diamond-Coated Cutting Tools, R. THOMPSON, D. NOLEN, Vista Engineering, **F. QIN**, K. CHOU, University of Alabama
8:40 am	**G3-3 Invited** Surface Modification of Inks, Coatings and Adhesives - The Interfacial Effects, **R. WOLF**, Enercon Industries Corporation	**G4/F4-4** Influence of Edge Micro-Geometry and Coating Design on the Drilling of Titanium Alloys with Carbide Drills, **A. PILKINGTON**, S.J. DOWEY, J.T. TOTON, RMIT University and Defence Materials Technology Centre, Australia, D. GRIFFETT, Cuttertec Pty, Australia, O. SMITH, Sutton Tools Pty, Australia, E.D. DOYLE, RMIT University and Defence Materials Technology Centre, Australia
9:00 am	Invited talk continued.	**G4/E4-5 Invited** Coating and Tool Wear in Composite Machining, **J. BOHLMARK**, Sandvik Tooling Stockholm SE, Sweden, E. MERSON, W.T. GOH, Sandvik Tooling Sheffield, UK
9:20 am	**G3-6** Effects of Coating Morphology on *In-Situ* Impedance Spectra of Plasma Electrolytic Oxidation Process, **C.-J. LIANG**, A. YEROKHIN, University of Sheffield, UK, E.V. PARFENOV, Ufa State Aviation Technical University, Russia, A. MATTHEWS, University of Sheffield, UK	Invited talk continued.
9:40 am	**G3-7** The Effect of Current Mode and Discharge Type on the Corrosion Resistance of Plasma Electrolytic Oxidation (PEO) Coated Magnesium Alloy AJ62., R.O. HUSSEIN, P. ZHANG, X. NIE, **D.O. NORTHWOOD**, University of Windsor, Canada	**G4/E4-7** Fatigue Behavior of TiN Coating on WC-Co Cemented Carbides, **J.-F. SU**, X. NIE, H. HU, University of Windsor, Canada
10:00 am	**G3-8 Invited** An Integrated Microwave Atmospheric Plasma Source, **R. GESCHE**, Ferdinand-Braun-Institut, Berlin, Germany	**G4/E4-8** Improved Cutting Processes of Austenitic Steels with γ-Alumina Based PVD Coating Systems, **S.E. CORDES**, RWTH Aachen University, Germany
10:20 am	Invited talk continued.	**G4/E4-9** An Investigation into the Tribological Performance of PVD Coatings on High Thermal Conductivity Cu Alloy Substrates and the Effect of an Intermediate Electroless Ni-P Layer Prior to PVD Treatment, J.C. AVELAR-BATISTA WILSON, Tecvac Ltd, UK, S. BANFIELD, Tecvac Ltd and University of Sheffield, UK, J. EICHLER, A. LEYLAND, A. MATTHEWS, The University of Sheffield, UK, **J. HOUSDEN**, Tecvac Ltd, UK
10:40 am	**G3-10** Nanocoating System with Focused ICP Atmospheric Plasma Torch for Anti-Reflective Coating, **Y. GLUKHOY**, A. USENKO, American Advanced Ion Beam Inc.	**G4/E4-10** Mechanical Properties of Partially Oxidized Silicon Nitride Films Deposited by RF Reactive Magnetron Sputtering, J. FILLA, C. AGUZZOLI, V. SONDA, CLG. AMORIM, Universidade de Caxias do Sul, Brazil, GV. SOARES, I. BAUMVOL, Universidade Federal do Rio Grande do Sul, Brazil, **C.A. FIGUEROA**, Universidade de Caxias do Sul, Brazil
11:00 am	**G3-12** Plasma Characteristics of Hollow Cathode Discharge in Plasma Ion Implantation of Slender Bore, **C.Z. GONG**, X.B. TIAN, H.F. JIANG, S.Q. YANG, Harbin Institute of Technology, China, R.K.Y. FU, P.K. CHU, City University of Hong Kong, China	**G4/E4-11 Invited** Carbon Based Coatings for Machining of Aluminum and Magnesium Alloys, **A.T. ALPAS**, S. BHOWMICK, University of Windsor, Canada, M.J. LUKITSCH, General Motors Research and Development Center
11:20 am		Invited talk continued.
	Exhibition Closes Today at 2:00 pm **CSM FTS at 12:15 - 1:15 pm California Room**	**Exhibition Closes Today at 2:00 pm** **CSM FTS at 12:15 - 1:15 pm California Room**

Wednesday Afternoon, May 4, 2011

	Coatings for Use at High Temperature	Hard Coatings and Vapor Deposition Technology
	Room: Sunrise - Session A1-2 - Coatings to Resist High Temperature Oxidation, Corrosion and Fouling **Moderators:** Y. Zhang, Tennessee Technological University, J.R. Nicholls, Cranfield University, L.G. Johansson, Chalmers University of Technology, D. Naumenko, Forschungszentrum Julich	**Room: Golden West - Session B6-2** **Application-Oriented Coating Design and Architectures** **Moderators:** C. Mitterer, Montanuniversität Leoben, M. Stueber, Karlsruhe Institute of Technology
1:30 pm	**A1-2-1** Effect of Increased Water Vapor Levels on TBC Lifetime, A. VANDEPUT, CIRIMAT - ENSIACET Toulouse, **B.A. PINT**, J.A. HAYNES, Oak Ridge National Laboratory, Y. ZHANG, Tennessee Technological University	**B6-2-1 Invited** Various Approaches to Reveal the Architecture of Nanocomposite Thin Films, **C. SANDU**, T. YAMADA, S. HARADA, R. SANJINÉS, EPFL, Switzerland, A. CAVALEIRO, Coimbra University, Portugal, N. SETTER, EPFL, Switzerland
1:50 pm	**A1-2-2** Oxidation Resistance of Nanocomposite CrAlSiN under Long-Time Heat Treatment, **H.-W. CHEN**, Y.-C. CHAN, National Tsing Hua University, Taiwan, J.-W. LEE, Mingchi University of Technology, Taiwan, J.-G. DUH, National Tsing Hua University, Taiwan	Invited talk continued.
2:10 pm	**A1-2-3** HRTEM Study of Arc-Sputtered Nanocomposite TiSiN Thin Films, **J. MOONEY**, E.I. MELETIS, University of Texas at Arlington, Y.H. CHENG, American Eagle Instruments, Inc.	**B6-2-3** Effect of Cathodic Arc Plasma Treatment on the Properties of WC-Co Based Hard Metals, **S.A. AKKAYA**, Istanbul Technical University, Turkey, E.S. SIRELI, Böhler Sert Maden ve Takım Inc, Turkey, M.K.K. KAZMANLI, M. URGEN, Istanbul Technical University, Turkey
2:30 pm	**A1-2-4 Invited** Moisture-Induced Desktop Spallation of TBCs, **J.L. SMIALEK**, NASA Glenn Research Center	**B6-2-4** Influence of Coating Architecture on Thermal Stability and Mechanical Properties of CrN Based Coatings, **M. SCHLÖGL**, F. ROVERE, J. PAULITSCH, J. KECKES, P.H. MAYRHOFER, Montanuniversität Leoben, Austria
2:50 pm	Invited talk continued.	**B6-2-5** Stress Design of Hard Coatings, **R. DANIEL**, J. KECKES, C. MITTERER, Montanuniversität Leoben, Austria
3:10 pm	**A1-2-6** A Single Step Process to Form an In-Situ Oxidized Alumina Foam Coating for Alloys for Extreme Environments at High Temperatures, **X. MONTERO**, M. GALETZ, M. SCHÜTZE, Dechema e.V., Germany	**B6-2-6** Nano-Beam X-Ray Diffraction Reveals Strain, Composition, Texture and Crystal Size Gradients Across Nano-Crystalline Thin Films, **J. KECKES**, R. DANIEL, M. BARTOSIK, C. MITTERER, Montanuniversität Leoben, Austria, S. SCHOEDER, M. BURGHAMMER, ESRF, Grenoble, France
3:30 pm	**A1-2-7** Oxidation Behavior of Slurry Aluminide Coatings on Stainless Steel Alloy CF8C-Plus, **J.A. HAYNES**, B.L. ARMSTRONG, S. DRYEPONDT, Oak Ridge National Laboratory, Y. ZHANG, Tennessee Technological University	**B6-2-7** Numerical Modeling of the Stress Degradation Process in Hard Coatings, **W. ECKER**, W. EßL, G. MAIER, R. EBNER, Materials Center Leoben Forschung GmbH, Austria, C. MITTERER, J. KECKES, Montanuniversität Leoben, Austria
3:50 pm	**A1-2-8** Nitriding and Coating of a Stainless Steel for Corrosion Protection in Carburizing Atmospheres, V. MELO, TRAMES SA de CV, Mexico, **M. SALAS**, E. OSEGUERA, ITESM, Mexico, R. TORRES, Pontifícia Universidade Católica do Parana, Brazil, R.M. SOUZA, University of Sao Paulo, Brazil	**B6-2-8** Application-Driven Design of Wear-Resistant Coatings by Means of an Integrated Multi-Scale Coating Design Tool, **M. FUCHS**, Saxonian Institute of Surface Mechanics, Germany, K. HOLMBERG, VTT Technical Research Centre of Finland, N. SCHWARZER, Saxonian Institute of Surface Mechanics, Germany, P. KELLY, Manchester Metropolitan University, UK
4:10 pm		**B6-2-9** Coating Design for Metalcutting Applications, **A. INSPEKTOR**, R. PENICH, Kennametal Inc., P.A. SALVADOR, N. PATEL, Carnegie Mellon University
4:30 pm		**B6-2-10** The Effect of an AlCrN Based Coating and Post Treatment on Uncoated Carbide Drills Designed for Ti Alloys, in Drilling of Mill Annealed Ti_6Al_4V., **S.J. DOWEY**, Surface Technology Coatings, Australia, A. PILKINGTON, J.T. TOTON, E.D. DOYLE, RMIT University, Australia, O. SMITH, Sutton tools Pty, Australia
4:50 pm		**B6-2-11** Towards an Improved Understanding of the Drill Test. A study of Cutting Parameters, Work Piece Material, Coatings and Finish and their Influence on Cutting Forces Measured during Drilling, **J.T. TOTON**, RMIT University, Australia, S.J. DOWEY, Surface Technology Coatings, Australia, A.
5:10 pm		**B6-2-12** TiN Multilayer Systems for Compressor Airfoil Liquid Droplet Erosion Protection, **A. FEUERSTEIN**, M. BRENNAN, M. ROMERO, Praxair Surface Technologies, Inc
	Awards Convocation **California Room – 5:30 pm**	**Awards Convocation** **California Room – 5:30 pm**
	Awards Buffet Reception: **Poolside near the Tiki Pavilion – 7:30 pm**	**Awards Buffet Reception:** **Poolside near the Tiki Pavilion – 7:30 pm**

Wednesday Afternoon, May 4, 2011

	Tribology and Mechanical Behavior of Coatings and Thin Films **Room: California - Session E5** **Nano- and Microtribology** **Moderators:** N. Randall, CSM Instruments, J.-H. Hahn, Korea Research Institute of Standards and Science	**New Horizons in Coatings and Thin Films** **Room: Sunset - Session F3** **New Boron, Boride and Boron Nitride Based Coatings** **Moderators:** H. Hoegberg, Linkoping University, M. Keunecke, Fraunhofer Institute for Surface Engineering & Thin Films
1:30 pm	**E5-1** Microstructural Tailoring of Metallic Multilayer Thin Films by Laser Interference Metallurgy for Enhanced Tribological Properties, **C. GACHOT**, F.TH. MUECKLICH, University of Saarland, Germany	**F3-1** Hardness, Thermal Stability and Oxidation Resistance of Cr_5B_3 Films, **D. PILLOUD**, J.-F. PIERSON, Ecole des Mines de Nancy, France
1:50 pm	**E5-2** Nanotribological Properties of CrN Films Deposited in an Industrial Chamber by HIPIMS and DC Magnetron Sputtering, **E. BROITMAN**, G. GRECZYNSKI, L. HULTMAN, Linköping University, Sweden	**F3-2** Direct Current Magnetron Sputtering of ZrB_2 Thin Films from a Compound Target in an Industrial Scale Deposition System, **H. HÖGBERG**, Linköping University, Sweden, M. OTTOSSON, Uppsala University, Sweden, J. LU, J. JENSEN, M. SAMUELSSON, L. HULTMAN, Linköping University, Sweden
2:10 pm	**E5-3** Nano-/Micro Scale Fretting and Reciprocating Wear of Thin Films and Si(100), B. BEAKE, Micro Materials Ltd, UK, **T.W. LISKIEWICZ**, University of Leeds, UK, J.F. SMITH, Micro Materials Ltd, UK	**F3-3 Invited** A Combinatorial Effect of Substrate and Surface Terminating Species on Phase Pure Growth of c-BN, **K. LARSSON**, Uppsala University, Sweden
2:30 pm	**E5-4** The Effect of Environmental and Contact Conditions on Micro-Tribology Experiments on Engineering Coatings, **M. GEE**, J.W. NUNN, L.P. ORKNEY, National Physical Laboratory, UK	Invited talk continued.
2:50 pm	**E5-6** Nanomechanics of Thin Films: a Cross Sectional Approach, C.A. BOTERO VEGA, **E. JIMENEZ-PIQUÉ**, Universitat Politècnica de Catalunya, Spain, T. KULKARNI, Boston university, L.M. LLANES PITARCH, Universitat Politècnica de Catalunya, Spain, V.K. SARIN, Boston University	**F3-5** Chemical Vapor Deposition of MB_2 and M-B-N Alloys Below 300°C: Highly Conformal, Hard and Wear-Resistant Films, **A.N. CLOUD**, J.R. ABELSON, University of Illinois at Urbana-Champaign
3:10 pm	**E5-7** Sub-Micro-Pillar Compression Tests on Nanocrystalline Nickel Tribofilms, **C.C. BATTAILE**, S.V. PRASAD, J.R. MICHAEL, B.L. BOYCE, Sandia National Laboratories	**F3-6** The Effect of Deposition Parameters on the Structure, Chemistry and Physical Properties of Deposited B-C-N Films, **M.F. GENISEL**, E. BENGU, Bilkent University, Turkey
3:30 pm	**E5-8** Nanoscale Mechanical Imaging of Multilayered Films for Flexible Display Using Contact Resonance Force Microscopy, **J.-H. HAHN**, Korea Research Institute of Standards and Science, Korea, D.-H. KIM, H.-S. AHN, Seoul National University of Science and Technlogy, Korea	**F3-7** Bonding Structure of B-C-N Ternary Compounds and Their Tribomechanical Properties, **I. CARETTI**, I. JIMÉNEZ, Instituto de Ciencia de Materiales de Madrid, Spain
3:50 pm	**E5-9 Invited** Effect of Surface Coating Topography on the Tribological Properties of Nanoparticle Films, **M. AKBULUT**, Texas A&M University	**F3-8** Influence of Nitrogen and Oxygen Addition on the Energy Flux in a rf-Magnetron Discharge for the Deposition of Superhard c-BN Coatings, **S. BORNHOLDT**, Christian-Albrechts-Universität zu Kiel, Germany, J. YE, S. ULRICH, Karlsruhe Institute of Technology (KIT), Germany, H. KERSTEN, Christian-Albrechts-
4:10 pm	Invited talk continued.	**F3-9** Electrochemical Boriding and Characterization of AISI D2 Tool Steel, **V. SISTA**, Argonne National Laboratory, O. KAHVECIOGLU, Istanbul Technical University, Turkey, O.L. ERYILMAZ, A. ERDEMIR, Argonne National Laboratory, S. TIMUR, Istanbul Technical University, Turkey
4:30 pm		**F3-10** Ultra Fast Boriding of Nickel Aluminide, **O. KAHVECIOGLU**, Istanbul Technical University, Turkey, V. SISTA, O.L. ERYILMAZ, A. ERDEMIR, Argonne National Laboratory, S. TIMUR, Istanbul Technical University, Turkey
5:30 pm	**ICMCTF Honorary Lecture** **Stan Veprek** **Technical University** **Munich Germany** **Search for Superhard Materials: Go Nano!** **Please View Abstract on** **Page xv**	
	Awards Convocation **California Room – 5:30 pm**	**Awards Convocation** **California Room – 5:30 pm**
	Awards Buffet Reception: **Poolside near the Tiki Pavilion – 7:30 pm**	**Awards Buffet Reception:** **Poolside near the Tiki Pavilion – 7:30 pm**

Wednesday Afternoon, May 4, 2011

	Applications, Manufacturing, and Equipment Room: Royal Palm 4-6 - Session G2 Coatings for Automotive and Aerospace Applications **Moderators:** H. Rudigier, OC Oerlikon Balzers AG, S. Roy, University of Newcastle	Surface Engineering for Thermal Transport, Storage, and Harvesting Room: Royal Palm 1-3 - Session TS3 **Moderators:** A.A. Voevodin, Air Force Research Laboratory, T.S. Fisher, Purdue University & Air Force Research Laboratory
1:30 pm	**G2-1** Highly Concentrated and Low Friction Slip-Rolling Contacts Through Thin Film Coatings and/or Alternative Steels?, **C. SCHOLZ**, D. SPALTMANN, M. WOYDT, Federal Institute for Materials Research and Testing, Germany	**TS3-1 Invited** New Approaches with Organic and Inorganic Films for Thermal Energy Conversion, **M. SHTEIN**, K.P. PIPE, University of Michigan, Y. JIN, H. SUN, Michigan State University, A. YADAV, University of Michigan
1:50 pm	**G2-2** Study on Fatigue and Wear Behaviors of a TiN Coating Using an Inclined Impact-Sliding Test, Y. CHEN, **X. NIE**, University of Windsor, Canada	Invited talk continued.
2:10 pm	**G2-3** Friction and Wear Behaviour of MoN-Cu Nanocomposite Coatings Under Lubricated Conditions, **O.L. ERYILMAZ**, J.-H. KIM, A. ERDEMIR, Argonne National Laboratory, M. URGEN, Istanbul Technical University, Turkey	**TS3-3** Effects of Ni Diffusion Barrier on CNT Growth on Metal Foils for Thermal Interface Applications, S.O. ADEWUYI, **A. BULUSU**, S. GRAHAM, B.A. COLA, Georgia Institute of Technology
2:30 pm	**G2-4** Effect of Si Addition on the Friction Coefficients of CrZr-Based Nitride Thin Films at Elevated Temperatures, **S.-Y. LEE**, Y.-S. KIM, J.-H. OH, Korea Aerospace University, Korea, J.-J. LEE, Seoul National University, Korea, W. Y. JEUNG, Korea Institute of Science and Technology, Korea	**TS3-4** Carbon Nanotube-Coated Foils as Low-Resistance Thermal Interface Materials, **S.L. HODSON**, Purdue Univ & Birck Nanotech Cntr, A. BULUSU, Georgia Inst of Tech, J.R. WASNIEWSKI, D.H. ALTMAN, Raytheon Integrated Defense Sys, B.A. COLA, S. GRAHAM, Georgia Inst of Tech, X. XU, Purdue Univ & Birck Nanotech Cntr, A. GUPTA, Raytheon Integrated Defense Sys, T.S. FISHER, Purdue Univ & AFRL
2:50 pm	**G2-5** Optimized DLC Coatings for Fuel Injection Components to Minimize Wear and Friction in Various Fuels, **A. HIEKE**, G. VAN DER KOLK, Ionbond Netherlands BV, Venlo, Netherlands, G. HAKANSSON, Ionbond Sweden AB, Sweden, F. GUSTAVSSON, P. FORSBERG, S. JACOBSON, Uppsala University, Sweden	**TS3-5** Crystalline Thin Film Materials with Anisotropic Thermal Conductivity, **C. MURATORE**, Air Force Research Laboratory, V. VARSHNEY, AFRL/UTC, J.J. GENGLER, AFRL/Spectral Energies, J. HU, J.E. BULTMAN, AFRL/UDRI, T. SMITH, A.A. VOEVODIN, AFRL
3:10 pm	**G2-6** Deposition and Characteristics of Chromium Nitride Thin Film Coatings on Precision Balls for Tribological Applications, M.D. DRORY, **R.D. EVANS**, The Timken Company	**TS3-6** Thermal Conductivity of Si-B-C-N Thin Films, **J.J. GENGLER**, Air Force Research Laboratory/Spectral Energies, J. HU, Air Force Research Laboratory/UDRI, J.G. JONES, A.A. VOEVODIN, Air Force Research Laboratory, P. STEIDL, J. VLCEK, University of West Bohemia, Czech Republic
3:30 pm	**G2-7 Invited** Recent Advancements in Coatings for Piston Rings, **K. HONDA**, Riken Corporation, Japan	**TS3-8** Thermal Properties of Diamond/Ag Composites Fabricated by Salt Bath Coating, **M.T. LEE**, J.-S. LIU, C.-Y. CHUNG, S.-J. LIN, National Tsing Hua University, Taiwan
3:50 pm	Invited talk continued.	**TS3-9** Homogeneous Solution of $Ca(BH_4)_2$ as a Thermal Energy Storage Material, **P.B. AMAMA**, J.E. SPOWART, A.A. VOEVODIN, Air Force Research Laboratory, T.S. FISHER, Purdue University & Air Force Research Laboratory, P. SHAMBERGER, Air Force Research Laboratory
4:10 pm	**G2-9** Surface Energy and Tribochemistry of Ti-DLC Coatings, **L.V. SANTOS**, M.S. OLIVEIRA, S.F. FISSMER, Tech Inst of Aeronautics, Brazil, L.C.D. SANTOS, C.A. ALVES, Univ Federal do Rio Grande do Norte, Brazil, P.A. RADI, Inst Nacional de Pesquisas Espaciais - INPE, Brazil, M. MASSI, H.S. MACIEL, Tech Inst of Aeronautics, Brazil	**TS3-10** Infrared Study of Ta_2O_5 and HfO_2 Thin Films on Si Substrates, T.J. BRIGHT, **Z.M. ZHANG**, Georgia Institute of Technology, C. MURATORE, A.A. VOEVODIN, Air Force Research Laboratory
4:30 pm	**G2-10 Invited** Chromium Carbide: A New Coating Approach for Highly Loaded, Low Friction Applications, **M. KEUNECKE**, K. BEWILOGUA, Fraunhofer Institute for Surface Engineering and Thin Films, Germany, J. BECKER, A. GIES, M. GRISCHKE, OC Oerlikon Balzers AG, Liechtenstein	**TS3-11** Photonically Enhanced Flow Boiling from Nanostructured Surfaces, C. HUNTER, Air Force Research Laboratory, **S.K. ARUN**, Purdue Univeristy, S.A. PUTNAM, Universal Technology Corporation, N. GLAVIN, Air Force Research Laboratory, T.S. FISHER, Purdue University & Air Force Research Laboratory
4:50 pm	Invited talk continued.	**TS3-12** Enhanced Surfaces in Conjunction with Single and Two-Phase Flows for Power Electronics Cooling Applications, **S. NARUMANCHI**, P. MCCLUSKEY, G. MORENO, C. KING, National Renewable Energy Laboratory
5:10 pm		
	Awards Convocation California Room – 5:30 pm	**Awards Convocation California Room – 5:30 pm**
	Awards Buffet Reception: Poolside near the Tiki Pavilion – 7:30 pm	**Awards Buffet Reception: Poolside near the Tiki Pavilion – 7:30 pm**

Thursday Morning, May 5, 2011

	Coatings for Use at High Temperature **Room: Sunrise - Session A1-3 - Coatings to Resist High Temperature Oxidation, Corrosion and Fouling** **Moderators:** Y. Zhang, Tennessee Technological University, J.R. Nicholls, Cranfield University, L.G. Johansson, Chalmers University of Technology, D. Naumenko, Forschungszentrum Julich	**Hard Coatings and Vapor Deposition Technology** **Room: Golden West - Session B5-1** **Hard and Multifunctional Nano-Structured Coatings** **Moderators:** C.P. Mulligan, Benet Laboratories, US Army ARDEC, R. Sanjines, EPFL, P. Zeman, University of West Bohemia
8:00 am	**A1-3-1** Effect of Steam Exposure on the Creep Properties of Bare and Aluminized Fe- and Ni-Based Alloys, **S. DRYEPONDT**, B.A. PINT, Oak Ridge National Laboratory, Y. ZHANG, Tennessee Technological University	**B5-1-1** Structure and Properties of Ti-Al-Y-N Coatings Deposited from Filtered Vacuum-Arc Plasma, V.A. BELOUS, V.V. VASYLIEV, Kharkov Inst of Physi & Tech, Ukraine, **V.S. GOLTVYANYTSYA**, S.K. GOLTVYANYTSYA, Real Ltd., Ukraine, E.N. RESHETNYAK, V.E. STRELNITSKIJ, G.N. TOLMACHEVA, A.A. LUCHANINOV, Kharkov Inst of Phys & Tech, Ukraine, O.S. DANYLINA, Krivoy Rog Technical University, Ukraine
8:20 am	**A1-3-2** High Temperature Protection of Ferritic Steels by Nano-Structured Coatings: Supercritical Steam Turbines Applications, **F.J. PEREZ**, M.P. HIERRO, M.S. MATO, I. LASANTA, M. TEJERO, Universidad Complutense de Madrid, Spain, J.C. SANCHEZ-LOPEZ, Instituto de Ciencia de Materiales de Sevilla (CSIC-US), Spain, M. BRIZUELA, TECNALIA-Inasmet, Spain	**B5-1-2** Growth of Hard Amorphous Ti-Al-Si-N Thin Films, **H. FAGER**, A. FALLQVIST, N. GHAFOOR, Linköping University, Sweden, M. JOHANSSON, Seco Tools AB Fagersta, Sweden, P.O.Å. PERSSON, M. ODÉN, L. HULTMAN, Linköping University, Sweden
8:40 am	**A1-3-3** Isothermal and Thermal Cycling Oxidation Behavior of Hot-Dip Alumina Coating on Flake/Spheroidal Graphite Cast Iron, **M.-B. LIN**, C.-J. WANG, National Taiwan University of Science and Technology, Taiwan	**B5-1-3 Invited** Solid Solutions and nanostructures in Al(Si)N Hard Coatings, **J. PATSCHEIDER**, Empa, Switzerland
9:00 am	**A1-3-5 Invited** Coatings for Severe High Temperature Corrosion Conditions, **M. SCHUETZE**, Dechema e.V., Germany	Invited talk continued.
9:20 am	Invited talk continued.	**B5-1-6** Corrosion Resistance and Hardness of Nb-Si-N Coatings Deposited by Dual Magnetron Sputtering, **G. RAMÍREZ**, S.E. RODIL, S. MUHL, L. HUERTA, Universidad Nacional Autonoma de Mexico, E. CAMPS, L. ESCOBAR-ALARCÓN, Instituto Nacional de Investigaciones Nucleares, Mexico
9:40 am		**B5-1-7** Quaternary-Phase Coatings in the Cr-WC-N System, **M.J. WALOCK**, University of Alabama, Birmingham, I. RAHIL, Arts et Metiers ParisTech, France, Y. ZOU, University of Alabama, Birmingham, C. NOUVEAU, Arts et Metiers ParisTech, France, A.V. STANISHEVSKY, University of Alabama, Birmingham
10:00 am		**B5-1-8** Self-Organized ZrN/Si_3N_4 Lamellar Growth During Reactive Dual Magnetron Sputtering of $Zr_{1-x}Si_xN_y$ Thin Films at High Temperature, **N. GHAFOOR**, K. YUAN, J. BIRCH, J. JENSEN, L. HULTMAN, M. ODÉN, Linköping University, Sweden, J. WEN, University of Illinois at Urbana- Champaign, I. PETROV, University of Illinois at Urbana-Champaign
10:20 am		**B5-1-9** Modulation Structure and Mechanical Properties of W/ZrB_2 Multilayers, G.Q. LIU, Y.B. KANG, **D.J. LI**, X.Y. DENG, Tianjin Normal University, China
10:40 am		**B5-1-10** Growth and Properties of Cr_2GeC Epitaxial Nanolaminated Thin Films, **P. EKLUND**, Linköping University, Sweden, M. BUGNET, M. JAOUEN, S. DUBOIS, C. TROMAS, T. CABIOC'H, University of Poitiers, France
11:00 am		**B5-1-12** In-Situ Characterisation of Microstructure Evolution in $Ti_{1-x}Al_xN$ Coatings During Annealing, **CH. WUESTEFELD**, D. RAFAJA, V. KLEMM, M. DOPITA, M. MOTYLENKO, TU Bergakademie Freiberg, Germany, C. BAEHTZ, Forschungszentrum Dresden-Rossendorf, Germany, C. MICHOTTE, CERATIZIT, Luxembourg, M. KATHREIN, CERATIZIT, Austria
11:20 am		**B5-1-13** Laminated Structure in the Internal Oxidation of Ta-Ru Coatings, **Y.-I. CHEN**, S.-M. CHEN, National Taiwan Ocean University, Taiwan
11:40 am		**B5-1-11** Nanostructured Superhard Films Ti-Hf-Si-N, their Properties and Structure, **D. POGREBNJAK**, Sumy State Univ, Ukraine, M. BERESNEV, Kharkov Natl Univ, P.V. KONARSKI, Tele & Radio Res Inst, V. UGLOV, F. KOMARTOV, Belarus St Univ, M.V. KAVERIN, Sumy Inst for Surf Mod, D.A. KOLESNIKOV, Belgorod St Univ, V. GRUDNITSKIY, Kharkov Natl Univ, N.A. MAKHMUDOV, Samarkand Branch of Tashkent Inst of Information, M.V. IL'YASHENKO, G.V. KIRIK, Sumy State Univ
	2012 ICMCTF Planning Meeting **(open to all interested attendees)** **12:00 - 1:15 pm Royal Palm 1-3 Room** **Elsevier FTS 12:15 - 1:15 PM California Room**	**2012 ICMCTF Planning Meeting** **(open to all interested attendees)** **12:00 - 1:15 pm Royal Palm 1-3 Room** **Elsevier FTS 12:15 - 1:15 PM California Room**

Thursday Morning, May 5, 2011

	Tribology and Mechanical Behavior of Coatings & Thin Films **Room: California - Session E2-1** **Mechanical Properties and Adhesion** **Moderators:** M.-T. Lin, National Chung Hsing University & Chaoyang University of Technology, J. Michler, Empa	**New Horizons in Coatings and Thin Films** **Room: Sunset - Session F1-2** **Nanomaterials, Nanofabrication, and Diagnostics** **Moderators:** S. Kodambaka, University of California at Los Angels, Y.A. Gonzalvo, Hiden Analytical
8:00 am	**E2-1-1 Invited** Theoretical Model Developed for the Pop-In Arising in the Thin Solids Films and Its Testification by Nanoindentations, **J.-F. LIN**, C.-F. HAN, National Cheng Kung University, Taiwan	**F1-1-1** Ordered ZnO/AZO/PAM Nanowire Arrays Prepared by Seed Layer Assisted Electrochemical Deposition, **Y.-M. SHEN**, C.-H. PAN, National Cheng Kung University, Taiwan, S.-C. WANG, Southern Taiwan University, Taiwan, J.-L. HUANG, National Cheng Kung University, Taiwan
8:20 am	Invited talk continued.	**F1-1-2** Hierarchical and Core-Shell ZnO/TiO_2 Photocatalytic Heterostructures, **J. MIGAS**, D. STONE, L. WANG, M.E. MCCARROLL, S.M. AOUADI, Southern Illinois University, Carbondale
8:40 am	**E2-1-3** Time Resolved Mechanical Surface Testing and Subsequent Physical Analysis, **N. SCHWARZER**, Saxonian Institute of Surface Mechanics, Germany	**F1-1-3** Photo-Degradation Behavior of N-Doped TiO_2 Nanotubes Prepared by Anodic Oxidation and Nitrogen Implantation, **J. LI**, F. HUANG, Q.-J. XUE, CAS Ningbo Institute of Materials Technology and Engineering, China
9:00 am	**E2-1-4** Mechanical Stress Effect on the Formation of Copper-Tin Intermetallic Thin Films, **M.-T. LIN**, C.-C. YANG, S.-N. LI, T.-C. CHEN, C.-M. CHEN, National Chung Hsing University & Chaoyang University of Technology, Taiwan	**F1-1-4** Low Temperature Growth Mechanisms of Vertically Aligned Carbon Nanofibers (CNFs) and Carbon Nanotubes (CNTs) by RF-PECVD, **H. WANG**, J.J. MOORE, Colorado School of Mines
9:20 am	**E2-1-5** What Qualifies a Well Adherent Cr-Based Adhesion Layer for Diamond-Like Carbon Coating Systems?, **J. SCHAUFLER**, C. SCHMID, G. YUANG, M. GÖKEN, K. DURST, University Erlangen-Nuremberg, Germany	**F1-1-5** Inkjet-Printed Carbon Nanotube Films, **A.R. HOPKINS**, D.C. STRAW, The Aerospace Corporation
9:40 am	**E2-1-6** Evidence of Vacuum Below Buckling Structures, **E. DION**, C. COUPEAU, J. COLIN, J. GRILHE, Université de Poitiers, France	**F1-1-6** Super-Hydrophobic Surfaces via Synthesis of Vertically Aligned Carbon Nanotube Arrays on Aluminum-Iron Matrix, B. BAYKAL, G. KUCUKAYAN, **E. BENGU**, Bilkent University, Turkey
10:00 am	**E2-1-7** Investigation of the Mechanical Properties of DLC-Coatings by Means of Nanoindentation and It's Modelling, **A. GIES**, OC Oerlikon Balzers AG, Liechtenstein, N. SCHWARZER, Saxonian Institute of Surface Mechanics, Germany, J. BECKER, H. RUDIGIER, OC Oerlikon Balzers AG, Liechtenstein	**F1-1-7** Fabrication of Nanoimprint Molds by Sub-Micron Sphere Lithography, **S. PORTAL**, C. CORBELLA, E. CABRERA, V.-M. FREIRE, E. PASCUAL, J.-L. ANDÚJAR, E. BERTRAN, Universitat de Barcelona, Spain
10:20 am	**E2-1-8** Fracture Behavior of Hard Multilayered Thin Films on Soft Substrates, C.G. OLIVA, Politecnico di Torino, Italy, R. GHISLENI, R. RAGHAVAN, Empa, Switzerland, D. UGUES, Politecnico di Torino, Italy, **J. MICHLER**, Empa, Switzerland	**F1-1-9** Gas Sensors with Porous Three-Dimentional Framework Using TiO_2/Polymer Double-Shell Hollow Microsphere, **C.-J. CHANG**, C-.K. LIN, Feng Chia University, Taiwan, C.-C. CHEN, National United University, Taiwan, C.-Y. CHEN, E.H. KUO, Feng Chia University, Taiwan
10:40 am	**E2-1-9** Correcting Time Dependent Displacement Effects in Nanoindentation Analysis, **M.I. DAVIES**, Univeristy of Nottingham, UK, N. SCHWARZER, Saxonian Institute of Surface Mechanics, Germany, B. BEAKE, Micro Materials Ltd, UK, N.M. EVERITT, University of Nottingham	**F1-1-10** Abnormal Retention Characteristics of $NiSi_2$/SiN_X Compound Nanocrystal Memory at Elevated Temperature, **Y.-T. CHEN**, National Sun Yat-sen University, Taiwan
11:00 am	**E2-1-10** Measuring Substrate-Independent Young's Modulus of Thin Films, **J. HAY**, Agilent Technologies	**F1-1-11** A Novel Fabrication Technique for Free Standing Nickel Nanowires and their Possible Applications, M. URGEN, **F.B. BAYATA**, N.S. SOLAK, Istanbul Technical University, Turkey
11:20 am	**E2-1-11** Interfacial Indentation Test of FeB/Fe_2B Coatings, M.A. DOÑU-RUIZ, I.E. CAMPOS-SILVA, J. MARTINEZ-TRINIDAD, **G. RODRIGUEZ-CASTRO**, E. HERNANDEZ-SANCHEZ, Instituto Politécnico Nacional, Mexico	
11:40 am	**E2-1-12** Indentation Size Effect on Fe_2B/Substrate Interface, I.E. CAMPOS-SILVA, **E. HERNANDEZ-SANCHEZ**, Instituto Politécnico Nacional, Mexico, M. ORTIZ-DOMÍNGUEZ, Instituto Politecnico Nacional, Mexico, A. RODRIGUEZ-PULIDO, G. RODRIGUEZ-CASTRO, Instituto Politécnico Nacional, Mexico	
	2012 ICMCTF Planning Meeting **(open to all interested attendees)** **12:00 - 1:15 pm Royal Palm 1-3 Room** **Elsevier FTS 12:15 - 1:15 PM California Room**	**2012 ICMCTF Planning Meeting** **(open to all interested attendees)** **12:00 - 1:15 pm Royal Palm 1-3 Room** **Elsevier FTS 12:15 - 1:15 PM California Room**

Thursday Morning, May 5, 2011

	New Horizons in Coatings and Thin Films Room: Royal Palm 1-3 - Session F5 New Oxynitride Coatings **Moderators:** W. Kalss, Oerlikon Balzers, S. Ulrich, Karlsruhe Institute of Technology (KIT)	Applications, Manufacturing, and Equipment Room: Royal Palm 4-6 - Session G1 Innovations in Surface Coatings and Treatments **Moderators:** A. Leyland, University of Sheffield, R. Cremer, KCS Europe
8:00 am	**F5-1 Invited** Oxynitride Coatings - Opportunities and Challenges from an Industrial Perspective, **J. SJÖLÉN**, Seco Tools AB, Sweden, A. KHATIBI, L. HULTMAN, Linköping University, Sweden	**G1-1** Electrical Measurement of Contamination Films in Plasma Reactors, **B.P. O'SHAUGHNESSY**, S.H. JANG, University of Texas at Dallas, J.S. LEE, DMS, G.S. LEE, University of Texas at Dallas
8:20 am	Invited talk continued.	**G1-2** Hierarchical Homo- and Hetero-Structures Produced using Unbalanced Magnetron Sputtering Techniques, **S.M. AOUADI**, B. SIROTA, D. STONE, L. WANG, M.E. MCCARROLL, Southern Illinois University, Carbondale
8:40 am	**F5-3** Deposition and High Temperature Stability of Reactively Magnetron Sputtered Al-Cr-O and Al-Cr-O-N Thin Films, **D. DIECHLE**, Karlsruhe Institute of Technology, Germany, A. CAVALEIRO, Coimbra University, Portugal, H. LEISTE, Karlsruhe Institute of Technology, Germany, V. SCHIER, Walter AG, Tübingen, Germany, M. STUEBER, S. ULRICH, Karlsruhe Institute of Technology, Germany	**G1-4 Invited** Synthesis, Interface Engineering, and Applications of Cubic Boron Nitride Films, **W.J. ZHANG**, B. HE, Q. YE, Y. YANG, I. BELLO, S.T. LEE, City University of Hong Kong
9:00 am	**F5-4** Synthesis of the Al-Cr-O-N Coatings by Reactive Cathodic Arc Evaporation, **D. KURAPOV**, H. RUDIGIER, T. BACHMANN, OC Oerlikon Balzers AG, Liechtenstein, M. DOEBELI, Ion Beam Physics, ETH Zürich, Switzerland	Invited talk continued.
9:20 am	**F5-5** Effect of Heat Treatment on the Structural Properties of LARC-Deposited AlCr-Based Oxynitride Coatings, H. NAJAFI, A. KARIMI, EPFL, Switzerland, P. DESSARZIN, **M. MORSTEIN**, Platit AG, Switzerland	**G1-6** Solution-Based Diamond-Like Carbon Coatings, **V.Z. POENITZSCH**, C. ELLIS-TERREL, R. WEI, K. COULTER, Southwest Research Institute
9:40 am	**F5-8** Dedicated Oxynitride Coating Systems for Heavy Machinable Materials, P. MAHR, **H. FRANK**, S. REICH, GFE Schmalkaden e.V., Germany	**G1-7** Microstructure and Corrosion Behavior of Magnetron Sputtering Ni-P-Based Alloy Thin Films, **F.-B. WU**, C.-C. WU, Y.-C. HSIAO, National United University, Taiwan
10:00 am	**F5-9** Fabrication and Optical Performance of Zirconium Oxynitride Coatings, **C.V. RAMANA**, I.C. FERNANDEZ, University of Texas at El Paso, A.L. CAMPBELL, Wright-Patterson Air Force Base (WPAFB)	**G1-8** An Investigation into the Effect of Triode Plasma Oxidation (TPO) on the Properties of Ti-6Al-4V, **S. BANFIELD**, Tecvac Ltd and University of Sheffield, UK, J.C. AVELAR-BATISTA WILSON, Tecvac Ltd, UK, G. CASSAR, A. LEYLAND, A. MATTHEWS, University of Sheffield, UK, J. HOUSDEN, Tecvac Ltd, UK
10:20 am	**F5-10** Characterization of Nanostructured Hydrophobic Zirconium Oxynitride Coatings Deposited by RF Magnetron Sputtering, S.K. RAWAL, A.K. CHAWLA, V. CHAWLA, R. JAYAGANTHAN, **R. CHANDRA**, Indian Institute of Technology, Roorkee, India	**G1-10** Interfacial Reaction of $Sn_{3.0}Ag_{0.5}Cu$ Solder with novel $Ni_{-x}Zn$ Under Bump Metallization, **H.-M. LIN**, J.-G. DUH, National Tsing Hua University, Taiwan
10:40 am		**G1-11** A Novel Preparation of Sn,Sb-O_{2-x} Coatings by Pulsed Fiber Laser Annealing, **C.-M. WANG**, National Cheng Kung University, Taiwan, C.-C. HUANG, H.-T. LIN, Cheng Shiu University, Taiwan, J.-L. HUANG, National Cheng Kung University, Taiwan
11:00 am		**G1-12** An analysis of the Temperature-Induced Supersaturation Effects on Structure and Properties of Sono-Electrodeposited Copper Thin Films, **A. MALLIK**, B.C. RAY, National Institute of Technology, India
11:20 am		**G1-9** The Stratified - Equiaxed Microstructure Transition of 316L Coatings by Low Pressure Plasma Spraying, **D.-M. YANG**, B.-H. TIAN, Y. GAO, The Thermal Spraying Center of Dalian Maritime University, China
11:40 am		**G1-3** The Titanium Oxide Film for Vascular Stent Modification, **Y.X. LENG**, Southwest Jiaotong University, China
	2012 ICMCTF Planning Meeting **(open to all interested attendees)** **12:00 - 1:15 pm Royal Palm 1-3 Room** **Elsevier FTS 12:15 - 1:15 PM California Room**	**2012 ICMCTF Planning Meeting** **(open to all interested attendees)** **12:00 - 1:15 pm Royal Palm 1-3 Room** **Elsevier FTS 12:15 - 1:15 PM California Room**

Thursday Morning, May 5, 2011

Coatings for Microelectronics and Active Devices
Room: Tiki Pavilion - Session TS6

Moderators: S.J. Bull, Newcastle University,
U. Helmersson, Linköping University

NOTES

Time	Session
8:00 am	**TS6-1** Improvement of Resistance Switching Behavior by Localizing Filament with Si Injection WO_X Switching Layer, **Y.E. SYU**, National Sun Yat-Sen University, Taiwan
8:20 am	**TS6-2** Mechanism and Characteristic Studies of Resistive Switching Effects on a Thin FeO_x-Transition Layer of the $TiN/SiO_2/FeO_x/Fe$ Structure by Thermal Annealing Treatments, **Y.-F. CHANG**, C.-Y. CHANG, National Chiao Tung University, Taiwan, T.-C. CHANG, National Sun Yat-Sen University, Taiwan
8:40 am	**TS6-3 Invited** Integration of Nickel Silicides in VLSI Circuits: A Mateirals Science Perspective, **P. DESJARDINS**, Ecole Polytechnique, Montreal, Canada
9:00 am	Invited talk continued.
9:20 am	**TS6-5** Resistive SwitchingCharacteristics of Ytterbium Oxide Thin Film for Nonvolatile Memory Application, **H.-C. TSENG**, National Sun Yat-sen University, Taiwan
9:40 am	**TS6-11** Study of Micro-Imprint by Electroless Nickel Plating Method, **H.-T. HSU**, M.-J. HO, T.-J. YANG, Feng Chia University, Taiwan
10:00 am	**TS6-8** Effect of the Thermal Stability and Electrical Behavior of Nickel Silicide by using Nickel Nitride, **C.-T. WU**, W-.H. LEE, C.-Y. WU, S-A. YAN, National Cheng-Kung University, Taiwan
10:20 am	**TS6-9** Inkjet-Printed High-k Nanocomposite Dielectric Film for OTFT Applications, **C.-T. LIU**, W-.H. LEE, T.-L. SHIH, H.-J. YAN, National Cheng-Kung University, Taiwan
10:40 am	**TS6-10** Resistive Switching Characteristics of Gallium Oxide for Nonvolatile Memory Application, **J.-J. HUANG**, National Sun Yat-Sen University, Taiwan
11:00 am	**TS6-6** Study of Sputter Deposited $SiO_2/Co/Pt/SiO_2$ Multilayers for Magnetic Storage, **R. WALIA**, Indian Institute of Technology, Roorkee, India, A.K. CHAWLA, R. CHANDRA, R. JAYAGANTHAN, Indian Institute of Technology Roorkee, India
11:20 am	
11:40 am	

2012 ICMCTF Planning Meeting
(open to all interested attendees)
12:00 - 1:15 pm Royal Palm 1-3 Room

Elsevier FTS 12:15 - 1:15 PM California Room

2012 ICMCTF Planning Meeting
(open to all interested attendees)
12:00 - 1:15 pm Royal Palm 1-3 Room

Elsevier FTS 12:15 - 1:15 PM California Room

Thursday Afternoon, May 5, 2011

	Coatings for Use at High Temperature Room: Sunrise - Session A2-1 Thermal and Environmental Barrier Coatings **Moderators:** R. Wellman, Cranfield University, B.T. Hazel, Pratt & Whitney, R. Trice, Purdue University	Hard Coatings and Vapor Deposition Technology Room: Golden West - Session B5-2 Hard and Multifunctional Nano-Structured Coatings **Moderators:** C.P. Mulligan, Benet Laboratories, US Army ARDEC, R. Sanjines, EPFL, P. Zeman, University of West Bohemia
1:30 pm	**A2-1-1 Invited** Effect of (CMAS-Assisted) Sintering under Service Conditions on the Thermo-Mechanical Stability of Plasma-Sprayed TBCs, **T.W. CLYNE**, M. SHINOZAKI, Cambridge University, UK	**B5-2-1 Invited** Wear-Resistant PTFE Based Nanocomposites, **T.A. BLANCHET**, S.S. KANDANUR, Rensselaer Polytechnic Institute
1:50 pm	Invited talk continued.	Invited talk continued.
2:10 pm	**A2-1-3** Degradation of YSZ Thermal Barrier Coatings by CMAS Infiltration, **V. KOLARIK**, M.M. JUEZ-LORENZO, Fraunhofer ICT, Germany, W. STAMM, Siemens Power Generation, Germany, H. FIETZEK, Fraunhofer ICT, Germany	**B5-2-3** Comparison of Different Bionic Structures Coated with CrAlN, W. TILLMANN, **J. HERPER**, Technische Universität Dortmund, Germany
2:30 pm	**A2-1-4** The Effect of Volcanic Ash on Sintering of Plasma Sprayed Thermal Barrier Coatings, **M. SHINOZAKI**, T.W. CLYNE, Cambridge University, UK	**B5-2-4** Surface Modification of Nanostructured NiTi Shape Memory Alloy Thin Films Using Various Passivation Layers by dc Magnetron Sputtering, N. CHOUDHARY, **D. KAUR**, Indian Institute of Technology Roorkee, India
2:50 pm	**A2-1-5 Invited** Mechanical Charactersation of Thermal Barrier Coatings After Thermal Treatments, **P. XIAO**, X. ZHAO, A. SHINMI, J. LIU, Y. ZHAO, I. SHAPIRO, University of Manchester, UK	**B5-2-6** Mechanical Properties, Tribological and Corrosion Resistance Evaluation of Cathodic Arc Deposited ZrN/CrN Multilayer Coatings, S.-F. CHEN, Natl Taiwan Univ of Sci & Tech, **J.-W. LEE**, Mingchi Univ of Tech, Taiwan, S.-H. HUANG, Natl Chiao Tung Univ, C.-J. WANG, Natl Taiwan Univ of Sci & Tech, T.-E. HSIEH, Natl Chiao Tung Univ, Y.-C. CHAN, H.-W. CHEN, J.-G. DUH, Natl Tsing Hua Unive, Taiwan, J.-W. CHEN, Gigastorage Corporation
3:10 pm	Invited talk continued.	**B5-2-7** High Temperature Crystallisation of Cr_2AlC MAX-Phase Coatings Sputter-Deposited at Room Temperature, **J.S. COLLIGON**, O. CRISAN, P. DOBROSZ, V. VISHNYAKOV, Manchester Metropolitan University, UK
3:30 pm	**A2-1-7** Interfacial Strength Measurement of Oxidized EB-PVD Thermal Barrier Coatings by the Laser Shock Adhesion Test (LASAT), **G. FABRE**, V. GUIPONT, M. JEANDIN, Centre des Materiaux - Mines ParisTech, France, A. PASQUET, J.Y. GUEDOU, SNECMA Safran Group, France, M. BOUSTIE, Institut PPRIME ENSMA, France, F.L. BERTHE, PIMM ENSAM, France	**B5-2-8 Invited** Recent Advances in Transition Metal Nitride–Based Nanostructured Hard and Superhard Coatings, **H.C. BARSHILIA**, K.S. RAJAM, NAL, Bangalore, India
3:50 pm	**A2-1-8** Observations of Ferroelastic Switching by Raman Spectroscopy, **A. BOLON**, M. GENTLEMAN, Texas A&M University	Invited talk continued.
4:10 pm	**A2-1-9** Factors to Consider in Cyclic Oxidation Testing of Thermal Barrier Coatings with MCrAlY-Bondcoats, **D. NAUMENKO**, P. SONG, L. SINGHEISER, W.J. QUADAKKERS, Forschungszentrum Julich, Germany	**B5-2-12** Comparison of Superhard and Superelastic Ti-Based Nanocomposite Erosion Resistant Coatings on Ti-6Al-4V Substrates Prepared by PECVD, S. HASSANI, **E. BOUSSER**, S. GURUVENKET, D. LI, J. KLEMBERG-SAPIEHA, L. MARTINU, Ecole Polytechnique de Montreal, Canada
4:30 pm	**A2-1-11** Characterization of the Alumina Scale Formed on Coated and Uncoated Doped, **K.A. UNOCIC**, B.A. PINT, Oak Ridge National Laboratory	**B5-2-10** Effects of Nanostructure Formation on the Fundamental Physical Properties of Epitaxial $Hf_{1-x}Al_xN(001)$ Alloys, **B.M. HOWE**, Univ of Illinois, T.W.H. OATES, ISAS, Germany, S.A. PUTTNAM, AFRL, J. WEN, Univ of Illinois, M.R. SARDELA, JR., Frederick-Seitz Matl Res Lab, A.A. VOEVODIN, AFRL, H. ARWIN, Linköping Univ, Sweden, J.E. GREENE, Univ of Illinois, L. HULTMAN, Linköping University, Sweden, I. PETROV, University of Illinois
4:50 pm	**A2-1-12** Laser Cycling Exposure of Thermal Barrier Coatings on Copper Substrates, **J. SCHLOESSER**, M. BÄKER, J. RÖSLER, Technische Universität Braunschweig, Germany	
5:10 pm	**A2-1-13** Processing, Repairing and Cyclic Oxidation Behaviour of Sol-Gel Thermal Barrier Coatings, L. PIN, Institut Clément Ader Mines Albi, France, F. ANSART, J.-P. BONINO, Cirimat Cnrs-Inpt-Ups Ensiacet, France, Y. LE MAOULT, **P. LOURS**, Institut Clément Ader Mines Albi, France	
	Poster Session: 5:00 - 7:00 pm **Town & Country Room** **Poster Reception: 6:00 - 7:00 pm**	**Poster Session: 5:00 - 7:00 pm** **Town & Country Room** **Poster Reception: 6:00 - 7:00 pm**

Thursday Afternoon, May 5, 2011

	Tribology and Mechanical Behavior of Coatings & Thin Films Room: California - Session E2-2 Mechanical Properties and Adhesion **Moderators:** M.-T. Lin, National Chung Hsing University & Chaoyang University of Technology, J. Michler, Empa	New Horizons in Coatings and Thin Films Room: Sunset - Session F1-2 Nanomaterials, Nanofabrication, and Diagnostics **Moderators:** S. Kodambaka, University of California at Los Angels, Y.A. Gonzalvo, Hiden Analytical
1:30 pm	**E2-2-1 Invited** Fatigue Damage in Ultra Thin Cu Films, **C.A. VOLKERT**, C. TRINKS, Institute for Materials Physics, University of Göttingen, Germany	**F1-2-1** Fabrication of Aluminum Nanodot Assisted Growth of Nanoroots for Application in Amorphous/Crystalline Silicon Composite Thin Film Solar Cells, **B. NEWTON**, H.K. MOHAMMED, H. ABU-SAFE, S.Q. YU, H.A. NASEEM, University of Arkansas
1:50 pm	Invited talk continued.	**F1-2-2** Platinum Doped Molybdenum Oxide Nanowires Alcohol Gas Sensor by Atomic Layer Deposition, **C.-C. CHANG**, National Tsing Hua University, Taiwan, H.-C. SHIH, Chinese Culture University, Taiwan
2:10 pm	**E2-2-3** Strain-Rate Sensitivity of Strength in Macro-to-Micro-to-Nano Crystalline Nickel, R.T. HUMPHREY, **A.F. JANKOWSKI**, Texas Tech University	**F1-2-3 Invited** Nanorods, Nanopipes, Nanosmiles, **D. GALL**, Rensselaer Polytechnic Institute
2:30 pm	**E2-2-4** Strain Rate Effects on Coated Surfaces' Response and their Film Fatigue Fracture: An Investigation by a Novel Impact Tester with Modulated Repetitive Force, **K.-D. BOUZAKIS**, G. MALIARIS, S. MAKRIMALLAKIS, Aristoteles University of Thessaloniki, Greece, CERTH, Greece & IPT, Germany	Invited talk continued.
2:50 pm	**E2-2-5** Microstructural Analysis of the Failure Mechanisms of Amorphous Carbon Coating Systems in Load-Scanning Tests, **H. HETZNER**, J. SCHAUFLER, S. TREMMEL, K. DURST, S. WARTZACK, University Erlangen-Nuremberg, Germany	**F1-2-5** Effects of Temperature and Pulse Mode on Nanoporous Anodic Aluminum Oxide Film by Potentiostatic Anodization, C.-K. CHUNG, **M.-W. LIAO**, H.-C. CHANG, National Cheng Kung University, Taiwan
3:10 pm	**E2-2-6** A Route to Avoid Thermo-Mechanical Fatigue Damage in Al Thin Films, W. HEINZ, **G. DEHM**, Montanuniversität Leoben, Austria	**F1-2-7** Epitaxial Si Layer Formed on ZrB_2 Thin Films - Silicene?, A. FLEURENCE, R. FRIEDLEIN, Y. WANG, F. BUSSOLOTTI, **Y. YAMADA-TAKAMURA**, School of Materials Science, JAIST, Japan
3:30 pm	**E2-2-7** Evaluation of Mechanical Properties in Cu Thin Films Under Various Substrate Conditions by Molecular Dynamics Simulation, J.-C. HUANG, **Y.-C. LIAO**, Tungnan University, Taiwan	**F1-2-8** Synthesis of Bioactive $NaHTi_3O_7$ Films on Ti-Coated Si by a Hydrothermal - Galvanic Couple Method, **C.-J. YANG**, L.-S. CHAO, National Chung Hsing University, Taiwan, Y.-C. CHIEH, Hsiuping Institute of Technology, Taiwan, F.-H. LU, National Chung Hsing University, Taiwan
3:50 pm	**E2-2-8** Comparison Titanium and Zirconia Dental Implants' Stress Analysis Using Finite Element Method, R. YESILDAL, **F. KARABUDAK**, M.P. YILDIRIM, F. BAYINDIR, Ataturk University, Turkey	**F1-2-9** Amorphous Phases and Crystallization Behaviour of Sputtered $Fe_{1-x}C_x$ Films with x Ranging between 0.32 and 0.50, **E. BAUER-GROSSE**, Nancy-University, France, G. LE CAËR, Universite de Rennes, France
4:10 pm	**E2-2-9** Effect of Nitrogen Flow Ratio on Microstructure and Property of Ta-Ti-N Thin Film by Reactive Sputtering of Ta-Ti Target, C.-K. CHUNG, **N.-W. CHANG**, T.-S. CHEN, National Cheng Kung University, Taiwan	**F1-2-11** Frost Reduction on the Micro/Nano Structured Superhydrophobic Aluminium Surface, **C.-T. YANG**, C.-H. LAN, St. John's University, Taiwan
4:30 pm	**E2-2-10** Mechanical Properties of Vapor Deposited Polyimide, **R. CHOW**, M. SCHMIDT, Lawrence Livermore National Laboratory	**F1-2-12** Micro/Nanostructured Surfaces of a-C:H:F Films with Anisotropic Properties, C. CORBELLA, **V.-M. FREIRE**, S. PORTAL, G. ONCINS, E. BERTRAN, J.-L. ANDÚJAR, Universitat de Barcelona, Spain
4:50 pm	**E2-2-11** Elastic Properties of Metastable $Mo_{1-x}Si_x$ Alloys: A Brillouin Light Scattering Study, **P. DJEMIA**, Université Paris, France, A. FILLON, G. ABADIAS, A. MICHEL, C. JAOUEN, University of Poitiers, France	**F1-2-13** Correlation Between Plasma and Properties of Cr_2AlC MAX Phase Coatings, **C. LEYENS**, O. SCHROETER, R. BASU, Technische Universität Dresden, Germany
5:10 pm	**E2-2-12** The Effect of Film Thickness Variations in Periodic Cracking: Shear Lag Analysis and Experiments, **AA. TAYLOR**, Erich Schmid Institute, Austria, V. EDLMAYR, Montanuniversität Leoben, Austria, R. RAJ, University of Colorado-Boulder, G. DEHM, Montanuniversität Leoben, Austria	
5:30 pm	**E2-2-13** Optimized Adhesion Strength of TiSiN Films Deposited by a Combination of DC and RF Sputtering, **A.R. BUSHROA**, H.H. MASJUKI, M.R. MUHAMAD, University of Malaya, Malaysia, B. BEAKE, Micro Materials Ltd, UK	**Poster Session: 5:00 - 7:00 pm** **Town & Country Room** **Poster Reception: 6:00 - 7:00 pm**

Thursday Afternoon, May 5, 2011

	New Horizons in Coatings and Thin Films Room: Royal Palm 1-3 - Session F2-1 **High Power Impulse Magnetron Sputtering** **Moderators:** R. Bandorf, Fraunhofer IST, . Sapieha, Ecole Polytechnique de Montreal	Applications, Manufacturing, and Equipment Room: Royal Palm 4-6 - Session G6 **Advances in Industrial PVD & CVD Deposition Equipment** **Moderators:** M. Rodmar, Sandvik Tooling Stockholm SE, K. Yamamoto, Kobe Steel Ltd.
1:30 pm	**F2-1-1 Invited** High Power Pulsed Magnetron Sputtering: a Review of Magnetron Ion Sputtering, **J. ALAMI**, Sulzer Metaplas, Germany, K. SARAKINOS, Linköping University, Sweden, K. KONSTANTINIDIS, CIRMAP, University of Mons, Belgium	**G6-1** Current and Future Applications of HIPIMS, **CH. SCHIFFERS**, T. LEYENDECKER, W. KÖLKER, S. BOLZ, CemeCon AG, Germany
1:50 pm	Invited talk continued.	**G6-2** Comparison of Hard Nitride Coatings Deposited by Industrial Scale AIP and HIPIMS Equipment, **K. YAMAMOTO**, S. TANIFUJI, J. MUNEMASA, H. NOMURA, Kobe Steel Ltd., Japan, R. CREMER, KCS Europe, Germany
2:10 pm	**F2-1-3** A Two-Zone Model for High-Power Pulsed Magnetron Sputtering Discharges, **T. KOZAK**, A.D. PAJDAROVA, University of West Bohemia, Czech Republic	**G6-3** Hybrid PVD Industrial Deposition Equipment for R&D Purposes, **L. PEETERS**, F. PAPA, R. TIETEMA, T. KRUG, Hauzer Techno Coating, Netherlands
2:30 pm	**F2-1-4** Temporal Evolution of the Radial Plasma Emission Profile in HIPIMS Plasma Discharge, **A. HECIMOVIC**, T. DE LOS ARCOS, M. BÖKE, J. WINTER, Institute for Experimental Physics II, Ruhr-Universität Bochum, Germany	**G6-4** Advantages of New Generation of Superior Arc Management Circuity, P. OZIMEK, **W. GLAZEK**, L. ZYSKOWSKI, Huettinger Electronic Sp. Z o.o., Poland
2:50 pm	**F2-1-5** The Influence of Pulse Arrangement and Off-Time Between Positive and Negative Pulse in Bipolar HIPIMS, **R. BANDORF**, M. RESCHKE, H. GERDES, G. BRÄUER, Fraunhofer IST, Germany	**G6-5 Invited** PVD Systems and Technology for Dedicated Hard Coatings: Challenges and Solutions, **J. VETTER**, G. ERKENS, J. MÜLLER, J. CRUMMENAUER, Sulzer Metaplas GmbH, Germany
3:10 pm	**F2-1-6** A Study on the Deposition Rate of Modulated Pulse Power (MPP) Magnetron Sputtering of Metallic Thin Films, **J. LIN**, J.J. MOORE, Colorado School of Mines, W.D. SPROUL, USA Reactive Sputtering, INC	Invited talk continued.
3:30 pm	**F2-1-7** The Effect of Various Deposition Parameters on the Phase of Tantalum Thick Films Deposited by Modulated Pulse Power Magnetron Sputtering, **S. MYERS**, J. LIN, J.J. MOORE, Colorado School of Mines, W.D. SPROUL, Reactive Sputtering, Inc., S. LEE, US Army ARDEC Benet Labs	**G6-7** Laser-Arc-Module System Combined with a Novel Filtering Unit for Industrial ta-C Coating of Parts and Tools, **H.-J. SCHEIBE**, Fraunhofer IWS, Germany, M. FALZ, MA. HOLZHERR, VTD Vakuumtechnik Dresden GmbH, Germany, M. LEONHARDT, A. LESON, C.-F. MEYER, Fraunhofer IWS, Germany, K.-D. STEINBORN, VTD Vakuumtechnik Dresden GmbH, Germany
3:50 pm	**F2-1-8** Control of the Magnetic Field for HiPIMS Process Optimization, J. CAPEK, M. HALA, O. ZABEIDA, **J. KLEMBERG-SAPIEHA**, L. MARTINU, Ecole Polytechnique de Montreal, Canada	**G6-8** InlineCoater™ 300: A New PVD System for Fast Research and High Volume Production, M. SAMUELSSON, Linköping University, Sweden, S. ÅSTRÖM, T. JOELSSON, A. FLINK, B. WÄLIVAARA, N. ODELSTAM, **H. LJUNGCRANTZ**, Impact Coatings AB, Sweden
4:10 pm	**F2-1-9** TiAlN Coatings Grown by HIPIMS, **G. GRECZYNSKI**, J. JENSEN, L. HULTMAN, Linköping University, Sweden, M. JOHANSSON, Seco Tools AB Fagersta, Sweden, CH. SCHIFFERS, CemeCon AG, Germany	
4:30 pm	**F2-1-10** Titanium Aluminum Nitride Sputtered using HIPIMS Technology, **M. LECHTHALER**, J. WEICHART, O. GSTOEHL, OC Oerlikon Balzers AG, Liechtenstein	
4:50 pm		
5:10 pm		
	Poster Session: 5:00 - 7:00 pm **Town & Country Room** **Poster Reception: 6:00 - 7:00 pm**	**Poster Session: 5:00 - 7:00 pm** **Town & Country Room** **Poster Reception: 6:00 - 7:00 pm**

Thursday Afternoon, May 5, 2011

Post Deadline Discoveries and Innovations
Room: Tiki Pavilion - Session PD

Moderators: G. Ramanath, Rensselaer Polytechnic Institute, S.J. Bull, Newcastle University

NOTES

1:30 pm	**PD-1** Superhard Transition Metal Diboride Coatings, **V.A. RAVI**, A. SCHISSLER, B. HARRISON, A. LY, J. KOCH, California State Polytechnic University, A. LECH, R. KANER, University of California, Los Angeles	
1:50 pm	**PD-2** Intelligent Self-Healing Corrosion Resistant Vanadia Coating of Flower-Like Morphology for AA2-24 and Novel Magnesium Alloys, **A.S. HAMDY**, Max Planck Institute, Germany & King Fahd University, Saudia Arabia, I. DOENCH, H. MÖHWALD, Max Planck Institute, Germany	
2:10 pm	**PD-3** Life Time Analysis of MCrAlY Coatings for Industrial Gas Turbine Blades (Calculational and Experimental Approach), **P. KRUKOVSKY**, K. TADLYA, Institute of Engineering Thermophysics, Ukraine, A. RYBNIKOV, Polzunov Central Boiler and Turbine Institute, Russia, V. KOLARIK, Fraunhofer ICT, Germany	
2:30 pm	**PD-5** Development of Photonic Platforms from Hybrid Sol-Gel Thin Films, **M. OUBAHA**, R. COPPERWHITE, A. GORIN, C. MCDONAGH, Dublin City University, Ireland	
2:50 pm	**PD-6** Vertical Growth of Carbon Nanotubes on Bulk Copper Substrates for Charge Storage Applications, **G. ATTHIPALLI**, R. EPUR, KUMTA, Y. TANG, A. STAR, J.L. GRAY, University of Pittsburgh	
3:10 pm	**PD-7** Thickness Ratio Calculation of Bi-Layer TiNi Alloys to Enhance Shape Memory Behavior using Stress-Strain Properties of the Individual Thin Films, **M. MOHRI**, M. NILI-AHMADABADI, University of Tehran, Iran	
3:30 pm	**PD-8** Novel Geometry Filtered Cathodic Arc Source, **P. SATHRUM**, Fluxion Inc.	
3:50 pm		
4:10 pm		
4:30 pm		
4:50 pm		
5:10 pm		
	Poster Session: 5:00 - 7:00 pm **Town & Country Room** **Poster Reception: 6:00 - 7:00 pm**	**Poster Session: 5:00 - 7:00 pm** **Town & Country Room** **Poster Reception: 6:00 - 7:00 pm**

Coatings for Use at High Temperature
Room: Town & Country - Session AP

Symposium A Poster Session
5:00 – 7:00 pm

AP-1

Preparation and Annealing Study of CrTaN Coatings on WC-Co, Y.-I. CHEN, **Y.-T. LIN**, National Taiwan Ocean University, Taiwan

AP-2

Microstructural Evolution in NiAl-Cr-Zr Coated Superalloys During High Temperature Annealing and Oxidation, **J.P. ALFANO**, M.L. WEAVER, The University of Alabama

AP-3

Microstructural Evolution and Thermal Stability of Vertical-Cracked Thermal Barrier Coatings Through Cyclic Thermal Fatigue, **S.-W. MYOUNG**, K.-S. SONG, T.-W. KANG, Z. LU, Y.-G. JUNG, Changwon National University, Korea, U. PAIK, Hanyang University, Korea

AP-4

Effect of Pre-Nickel Plating on the Microstructure and Phase Constitution of Hot-Dipped Aluminide Coating on Mild Steel, **W.-J. CHENG**, C.-J. WANG, National Taiwan University of Science and Technology, Taiwan

AP-5

Non Destructive Assessment by Photo-Stimulated Luminescence of EB-PVD Thermal Barrier Coatings Damaged by Laser Shock Spallation, **G. FABRE**, V. GUIPONT, M. JEANDIN, Centre des Materiaux - Mines ParisTech, France, F. PASSILLY, T. MAFFREN, ONERA, France, A. PASQUET, J.Y. GUEDOU, SNECMA Safran Group, France

AP-6

Pore Density Control of Al Thin Films with Process Conditions of Magnetron Sputtering, **J.-H. YANG**, J.-I. JEONG, S.-H. JANG, H.-S. PARK, Research Institute of Industrial Science and Technology, Korea

AP-7

Thermal Stability and Corrosion Resistance of AlTiON/CrON Multilayered Coating, **W.-Y. HO**, L.-W. SHEN, Z.-S. YANG, C.-L. CHANG, D.-Y. WANG, Mingdao University, Taiwan

AP-9

Nano Modified NiCrAlY Coatings for High Temperature Applications, **S. SAHU**, A.S. KHANNA, Indian Institute of Technology, India

AP-11

Thermal Properties Characterization of Gradient $RE_2Zr_2O_7$/YSZ Bilayer Thermal Barrier Coatings Obtained by the APS Method, G. MOSKAL, **A. ROZMYSLOWSKA-GRUND**, Silesian University of Technology, Poland

AP-12

Characteristics of Microstructural Phenomena in TGO Zone of TBC Layer of $Re_2Zr_2O_7$ Type, G. MOSKAL, **R. SWADŹBA**, Silesian University of Technology, Poland

AP-13

Comparison of Surface Quality, Machining Time in P-20 Steel and Alumold in the Manufacture of Thermoplastic Injection Mold, **W. MATTES**, SENAI-SC, Brazil

AP-14

Phase Transformation of MoS2-Nb Composite Coated Films at the High Temperatures, **I. EFEOGLU**, Atatürk University, Turkey, -. ALTINTAS, Bogazici University, Turkey, E. ARSLAN, Atatürk University, Turkey, O. BARAN, Erzincan University, Turkey, D. UGUR, Bogazici University, Turkey

AP-15

Cyclic Oxidation Behavior of HVOF Bond Coatings Deposited on La- and Y-doped Superalloys, **M.A. BESTOR**, J.A. HAYNES, B.A. PINT, Oak Ridge National Laboratory

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

Symposium B Poster Session
5:00 – 7:00 pm

BP-2

Oxygen Impurities in Ti-Si-N System are Hindering the Phase Segregation, Formation of Stable Nanostructure and Degrading the Cutting Performance of Tools Coated with the Nanocomposites, **S. VEPREK**, M. VEPREK-HEIJMAN, Technical University Munich, Germany, M. JILEK, SHM Ltd., Czech Republic, M. PISKA, Brno Technical University, Czech Republic, X. ZENG, Singapore Inst. of Manufacturing Technology, Singapore, A. BERGMAIER, Universität der Bundeswehr, Germany, Q.F. FANG, Chinese Academy of Sciences, China

BP-3

Structural and Mechanical Properties of Multilayered ZrN/CrAlN Coatings Synthesized by a Cathodic-Arc Deposition Process, **T.-H. YANG**, Y.-Y. CHANG, C.-Y. HSIAO, Mingdao University, Taiwan

BP-4

Evaluation of Depth Profile of Residual Stress in a TiN Thin Film, **C.-J. LAN**, J.-H. HUANG, G.-P. YU, National Tsing Hua University, Taiwan

BP-5

Measurement of Fracture Toughness on TiN Thin Films, **A.-N. WANG**, G.-P. YU, J.-H. HUANG, National Tsing Hua University, Taiwan

BP-6

Nanocomposite PVD Coatings for Milling of Hardened Steels and Cast Ion, **P. IMMICH**, U. SCHUNK, U. KRETZSCHMANN, LMT Fette, Germany

BP-7

An Experimental Trial of Prediction and Control Technology of Film Properties by a Numerical Model in Vacuum Vapor Deposition, J.-I. JEONG, J.-H. YANG, **H.-S. PARK**, S.-H. JANG, Research Institute of Industrial Science and Technology, Korea

BP-8

The Effect of Laser Annealing on the Crystal Structure of Magnetron Sputtered Alumina Thin Films, **H. ABU-SAFE**, Lebanese American University, Lebanon, F. RAWWAGH, Yarmouk University, Lebanon, M. TABBAL, American University of Beirut, Lebanon, M. ROUMIE, the National Council for Research, Lebanon

BP-9

Wear and Corrosion Properties of TiSiN and TiSiN/CrN Coatings by Cathodic Arc Deposition, W.-Y. HO, **C.-H. HSIEH**, Y.-Y. CHANG, C.-L. CHANG, C.-J. WU, MingDao University, Taiwan

BP-10

Properties of Carbon-Based Coatings on Injection Mold Steel Prepared by Nitriding and PCVD Hybrid Process, **K.H. LEE**, J.W. PARK, K.S. PARK, D.W. KIM, Research Institute of Industrial Science and Technology, Korea

BP-13

Tetrahedral Amorphous Carbon Tetrahedral Amorphous Carbon Deposited by Filtered Cathodic Vacuum Arc Bombarded by Argon Ions, **E.F. MOTTA**, G.A. VIANA, D.S. SILVA, A.D.S. CORTÊS, F.C. MARQUES, Universidade Estadual de Campinas, Brazil

BP-14

Thermal Stability of V-Al-C Thin Films Grown by DC Magnetron Sputtering Using a Multi-component Target, **Y. JIANG**, R. ISKANDAR, T. TAKAHASHI, J. ZHANG, M. TO BABEN, M. JOACHIM, J.M. SCHNEIDER, RWTH Aachen University, Germany

BP-15

The Effect of Composition on the Structure, Mechanical Properties, and Thermal Stability of Sputter Coated Ternary Chromium-Molybdenum-Nitride Coatings, **Y. ZOU**, University of Alabama, Birmingham

BP-16

Oxidation Resistance and Microhardness of (Ti,Al,Si)N/(Cr,Al,Y)N Nano-Multilayered Film, **T. MORI**, K. YOSHIWARA, M. TAKAHASHI, Keio University, Japan, T. WATANABE, Kanagawa Industrial Technology Center, Japan, T. SUZUKI, Keio University, Japan

BP-17

Evaluation of Ti_3SiC_2 Coatings Deposited by HTCVD from Methyltrichlorosilane and Titanium Tetrachloride, A. CLAUDEL, S. LUCA, R. MARTIN, P-O. ROBERT, D. PIQUE, ACERDE, France, M. MORAIS, E. BLANQUET, **M. PONS**, SIMAP, France

BP-18

Annealing Effect on Microstructure and Mechanical Properties of Titanium Nitride Thin Film, S.-C. HER, **W. N. LIN**, C.-L. WU, Yuan Ze University, Taiwan

BP-19

Texture and Magnetic Properties of Electrodeposited FePd Films, **H.-P. LIN**, J.-C. KUO, National Cheng Kung University Taiwan

BP-20

Effect of Oxygen in Aerosol Assisted Chemical Vapor Deposition of TiO_2 Using Titanium tetra-*iso*-propoxide/acetylacetone Solutions., **F. MAURY**, D. DUMINICA, CIRIMAT CNRS-INPT-UPS ENSIACET, France

BP-21

Cylindrical Magnetrons Sputter Deposition of Ta on Carbon Steels using DC Magnetron Sputtering, HIPIMS and MPPMS, R. WEI, Southwest Research Institute, **S. LEE**, M. RILEY, US Army ARDEC Benet Labs

BP-22

Effects of Nitrogen Ratio on Resistive Switching Characteristics of Titanium Oxynitride Thin Films by DC Reactive Magnetron Sputtering, L.-C. CHANG, K.-H. CHANG, Ming Chi University of Technology, Taiwan, **K.-H. LIU** Chang Gung University, Taiwan, H.-J. TSAI, W.-Z. WANG, Ming Chi University of Technology, Taiwan

BP-23

Plasma Diagnostics for Pulsed-dc Plasma-Polymerizing Para-Xylene using QMS and OES, C-.M. CHOU, Feng Chia University & Taichung Veterans General Hospital, Taiwan, C.-C. CHUANG, C.-H. LIN, Feng Chai University, Taiwan, **C.-J. CHUNG**, Central Taiwan University of Science and Technology & Taipei Medical University, Taiwan, J.-L. HE, Feng Chai University, Taiwan

BP-24

Corrosion Evaluation of Ductile Iron Duplex-Treated by Electroless Ni-P and TiAlZrN Coating, C.-H. HSU, Tatung University, Taiwan, C-.K. LIN, Feng Chia University, Taiwan, **K.-L. CHEN**, Y-.H. CHANG, Tatung University, Taiwan, C.-Y. SU, National Taipei University of Technology, Taiwan

BP-26

Microstructures and Mechanical Properties of Nano-Structured TiAlCN/Amorphous Carbon Films, W.-H. WU, Y.-Y. CHANG, **H-.Y. KAO**, Mingdao University, Taiwan

BP-27

The Effect of Bias on The Structure and Property of (Ti,Zr)N Thin Film Deposited by Radio Frequency Magnetron Sputtering, **Y.-W. LIN**, Instrument Technology Research Center, Taiwan, J.-H. HUANG, National Tsing Hua University, Taiwan, G.-P. YU, National Tsing Hua University, Taiwan, Republic of China

BP-28

Microstructures and Mechanical Properties of Cr-Si-B-N Films Synthesized by Unbalanced Magnetron Sputtering, C.-L. CHANG, **C.-Y. HUNG**, Mingdao University, Taiwan, J.-Y. JAO, National Chung Hsing University, Taiwan,

BP-29

Multi Pulse Modulated Pulse Power (MPMPP) Magnetron Sputtering of the Structural Modulated Hard Tribological Coatings, **J. LIN**, J.J. MOORE, Colorado School of Mines, W.D. SPROUL, Reactive Sputtering, Inc., S. LEE, US Army ARDEC Benet Labs

BP-31

Multilayer Diamond Coatings for the Machining of Aircraft Materials, C. BAREISS, W. KOELKER, M. WEIGAND, **CH. SCHIFFERS**, O. LEMMER, CemeCon AG, Germany

BP-32

Characterization of NiAl / TiAlSiN Thin Films Deposited by Unbalanced Magnetron Sputtering for Glass Modeling Dies Application, D.-Y. WANG, **W.-C. CHEN**, T.-A. LI, Mingdao University, Taiwan

BP-33

Evaluation of Ca Doped $Ce_{0.8}$ $Gd_{0.2}O_{1.9}$ Electrolyte by Various Deposition Method, **S.H. YANG**, K.H. KIM, H.W. CHOI, Kyungwon University, Korea

BP-34

Large Scale Deposition of TiC/a-C Nanocomposite Coatings by Magnetron Sputtering using Novel Ceramic Compound Targets, **M. STUEBER**, S. ULRICH, H. LEISTE, Karlsruhe Institute of Technology, Germany, P. POLCIK, M. O`SULLIVAN, PLANSEE Composite Materials GmbH, Germany

BP-36

Enhanced Efficiency in Dye-Sensitized Solar Cells Based on TiO_2 Nanotube/Nanoparticle Composition Powder, **C.-H. LEE**, K.H. KIM, H.W. CHOI, Kyungwon University, Korea

BP-39

Theoretical Investigation of the Dynamical and Thermodynamic Stability of One Monolayer SiN_x Interfaced with TiN, T. MARTEN, E.I. ISAEV, **B. ALLING**, L. HULTMAN, I. ABRIKOSOV, Linköping University, Sweden

BP-41

Magnetron Sputtered ZrN/SiN_x Nanocomposite Thin Films: Relationship Between Chemical Composition, Film Morphology and Electrical Properties, D. OEZER, S.C. SANDU, **R. SANJINÉS**, EPFL, Switzerland

BP-42

The Effect of H_2S Addition on the Crystal Quality of the Nanocrystalline Diamond Films Grown by the Down-Flow Microwave Plasma-Assisted Chemical Vapor Deposition, H. GAMO, Toppan Printing Co., Ltd., Japan, M. KIKUCHI, K. SHIMADA, Toyo University, Japan, T. ANDO, Northeastern University, Japan, **M.N. GAMO**, Toyo University, Japan

BP-44

Characterization of Cu-Ag Alloy Thin Films, J.-H. HSIEH, **S.-Y. HUNG**, Ming Chi University of Technology, Taiwan

BP-46

A Comparative Research on Magnetron Sputtering and Arc Evaporation Deposition of Ti-Al-N Coatings, **L. CHEN**, S. WANG, ZhuZhou Cemented Carbide Cutting Tools Co., LTD, China

BP-48

Evaluation of Microstructures and Mechanical Properties of Niobium and Vanadium Carbide Coated H11 Tool Steels, **J.-W. LEE**, Mingchi University of Technology, Taiwan, C.-T. LIN, Unilift Corp., Taiwan, M.-K. WU, J.-C. HUANG, Tungnan University, Taiwan

BP-50

Effect of Nitrogen Content in SiC_xN_y Thin Films Deposited by Magnetron Co-Sputtering Technique, R.S. PESSOA, **H.S. MEDEIROS**, L.V. SANTOS, H.S. MACIEL, A. S. DA SILVA SOBRINHO, M. MASSI, Technological Institute of Aeronautics, Brazil

BP-52

Enhancement of Thermal Stability on DLC Nanofilm by Using Addition of Silicon Top-Layer, C.-K. CHUNG, T.-Y. CHEN, C-W. LAI, **M.-W. LIAO**, National Cheng Kung University, Taiwan

BP-53

Formation and Characteristics of ZnNO Thin Film From n-Type to p-Type Conductivity by Thermal Annealing, **Y.-J. CHEN**, T.-F. YOUNG, T.-C. CHAN, T.-M. TSAI, K.-C. CHANG, C.-H. LI, National Sun Yat-Sen University, Taiwan

BP-54

Microstructure and Properties of Arc Sprayed Coatings Prepared by Conventional and Nanocomposite Cored Wires, M. TUIPRAE, **S. WIROJANUPATUMP**, S. JIANSIRISOMBOON, ChiangMai University, Thailand

BP-56

Study of the Structural and Mechanical Properties of Tungsten Zirconium Nitride Nanostructured Coatings Deposited by by Physical Vapor Deposition, P. DUBEY, **R. CHANDRA**, Indian Institute of Technology Roorkee, India

BP-58

Coating of Superalloy with Laser Surface Alloying, **M.H. RHEE**, Korea Automotive Technology Institute, Korea, W. Y. JEUNG, Korea Institute of Science and Technology, Korea, J.W. MIN, W.Y. CHUNG, Korea Automotive Technology Institute, Korea

BP-60

Heat Treatment of Nanocrystaline TiZrN Film Deposited by Unbalanced Magnetron Sputtering, **Q.-Y. CHEN**, J.-H. HUANG, G.-P. YU, National Tsing Hua University, Taiwan, Y.-W. LIN, Instrument Technology Research Center, Taiwan

BP-61

Morphology and Growth Mechanism of SiC Films Synthesized by Liquid Phase Epitaxy Assisted Chemical Vapor Deposition, **P.-T. LEE**, National Cheng Kung University, Taiwan, S.-C. WANG, Southern Taiwan University, Taiwan, P.-K. NAYAK, National Cheng Kung University, Taiwan, J.-C. SUNG, KINIK Company, Taiwan, J.-L. HUANG, National Cheng Kung University, Taiwan

BP-62

Synthesis of CrN and CrAlN Coatings for High Temperature Wear Applications, **H. ALAGÖZ**, M.F. GENISEL, Bilkent University, Turkey, M. UĞRAŞ, Atılım University, Turkey, E. BENGÜ, Bilkent University, Turkey

BP-64

Hot Filament CVD Grown Diamond Films at Various Total Mass Flow Rates under Constant Residence Time, M.A. ALI, **M. URGEN**, Istanbul Technical University, Turkey

BP-65

Improved Adhesion and Tribological Properties of Hard Graphite-Like Hydrogenated Amorphous Carbon Films Grown by a Remote Plasma on Steel Substrates, **T. ZAHARIA**, Eindhoven University of Technology, Netherlands, R. GROENEN, N.V. Bekaert S.A., Belgium, **R. VAN DE SANDEN**, Eindhoven University of Technology, Netherlands

BP-66

Structure Characterization and Antibacteria Behavior of TaN-Ag, TaN-Cu and TaN(Ag,Cu) Nanocomposite Thin Films, **Y.-J. LIN**, J.-H. HSIEH, S.-Y. HUNG, Ming Chi University of Technology, Taiwan, C. LI, National Central University, Taiwan

Fundamentals and Technology of Multifunctional Thin Films: Towards Optoelectronic Device Applications
Room: Town & Country - Session CP

Symposium C Poster Session
5:00 – 7:00 pm

CP-2

AZO Coatings Deposited by Reactive HiPIMS for Modified TCO Properties on Polymeric Web, P. BARKER, **P. KELLY**, G.T. WEST, Manchester Metropolitan University, UK, J.W. BRADLEY, University of Liverpool, UK, H. ASSENDER, University of Oxford, UK

CP-4

Study of the Physical Properties of PLD Grown Cobalt Doped Nanocrystalline $Zn_{0.9}Cd_{0.1}S$ Thin Films, **A.K. CHAWLA**, S. SINGHAL, H.O. GUPTA, R. CHANDRA, Indian Institute of Technology Roorkee, India

CP-6

Thermal Properties of C-Si-O Composite Thin Films Deposited by PBII Method, **S. ABE**, N. MOOLSRADOO, S. WATANABE, Nippon Institute of Technology, Japan

CP-7

Influence of Substrate Temperature on Electrical and Optical Properties of Al-Doped ZnO Thin Film, S.-C. HER, **T.-C. CHI**, Yuan Ze University, Taiwan

CP-8

Temperature Effect on the Optical and Mechanical Properties of Silver Thin Film Deposited on Glass Substrate, **S.-C. HER**, Y.-H. WANG, Yuan Ze University, Taiwan

CP-9

Charge Trapping Induced Frequency-Dependence Degradation in n-MOSFETs with High-k/Metal Gate Stacks, **C.-H. DAI**, National Sun Yat-sen University, Taiwan

CP-10

Electrical and Optical Characterization of Fluorine Doped Tin Dioxide Film Grown by Spray Method, M. OSHIMA, Univeristy of Miyazaki, Japan, K. NAOMI, **K. YOSHINO**, University of Miyazaki, Japan

CP-11

Improving the Visible Transmittance of Low-e Titanium Nitride Based Coatings for Solar Thermal Applications, **M. YUSTE**, R. ESCOBAR GALINDO, O. SÁNCHEZ, J.M. ALBELLA, Instituto de Ciencia de Materiales de Madrid, Spain

CP-13

Processing of TiO_2 Films by dc Magnetron Sputtering and Pulsed dc Magnetron Sputtering., **L.C. FONTANA**, Universidade do Estado de Santa Catarina, Brazil, J. LIN, J.J. MOORE, Colorado School of Mines

CP-14

The Band Diagram Constructed by Scanning Surface Potential Microscopy (SSPM) in n-ITO/p-Si Heterojunction Solar Cells, P.-C. JUAN, Center for Coatings and Laser Applications, Taiwan, C.-H. LIU, National Taiwan Normal University, Taiwan, **J.-F. DAI**, Ming Chi University of Technology, Taiwan, C.-L. LIN, Feng Chia University, Taiwan

CP-15

Optical Optimized Transparent Electrode for Thin Film Solar Cell by Atomic Layer Deposition, C.-N. HSIAO, C-.C. YU, P.-K. CHIU, C-.C. KEI, **D. CHIANG**, National Applied Research Laboratories, Taiwan, H.-C. PAN, Gintech Energy Corporation, Taiwan

CP-16

Helical SiO_2 Film for Indiscriminatively Circular Polarization Handedness Inversion, Y.-D. KIM, Y. ZOU, **J.-J. KIM**, J.-B. KIM, C.-K. HWANGBO, Inha University, Korea

CP-17

The Electrical Impedance Spectra Characterization of Electrochromic Glass, **W.-D. JHENG**, National Chin-Yi University of Technology, Taiwan, C-.K. LIN, Feng Chia University, Taiwan, C.-C. CHEN, National United University, Taiwan

CP-18

Tantalum Oxide Films Prepared by Magnetron Sputtering for All Solid State Electrochromic Devices, **S.-C. WANG**, Southern Taiwan University, Taiwan, K.-Y. LIU, J.-L. HUANG, National Cheng Kung University, Taiwan

CP-19

Effect of Annealing Temperature on the Microstructure and Photoluminescence of Low Resistivity Si/Si-N/Ta-N Thin Films Using Magnetron Sputtering, C.-K. CHUNG, T.-S. CHEN, **N.-W. CHANG**, M.-W. LIAO, National Cheng Kung University, Taiwan

CP-20

Surfactant Assisted Growth of SnO_2 Thin Films for Gas Sensing Applications, **K. KHUN KHUN**, A. MAHAJAN, R.K. BEDI, Guru nanak dev University, Amritsar, India

CP-21

Structural Evolution and Photocatalytic Activity of Pulsed Magnetron Sputtered Titania-Based Coatings, N. FARAHANI, P. KELLY, G.T. WEST, M. RATOVA, Manchester Metropolitan University, UK, C. HILL, Cristal Global, UK, **J. KULCZYK-MALECKA**, Manchester Metropolitan University, UK

CP-23

Characterization of IZO-Based Thin Film Transistors Fabricated Using a Novel Two-Step Deposition Process, **W. KIM**, S.-H. LEE, J.-H. BANG, H.-S. UHM, J.-S. PARK, Hanyang University, Korea

CP-24

Effects of Additive Hydrogen Gas on the Instability Due to Air Exposure in ZnO-Based Thin Film Transistors, J.-H. BANG, **S.-H. LEE**, W. KIM, H.-S. UHM, J.-S. PARK, Hanyang University, Korea

CP-26

$CuInSe_2$ Thin Film Photovoltaic Absorber Formation by Rapid Thermal Annealing of Binary Stacked Precursors, **J. KOO**, S.-C KIM, H. PARK, W.-K. KIM, Yeungnam University, Korea

CP-27

Galvanic Corrosion Behaviour of Al Based Coatings in 0.6 M NaCl Solution, **O.A. FASUBA**, A. YEROKHIN, A. MATTHEWS, A. LEYLAND, University of Sheffield, UK

CP-28

In Situ Thermal Residual Stress Evolution in ZnO Thin Films Deposited by Magnetron Sputtering on Si, **P.-O. RENAULT**, C. KRAUSS, E. LE BOURHIS, P. GOUDEAU, University of Poitiers, France, E. BARTHEL, SVI, Aubervilliers, France, S.Y. GRACHEV, A. BENEDETTO, SGR, Saint Gobain, France

CP-29

X-ray Photoelectron Spectroscopy Depth Profiling of La_2O_3/Si Thin Films Deposited by Reactive Magnetron Sputtering, C.V. RAMANA, R.S. VEMURI, University of Texas at El Paso, **V. KAICHEV**, Boreskov Institute of Catalysis, Russia, V. KOCHUBEY, Institute of Semiconductor Physics, Russia, A. SARAEV, Novosibirsk State University, Russia, V.V. ATUCHIN, Institute of Semiconductor Physics, Russia

CP-30

Microstructure and Dispersive Optical Parameters of Thermally Evaporated Nickel Films, C.V. RAMANA, University of Texas at El Paso, **V.V. ATUCHIN**, T.I. GRIGORIEVA, V.N. KRUCHININ, Institute of Semiconductor Physics, Russia, D.V. LYCHAGIN, Tomsk State University of Architecture and Building, Russia, L.D. POKROVSKY, Institute of Semiconductor Physics, Russia

CP-31

Effect of Nitrogen Pressure on the Growth, Microstructure and Optical Properties of TiN Thin Films, C.V. RAMANA, N. ESPARAJA, V. RANGEL, **S. WHITE**, University of Texas at El Paso, A.L. CAMPBELL, Wright-Patterson Air Force Base (WPAFB)

CP-34

Large Area Colloidal Crystals for Photonic Applications, **S. PORTAL**, E. CABRERA, O. ARTEAGA, M.-A. VALLVÉ, Universitat de Barcelona, Spain, J. FERRE-BORRULL, Universitate Rovira i Virgili, Spain, J. IGNÉS-MULLOL, E. BERTRAN, Universitat de Barcelona, Spain

CP-35

Diamond Like Carbon/Metal Nanocomposite Films for Solar Harvesting Applications, H. ZOUBOS, University of Ioannina, Greece, S. KALOGIROU, G. CONSTANTINIDIS, P.C. KELIRES, Cyprus University of Technology, Cyprus, **P. PATSALAS**, University of Ioannina, Greece

CP-36

Temperature Effect on $Cu(InGa)Se_2$ Thin Film Photovoltaic Absorber Formation by Reactive Annealing of Metal Precursors, **H. PARK**, J. KOO, J.-S. HAN, W.-K. KIM, Yeungnam University, Korea

CP-38

Transportation Model Establishment of InGaZnO TFT by Using Vacuum System Measurement, Z.-Z. LI, Minghsin University of Science and Technology, Taiwan, **Z.-X. FU**, Y.-T. CHOU, P.-T. LIU, National Chiao Tung University, Taiwan, B.-M.. CHEN, Minghsin University of Science and Technology, Taiwan

CP-41

Electron Microscopy Analysis of the Growth and Interface Structure of Sputter-Deposited ZrO_2 Thin Films, **C.V. RAMANA**, R.S. VEMURI, A. FERRER, University of Texas at El Paso

CP-42

High Transparent Soluble Polyimide/Polyimide–Nanocrystalline-Titania Hybrid Optical Materials for Antireflective Applications, Y.-Y. YU, W.-C. CHIEN, **H.-H. YU**, Ming Chi University of Technology, Taiwan

CP-43

Preparation and Characterization of P3HT:$CuInSe_2$:TiO_2 Thin Film for Application on Hybrid Solar Cell, Y.-Y. YU, W.-C. CHIEN, **S.-H. CHEN**, Ming Chi University of Technology, Taiwan

CP-46

Electrical and Morphological Properties of Metal Doped-TiO_2 Sol-Gel Thin Films, R. VALASKI, Inmetro, Brazil, **M. CREMONA**, Pontifícia Universidade Católica do Rio de Janeiro, Brazil, C. ARANTES, C. LEGNANI, W. QUIRINO, C. ACHETE, Inmetro, Brazil

CP-47

Preparation of Impurity-Doped ZnO Transparent Electrodes Suitable for Thin-Film Solar Cell Applications by Various Types of Magnetron Sputtering Depositions, T. MINAMI, J. NOMOTO, T. HIRANO, **T. MIYATA**, Kanazawa Institute of Technology, Japan

CP-48

PL and EL Characteristics of Rare Earth-Activated $BaLa_2O_4$ Phosphor Thin Films with or without Co-doping of Bi, T. MIYATA, Y. NISHI, J.-I. ISHINO, **T. MINAMI**, Kanazawa Institute of Technology, Japan

CP-49

Exciton Wavefunction Coupled Surface Plasmon Resonance for In-doped ZnO Nanowires with Aluminum Cylindrical Micropillars, **C.-H. FANG**, Y.-T. LIANG, J.-C. WANG, T.-E. NEE, Chang Gung University, Taiwan

CP-50

Preparation and Post Annealing Effect on Physical Properties of Nanostructure ZTO Thin Films, **V.K. JAIN**, University of Rajasthan, India, P. KUMAR, National Physical Laboratory, India, P. JAIN, Indian Institute of Technology, India, S. SRIVASTAV, S. AGRAWAL, Y.K. VIJAY, University of Rajasthan, India

Biomedical Coatings
Room: Town & Country - Session DP

Symposium D Poster Session
5:00 – 7:00 pm

DP-1

A Study on Cell Adhesion and Hemocompatibility of CN_x Coated on Carbon Nanotubes, M.L. ZHAO, Y.C. YUE, **D.J. LI**, Tianjin Normal University, China

DP-2

Characterization and Antibacterial Performance of ZrCN/Amorphous Carbon Coatings Deposited on Titanium Implants, **Y.-Y. CHANG**, Mingdao University, Taiwan, H.-L. HUANG, China Medical University and Hospital, Taiwan, H-.Y. KAO, Mingdao University, Taiwan, C.-H. LAI, T.-M. SHIEH, China Medical University and Hospital, Taiwan

DP-3

Modification of the Surface of Porous Polymer Fibrous and Membranes by Deposition of Multifunctional Bioactive Nanostructured Films, **D.V. SHTANSKY**, A.N. SHEVEIKO, P.V. KIRUYKHANTSEV-KORNEEV, National University of Science and Technology "MISIS", Russia, N.A. GLOUSHANKOVA, Cancer Research Center of RAMS, A.S. GRIGORYAN, Cental Research Dental Institute

DP-4

Stable Superhydrophilic Surfaces on Titanium Substrates, R. FLEMING, **M. ZOU**, University of Arkansas

DP-5

Allylamine Plasma Enhanced Cytocompatibility of Porous NiTi Bone Implants, S.L. WU, City University of Hong Kong, X.M. LIU, Hubei University, China, K.W.K. YEUNG, **T. HU**, City University of Hong Kong, Z.S. XU, Hubei University, China, J.C.Y. CHUNG, P.K. CHU, City University of Hong Kong

DP-6

Antibacterial with Silver-Embedded Silica/ Polyethylene Nanocomposite, **C.-H. CHIEN**, K-.H. CHEN, National Tsing Hua University, Taiwan, Y.-C. PU, C.-M. LIU, Industrial Technology Research Institute Taiwan, H-C. SHIH, National Tsing Hua University, Taiwan

DP-10

Microscopical Observation of Osteoblast Growth on Micro-arc Oxidized Titanium Dioxide, **H.-T. CHEN**, Feng Chia University & China Medical University Hospital, Taiwan, C.-J. CHUNG, Central Taiwan University of Science and Technology & Taipei Medical University, Taiwan, T.-C. YANG, Feng Chai University, Taiwan, C.-H. TANG, China Medical University, Taiwan, K.-C. CHEN, J.-L. HE, Feng Chai University, Taiwan

DP-11

In vivo Osseointegration Performance of Titanium Dioxide Modified Polyetheretherketone Using Arc Ion Plating, **H.-K. TSOU**, Feng Chia University & Taichung Veterans General Hospital, Taiwan, M.H. CHI, Feng Chai University, Taiwan, Y.-W. HUNG, Taichung Veterans General Hospital & National Chung Hsing University, Taiwan, C.-J. CHUNG, Central Taiwan University of Science and Technology & Taipei Medical University, Taiwan, J.-L. HE, Feng Chai University, Taiwan

DP-12

Corrosion Behavior of Ag-Ti(C,N) Coatings for Biomedical Applications, **G. RAMÍREZ**, Universidad Nacional Autonoma de Mexico, N. MANNINEM, S. CARVALHO, Universidade do Minho, Portugal, S.E. RODIL, Universidad Nacional Autonoma de Mexico, M. HENRIQUES, I. CARVALHO, Universidade do Minho, Portugal

DP-13

Silver Diffusion and Ionization Mechanisms on Antibacterial Ag(Au)-TiCN Coatings, I. CARVALHO, Universidade do Minho, Portugal, **R. ESCOBAR GALINDO**, Instituto de Ciencia de Materiales de Madrid, Spain, S. CALDERON, M. HENRIQUES, Universidade do Minho, Portugal, C. PALACIO, Universidad Autónoma de Madrid, A. CAVALEIRO, Coimbra University, Portugal, S. CARVALHO, Universidade do Minho, Portugal

DP-15

Photocatalytical Performance of Silver Containing Titania Films by Reactive Sputtering, **C.-C. HSIEH**, M.-S. WONG, National Dong Hwa University, Taiwan, H.-H. CHANG, Tza Chi University, Taiwan

DP-16

Corrosive Nature of Orthopedic Implant Alloys: Influence of Protien and Corrosion Mechanisms, **M.T. MATHEW**, Rush University Medical Center, R. POURZAL, University of Duisburg-Essen, Germany, J. HALLAB, Rush University Medical Center, A. FISCHER, University of Duisburg-Essen, J. JACOBS, M.A. WIMMER, Rush University Medical Center

DP-17

Thick Polycrystalline Diamond Layers for Biomedical Application, **M. FIJALKOWSKI**, Technical University of Lodz, Poland, A. KARCZEMSKA, Technica University of Lodz, Poland, J.M. LYSKO, Institute of Electron Technology, Poland, A. BOLSHAKOV, D. SOVYK, V. RALCHENKO, Russian Academy of Science, Russia

DP-19

Tribocorrosion of Multi-Layered ZrN/(Ti,Al)N Thin Coatings Deposited by Magnetron Sputtering, **O. JIMENEZ-ALEMAN**, M. FLORES, E. RODRIGUEZ, Universidad de Guadalajara, Mexico

DP-21

Tribocorrosion Behavior of $TiAlPt_xN$ Coatings in a Ringer´s Solution, **M. FLORES**, O. JIMENEZ, Universidad de Guadalajara, Mexico, J. GARCIA, Universidad Panamericana, Mexico, E. RODRIGUEZ, Universidad de Guadalajara, Mexico, L. HUERTA, Universidad Nacional Autonoma de Mexico

DP-22

The Tribocorrosion Behavior of Cp- Titanium Deposited by Micro Arc Oxidation at Different Frequencies, **E.E. DEMIRCI**, E. ARSLAN, Y. TOTIK, Atatürk University, Turkey, O. BARAN, Erzincan University, Turkey, I. EFEOGLU, Atatürk University, Turkey

Thursday Afternoon Poster Sessions

Tribology and Mechanical Behavior of Coatings and Thin Films
Room: Town & Country - Session EP

Symposium E Poster Session
5:00 – 7:00 pm

EP-1

Textured Coatings with Ag_3VO_4 Solid Lubricant Reservoirs, **S. SCHWARTZ**, Valparaiso University, B. LUSTER, D.P. SINGH, D. STONE, Southern Illinois University, Carbondale, M. BABEN, J.M. SCHNEIDER, RWTH Aachen University, Germany, K. POLYCHRONOPOULOU, C. REBHOLZ, University of Cyprus, P. KOHLI, S.M. AOUADI, Southern Illinois University, Carbondale

EP-2

Formation of Micro- and Nanostructured Phases in Ni-Cr-B-Si-Fe Coatings Improving Their Protection Functions, **D. POGREBNJAK**, N. BRATUSHKA, M.V. IL'YASHENKO, G.V. KIRIK, P. SHYPYLENKO, Sumy State University, Ukraine, L. ALOTSEVA, V. PROHORENKOVA, East-Kazakstan State Technical University, Kazakhstan, V. PSHYK, A. DEMIANENKO, Sumy State University, Ukraine

EP-3

Tribological Properties and Thermal Stability of C-Si-O Composite Thin Films Deposited by PBII Method, **N. MOOLSRADOO**, S. ABE, S. WATANABE, Nippon Institute of Technology, Japan

EP-5

Analysis of Mechanical Properties and Structure of a-C:H DLC Thin Films, **A.N. BERTHELSEN**, S. LOURING, N.D. MADSEN, Aarhus University, Denmark, B.H. CHRISTENSEN, K.P. ALMTOFT, L.P. NIELSEN, Danish Technological Institute, Tribology Centre, Denmark, J. BØTTIGER, Aarhus University, Denmark

EP-6

Nano-Impact Test on a TiAlN Pvd Coating and Correlation Between Experimental and Fem Results, **K.-D. BOUZAKIS**, S. GERARDIS, G. SKORDARIS, Aristoteles University of Thessaloniki, Greece, CERTH, Greece & IPT, Germany, E. BOUZAKIS, Aristoteles University of Thessaloniki, Greece, CERTH, Greece & IPT, Germany, Greece

EP-10

Comparison of Gas Nitrided and Powder-Pack Borided AISI 4140 Steel Behaviour in Terms of Tribological Properties, L. LOPEZ, ITESM, Mexico, **J. SOLIS**, SEP-DGEST-ITTLA/ITESM, Mexico, U. FIGUEROA, E. OSEGUERA, ITESM, Mexico, O.A. GOMEZ, SEP-DGEST-ITTLA/ITESM, Mexico

EP-11

Optimized DLC Films for High-Performance Racing Engine Applications, **O. CODDET**, Platit AG, Switzerland, B. TORP, Platit Scandinavia, Denmark, G. BULAJA, Platit Inc., USA, C. GALAMAND, Platit AG, Switzerland, G. HUFFMAN, Calico Coatings, USA, T. CSELLE, Platit AG, Switzerland

EP-15

Structural, Surface and Mechanical Properties of a-C:H:Si:F and a-C:H:Si:Cl Films Produced by PECVD, T. MATIELLO, R. TURRI, M.B. APPOLINARIO, R. MARTINS, State University of São Paulo - UNESP, Brazil, C.U. DAVANZO, UNICAMP, Brazil, W.H. SCHREINER, State University of Paraná, Brazil, N. CRISTINO DA CRUZ, E. RANGEL, J.R. BORTOLETO, **S.F. DURRANT**, State University of São Paulo - UNESP, Brazil

EP-17

The Study on the Mechanical Properties of Perfect Lattice and Sputtering of Al/Cu Multilayer Thin Film by Molecular Dynamics Simulation, J.-C. HUANG, **Y.-C. LIAO**, Tungnan University, Taiwan

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

Symposium F Poster Session
5:00 – 7:00 pm

FP-2

The Preparation and Photo-Sensing of Thermal Evaporated ZnS/ZnO Core-Shell Nanowires, **Y.-W. CHENG**, National Cheng Kung University Taiwan, H.-C. SHIH, Chinese Culture University, Taiwan, C.-P. LIU, National Cheng Kung University Taiwan

FP-4

Defects and Oxygen Incorporation in TiAlN, M. TO BABEN, L. RAUMANN, **J.M. SCHNEIDER**, RWTH Aachen University, Germany

FP-5

Aluminum Films with Protruding Nanoislands by Thermal Evaporation, **R. FLEMING**, M. ZOU, University of Arkansas

FP-8

The Nano-Depth Profiling Analysis of La-Substituted $BiFeO_3$ Multiferroic Thin Films Sputtered on Silicon Surface with Different Postannealing Temperatures, P.-C. JUAN, **C.-W. HSU**, Ming Chi University of Technology, Taiwan, C.-H. LIU, National Taiwan Normal University, Taiwan

FP-9

Two-Step Synthesis and Electrical Transport Properties of Tungsten Oxide Nanowires Bundles, T. HSIEH, **L.-W. CHANG**, C.-C. CHANG, National Tsing Hua University, Taiwan, B.J. WEI, National Chung Hsing University, Taiwan, H-C. SHIH, National Tsing Hua University, Taiwan

FP-10

Position and O_2 Concentration Effects on Growth of Carbon Nanotubes (CNTs) by DC-PECVD at Low Temperature, **H. WANG**, J.J. MOORE, Colorado School of Mines

FP-11

Novel Nanoplate Thin Film Solar Cell Using Amorphous Silicon-Based Materials, **B.-F. HSIEH**, J.-W. FAN, S.-T. CHANG, C.-Y. LIN, National Chung Hsing University, Taiwan

FP-12

Recycling of Used DLC-Coated WC/Co Dies for Practical Dry Stamping, **T. AIZAWA**, Shibaura Institute of Technology, Japan, Y. MORITA, Nano-Coat and Film LLC, Japan

FP-15

The Effect of Thickness on Structure and Properties of Tantalum Thin Films Deposited by Modulated Pulse Power Magnetron Sputtering, **S. MYERS**, J. LIN, J.J. MOORE, Colorado School of Mines, W.D. SPROUL, Reactive Sputtering, Inc., S. LEE, US Army ARDEC Benet Labs

FP-16

Graphene Layers Deposited by Hot Wire CVD, **C. CORBELLA**, J. BADIA-CANAL, V.-M. FREIRE, E. BERTRAN, J.-L. ANDÚJAR, Universitat de Barcelona, Spain

FP-18

Analysis of the Inorganic Component of Autogenous Tooth Bone Graft Material, **S.-C. JIN**, S.-G. KIM, J.-H. BYEON, Y.-K. KIM, Chosun University, Korea, S.-Y. KIM, Yeungnam University, Korea, I.-W. UM, Dentist - Private Practice, Korea

FP-19

Non-Catalytic Method to Prepare Organized Nickel–Carbon Nanofibers on Nanopatterned Silicon Substrates, **A.-A. EL MEL**, Université de Nantes, France, W. XU, C.-H. CHOI, Stevens Institute of Technology, E. GAUTRON, B. ANGLERAUD, A. GRANIER, P.-Y. TESSIER, Université de Nantes, France

FP-20

Stable Electron-Emission from a Tip-Type Carbon Nanotube-Based Emitter via Formation of Interlayers, **J.-P. KIM**, H.-B. CHANG, Y.-R. NOH, Hanyang University, Korea, J.-U. KIM, Korea Electrotechnology Research Institute, Korea, J.-S. PARK, Hanyang University, Korea

FP-21

Small Angle Neutron Scattering (SANS) Characterization of Electrically Conducting Polyaniline Nanofiber/Polyimide Nanocomposites, **A.R. HOPKINS**, The Aerospace Corporation, S.J. TOMCZAK, AFRL/RZSM, Edwards Air Force Base, V. VANDANA, AFRL/PRSM, Edwards AFB, A.J. JACKSON, NIST

FP-24

Effects of Tip-Curvatures and Selective Growth on Electron Emission Behavior in Conical-Type Carbon Nanotube Field-Emitters, Y.-R. NOH, J.-P. KIM, **H.-B. CHANG**, J.-S. PARK, Hanyang University, Korea

FP-25

Plasma Species Influence on the Properties of Oxynitrided Titanium Surface, **C.A. ALVES**, Federal University of Rio Grande do Norte - Brazil, D.C. BRAZ, J.C.P. BARBOSA, R.C.S. ROCHA, UFRN, Brazil, A. NUNES, Federal University of Rio Grande do Norte - Brazil, C. KRUG, Federal University of Rio Grande do Sul - Brazil

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

Symposium G Poster Session
5:00 – 7:00 pm

GP-2

Improvement on Corrosion Resistance of Austempered Ductile Iron via Low Temperature Duplex Coatings, C.-H. HSU, **K.-H. HUANG**, Y.-T. CHEN, Tatung University, Taiwan, P.-L. SUN, C-.K. LIN, Feng Chia University, Taiwan

GP-8

Fabrication and Mechanical Characteristics of Metal Matrix Composite with Homogeneously Dispersed Ceramic Particles, E.-H. KIM, W.-R. LEE, Changwon National University, Korea, C.-G. LEE, M.-K. LEE, J.-J. PARK, Korea Atomic Energy Research Institute, Korea, C-.S. LEE, METIA Corporation, Korea, **Y.-G. JUNG**, Changwon National University, Korea

GP-9

Synthesis of Hydrogenated Amorphous Carbon Films with a Line Type Atmospheric-Pressure Plasma CVD Apparatus, **M. AGEMI**, K. KAYAMA, M. NOBORISAKA, Keio University, Japan, A. SHIRAKURA, Kanagawa Academy of Science and Technology (KAST), Japan, T. SUZUKI, Keio University, Japan

GP-10

Influence of the Deposition Pressure on Properties of a-C:H Films Synthesized Using a Dielectric Barrier Discharge, **R. HORIKOSHI**, K. KAYAMA, M. NOBORISAKA, Y. TACHIMOTO, Keio University, Japan, T. WATANABE, Kanagawa Industrial Technology Center, Japan, A. SHIRAKURA, Kanagawa Academy of Science and Technology (KAST), Japan, T. SUZUKI, Keio University, Japan

GP-12

Surface Texture and Stress State in Post Polished Cathodic Arc PVD Coatings, **A. PILKINGTON**, S.J. DOWEY, J.T. TOTON, RMIT University and Defence Materials Technology Centre, Australia, L. WARD, RMIT University, Australia, D. GRIFFETT, Cuttertec Pty, Australia, E.D. DOYLE, RMIT University and Defence Materials Technology Centre, Australia

GP-13

Thermal Annealing Effect on Material and Electrical Properties of NbN_x Gates on HfO_2 Gate Dielectrics, **S.-Y. LIN**, Y.-S. LAI, National United University, Taiwan

GP-15

Electrochemical Behavior of the Ti_6Al_4V Alloy Implanted by Nitrogen PIII, G.S. SAVONOV, Instituto Tecnologico de Aeronautica - ITA & Instituto Nacional de Pesquisas Espaciais - INPE, Brazil, **M. UEDA**, R.M. OLIVEIRA, Instituto Nacionale de Pesquisas Espaciais - INPE, Brazil, C. OTANI, Instituto Tecnologico de Aeronautica - ITA, Brazil

GP-17

Hydrophilicity of TiO_x Thin Films by Atmospheric Pressure Plasma Enhanced Chemical Vapor Deposition, **S.-S. KIM**, J.-U. SHIN, S.-C. OH, Institue for Advanced Engineering, Korea

GP-19

Uniformity Enhancement of Incident Dose on Concave Surface in Plasma Immersion Ion Implantation Assisted by Pulsed Beam-Line Plasma, Z.T. ZHU, X.B. TIAN, Z.J. WANG, **C.Z. GONG**, S.Q. YANG, Harbin Institute of Technology, China, R.K.Y. FU, P.K. CHU, City University of Hong Kong, China

GP-22

Liquid-Phase Deposition of Low-k Carbon Nitride Films, **H. KIYOTA**, M. HIGASHI, T. KUROSU, M. CHIBA, Tokai University, Japan

GP-23

Deposition of $In_{2-x}Fe_xO_3$ Films by Ultrafast Microwave Annealing Technique, S.B. QADRI, Naval Research Laboratory, **C. FAHED**, George Mason University, N.A. MAHADIK, H. KIM, M. OSOFSKY, Naval Research Laboratory, M.V. RAO, George Mason University, Y. TIAN, L. T. Technologies

GP-24

Incorporation of Silver Nanoparticles in DLC Films for Spatial Application, **S.F. FISSMER**, L.V. SANTOS, M. MASSI, Technological Institute of Aeronautics, Brazil, P.A. RADI, Instituto Nacional de Pesquisas Espaciais - INPE, Brazil

GP-25

The Electrical Contact Resistance Endurance of Thin Silver Coatings Subjected to Fretting Wear: Influence of the Coating Thickness, P. JEDRZEJCZYK, Ecole Centrale de Lyon - LTDS, France, **S. FOUVRY**, CNRS - ECL, France, P. CHALANDON, PSA, France

GP-26

Plasma Nitrocarburizing of AISI 304 Stainless Steel Under Floating Potential, **T.R. DA ROSA**, Technological Institute of Aeronautics, Brazil, L.C. FONTANA, M. TOMIYAMA, J.H.C.P. SANTOS, Universidade do Estado de Santa Catarina, Brazil, H.S. MACIEL, Technological Institute of Aeronautics, Brazil

GP-28

The Characteristics of Interface for Pentacene/ZnO Hybrid p-n Junction Diode, **J-B. KWON**, H.-H. KIM, M.-S. KIM, J.-H. HAN, D.-H. LEE, B.-H. O, S.-G. LEE, E.-H. LEE, S.-G. PARK, Inha University, Korea

GP-30

Improved Nucleation and Transition in Fast Response Liquid Crystal Displays by Atmospheric Plasma Treatments, **G.M. WU**, H.W. CHIEN, C.C. HUANG, Chang Gung University

GP-31

Nitriding of Tool Steels in Electron Beam Excited Plasma, **P. ABRAHA**, J. MIYAMOTO, Meijo University, Japan

GP-32

Multi-Functional ECR Plasma Sputtering System for Preparing Amorphous Carbon and Al-O-Si Films, X. FAN, D. DIAO, K. WANG, **C. WANG**, Xian Jiaotong University, China

Symposium T Poster Session
Room: Town & Country - Session TSP

TP Poster Session
5:00 – 7:00 pm

TSP-2

Fabrication and Characterization of Nanocomposite Films, S.-C. HER, T.-Y. SHIU, **S.J. LIU**, Yuan Ze University, Taiwan

TSP-3

Alumina Template Assistance in Pt/Sn Core-Shell Nano-Sphere Fabrication, **C.-L. CHEN**, C.-C. CHEN, Y.-S. LAI, National United University, Taiwan

TSP-10

Why Taking Creep Material Behavior Into Account is of Great Importance, **P. HEUER-SCHWARZER**, N. BIERWISCH, Saxonian Institute of Surface Mechanics, Germany

TSP-11

Interfacial Structure and Electrical Properties of Epitaxial $NiSi_2$/Si Contacts Formed by a Solid-Phase Reaction in Ni-P/Si(100) System, **H.-F. HSU**, C.-L. WU, T.-H. CHEN, H.-Y. WU, National Chung Hsing University, Taiwan

TSP-12

GDOES for Accurate and Well Resolved Thin Film and Coating Analysis, **P. SCHAAF**, M. WILKE, L. SPIEß, G. TEICHERT, H. ROMANUS, TU Ilmenau, Institut für Werkstofftechnik, Germany

TSP-14

Characterization and Properties of Multilayered BN/SiO_2 Thin Films for Tailoring Thermal and Mechanical Contact Interfaces, **J. HU**, J.E. BULTMAN, Air Force Research Laboratory/UDRI, J.J. GENGLER, Air Force Research Laboratory/Spectral Energies, C. MURATORE, A.A. VOEVODIN, Air Force Research Laboratory

TSP-15

Atom Probe Reconstruction Limitations in the Quantification of Interfacial Intermixing in Multilayered Thin Films, J.G. BRONS, University of Alabama, A.A. HERZING, I.M. ANDERSON, NIST, **G.B. THOMPSON**, University of Alabama

TSP-16

Wear Properties of Thick TiSiCN Coatings, J.-F. SU, Y. CHEN, X. NIE, University of Windsor, Canada, R. WEI, Southwest Research Institute, **S. CUI**, University of Windsor, Canada

TSP-17

Pressure Cell for Thermal Conductivity Measurement of Thin Films under Applied Stress with the Time Domain Thermoreflectance Technique, **J.E. BULTMAN**, A.J. SAFRIET, Air Force Research Laboratory/UDRI, J.J. GENGLER, Air Force Research Laboratory/Spectral Energies, A.R. WAITE, Air Force Research Laboratory/UTC, C. MURATORE, J.G. JONES, Air Force Research Laboratory, B.M. HOWE, I. PETROV, University of Illinois at Urbana-Champaign

TSP-20

Thermal Properties of Metal/Carbon Interfaces, **C. MURATORE**, Air Force Research Laboratory, S. SHENOGIN, UES/Air Force Research Laboratory, J.J. GENGLER, Air Force Research Laboratory/Spectral Energies, J. HU, Air Force Research Laboratory/UDRI, A. ROY, A.A. VOEVODIN, Air Force Research Laboratory

TSP-21

Pressure Dependence on Thermal Conductivity and Interface Conductance of Interface Materials for Thermal Switching, **A.R. WAITE**, Air Force Research Laboratory/UTC, J.J. GENGLER, Air Force Research Laboratory/Spectral Energies, J.G. JONES, C. MURATORE, A.A. VOEVODIN, Air Force Research Laboratory

Friday Morning, May 6, 2011

	Coatings for Use at High Temperature **Room: Sunrise - Session A2-2** **Thermal and Environmental Barrier Coatings** **Moderators:** R. Wellman, Cranfield University, B.T. Hazel, Pratt & Whitney, R. Trice, Purdue University	**Hard Coatings and Vapor Deposition Technology** **Room: Golden West - Session B7** **Thermodynamics and Kinetic Considerations for Coating Growth** **Moderators:** V. Gorokhovsky, Southwest Research Institute, San Antonio Texas, P. Patsalas, University of Ioannina
8:00 am	**A2-2-1 Invited** Synchrotron Studies of Environmental Barrier Coatings, **K.T. FABER**, Northwestern University	**B7-1 Invited** Suppression of Intermixing in Strain-Relaxed Epitaxial Layers, T.L. LEONTIOU, Cyprus University of Technology, Cyprus, J.D. TERSOFF, IBM, **P.C. KELIRES**, Cyprus University of Technology, Cyprus
8:20 am	Invited talk continued.	Invited talk continued.
8:40 am	**A2-2-3** Low Thermal Conductivity Multi-Phase Thermal Barrier Coatings, **V. TOLPYGO**, W. BAKER, Honeywell, R. LECKIE, C.G. LEVI, University of California, Santa Barbara, A. LIMARGA, D. CLARKE, Harvard University, K. MURPHY, Alcoa Howmet	**B7-3** Theoretical Investigation of Atomistic Surface Processes in Multinary Nitrides Materials, **B. ALLING**, L. HULTMAN, Linköping University, Sweden
9:00 am	**A2-2-4** Deposition of Thick and 50 % Porous YpSZ Layer by Spraying Nitrate Solution in a Low Pressure Plasma Reactor, C. FOURMOND, **F. ROUSSEAU**, D. MORVAN, F. PRIMA, Chimie ParisTech, France, M.H. VIDAL-SETIF, O. LAVIGNE, ONERA, France	**B7-5** Fundamental Aspects of Mixed Oxide Thin Film Growth, **M. SARAIVA**, Ghent University, Belgium, V. GEORGIEVA, N. JEHANATHAN, University of Antwerp, Belgium, S. MAHIEU, W.P. LEROY, Ghent University, Belgium, R. PERSOONS, Flemish Institute for Technological Research (VITO), Belgium, G. VAN TENDELOO, A. BOGAERTS, University of Antwerp, Belgium, D. DEPLA, Ghent University, Belgium
9:20 am	**A2-2-5 Invited** Foreign Object Damage Phenomena of Various Thermal and Environmental Barrier Coatings, **S.R. CHOI**, Naval Air Systems Commands	**B7-6** Modelling Reactive Sputter Deposition of Titanium Nitride in a Triode Magnetron Sputtering System, J.C. SAGÁS, D.A. DUARTE, Technological Institute of Aeronautics, Brazil, L.C. FONTANA, Universidade do Estado de Santa Catarina - Brazil, **T.R. ROSA**, D.R. IRALA, Technological Institute of Aeronautics, Brazil
9:40 am	Invited talk continued.	**B7-7 Invited** Thermodynamics of Small Systems Applied to Fluid Mixtures of Condensing Films at Critical Consulate Points, **M.A. MILLER**, Southwest Research Institute
10:00 am	**A2-2-7** Effect of Composition on the Growth and Microstructure of Hafnia-Zirconia Based Thermal Barrier Coatings, **M. NOOR-A-ALAM**, A. CHOUDHURI, C. RAMANA, University of Texas at El Paso	Invited talk continued.
10:20 am	**A2-2-8** Characterization of Microstructure, Thermal and Electric Properties of $RE_2Zr_2O_7$ of the TBC Thermal Barrier Coatings Obtained by the APS Method, **A. ROZMYSLOWSKA-GRUND**, G. MOSKAL, Silesian University of Technology, Poland	**B7-9** Understanding the Catalytic Effect of H_2S on CVD-Growth of α-Al_2O_3:Thermodynamic Gas Phase Simulations and ab Initio Theory, A. BLOMQVIST, Uppsala Univ, Sweden, **C. ÅRHAMMAR**, Sandvik Tooling Stockholm SE, Sweden, S. NORGREN, Sandvik Mining & Construction AB, Sweden, F. SILVEARV, Uppsala Univ, Sweden, M. RODMAR, Sandvik Tooling Stockholm SE, Sweden, R. AHUJA, Uppsala Univ, Sweden
10:40 am	**A2-2-9** Strain Localisation in Thermal Barrier Coatings Mechanical Compressive Test, **V. MAUREL**, Centre des Materiaux - Mines ParisTech, France, P. DE BODMAN, SNECMA Safran Group, France, L. RÉMY, Centre des Materiaux - Mines ParisTech, France	**B7-10** Study of Structural Properties of PVD Coatings on Inclined Substrates, K. KUMAR, **S. MUKHERJEE**, Institute for Plasma Research, India
11:00 am	**A2-2-11** Analysis of Thermoelastic Characteristics for Vertical-Cracked Thermal Barrier Coatings Through Mathematical Approaches, **J. GO**, Y.-G. JUNG, S. KIM, Changwon National University, Korea, U. PAIK, Hanyang University, Korea	**B7-11** Structural Analysis of Alumina Thin Films Deposited by Dual Magnetron Sputtering, **W. ENGELHART**, V. SCHIER, Walter AG, Tübingen, Germany, W. DREHER, NMI Naturwissenschaftliches und Medizinisches Institut, Germany, O. EIBL, Universität Tübingen, Germany
11:20 am		
	Thank You & See You Next Year Party **12:30 – 1:30 pm** **Trellises Courtyard near Pool**	**Thank You & See You Next Year Party** **12:30 – 1:30 pm** **Trellises Courtyard near Pool**
	Award Nominations Deadline **October 1, 2011**	**Award Nominations Deadline** **October 1, 2011**

Friday Morning, May 6, 2011

	Tribology and Mechanical Behavior of Coatings and Thin Films **Room: California - Session E2-3** **Mechanical Properties and Adhesion** **Moderators:** M.-T. Lin, National Chung Hsing University & Chaoyang University of Technology, J. Michler, Empa	**New Horizons in Coatings and Thin Films** **Room: Royal Palm 1-3 - Session F2-2** **High Power Impulse Magnetron Sputtering** **Moderators:** R. Bandorf, Fraunhofer IST, J. Sapieha, Ecole Polytechnique de Montreal
8:00 am	**E2-3-1** Optimization of the Scratch Test for Specific Coating Designs, **G. FAVARO**, CSM Instruments SA, Switzerland, N. BIERWISCH, Saxonian Institute of Surface Mechanics, Germany, Q.-H. DUONG, P. KEMPE, CSM Instruments SA, Switzerland, J. RAMM1, Oerlikon Balzers AG, Switzerland, N. SCHWARZER, Saxonian Institute of Surface Mechanics, Germany, B. WIDRIG, OC Oerlikon Balzers AG, Germany	**F2-2-1 Invited** The influence of High Power Impulse Magnetron Sputtering (HIPIMS) Pulse Parameters on Plasma, Target and Substrate Interactions for Chromium, **F. PAPA**, Hauzer Techno Coating, BV, Netherlands, H. GERDES, R. BANDORF, Fraunhofer IST, Germany, A.P. EHIASARIAN, Sheffield Hallam University, UK, I. KOLEV, R. TIETEMA, Hauzer Techno Coating, BV, Netherlands, G. BRAEUER, Fraunhofer IST, Germany, T. KRUG, Hauzer Techno Coating, BV, Netherlands
8:20 am	**E2-3-2** A Modified Scratch Test for the Mechanical Characterization of Scratch Resistance and Adhesion of Thin Hard Coatings on Soft Substrates, **T. SANDER**, S. TREMMEL, S. WARTZACK, University Erlangen-Nuremberg, Germany	Invited talk continued.
8:40 am	**E2-3-3 Invited** The Plastic Deformation of Metallic Thin Films on Substrate Seen Through In Situ TEM Experiments, **M. LEGROS**, CEMES-CNRS, France	**F2-2-3** A Comparison of PET Plasma Pre-Treatment Using Medium Frequency and Low Frequency-High Power Pulse Oxygen-Containing Discharges, M. AUDRONIS, V. BELLIDO-GONZALEZ, Gencoa Ltd, UK, S. HINDER, **M. BAKER**, University of Surrey, UK, A. MATTHEWS, University of Sheffield, UK
9:00 am	Invited talk continued.	**F2-2-4** Growth of HfO_2-Based High-k Dielectric Films by High Power Impulse Magnetron Sputtering, **K. SARAKINOS**, B. LÜ, H. ARWIN, Linköping University, Sweden, K. KONSTANTINIDIS, CIRMAP, University of Mons, Belgium, M. TO BABEN, D. MUSIC, J.M. SCHNEIDER, RWTH Aachen University, Germany, U. HELMERSSON, Linköping University, Sweden
9:20 am	**E2-3-5** Correlation between Adhesion Strength and Coating/Substrate Mechanical Properties using the Scratch Test Technique, **B. ZHOU**, N. RANDALL, CSM Instruments	**F2-2-5** Growth of V-Al-C Thin Films by HPPMS and DC Magnetron Sputtering Using a Multi-Component Target, **Y. JIANG**, S. MRAZ, T. TAKAHASHI, RWTH Aachen University, Germany
9:40 am	**E2-3-6** Numerical and Experimental Analyses of Scratch Tests Conducted on Coated Systems with Residual Stress Gradients, N.K. FUKUMASU, **R.M. SOUZA**, University of Sao Paulo, Brazil, A.A.C. RECCO, University of Santa Catarina, Brazil, A.P. TSCHIPTSCHIN, University of Sao Paulo, Brazil	**F2-2-7** Rotatable Magnetron Sputtering of Aluminium in Continuous and Pulse Modes Using Different Strength Magnetic Arrays, **M. AUDRONIS**, V. BELLIDO-GONZALEZ, R. BROWN, Gencoa Ltd, UK
10:00 am	**E2-3-7** Mechanical and Wear Characterization of Electroless Nickel-Boron Coatings, V. VITRY, A.-F. KANTA, **F. DELAUNOIS**, Université de Mons, Belgium	
10:20 am	**E2-3-12** Micro-Scratch Testing for Interface Characterizations of Diamond-Coated Tools, **P. LU**, University of Alabama, X. XIAO, M.J. LUKITSCH, General Motors Research and Development Center, K. CHOU, The University of Alabama	
10:40 am	**E2-3-8** Investigation of the Mechanical Properties of Hierarchically Structured Gold Nanoparticles, **A.J. SMITH**, Y.W. HAO, E.I. MELETIS, University of Texas at Arlington	
11:00 am	**E2-3-10** Influence of the Nitriding and TiAlN/TiN Coating Thickness on the Mechanical Properties and Adhesion of Duplex Treated AISI H13 Steel, **R. TORRES**, P.C. SOARES, Pontifícia Universidade Católica do Parana, Brazil, C.M. LEPIENSKI, Universidade Federal do Parana, Brazil, R.M. SOUZA, M. FARIA, A.P. TSCHIPTSCHIN, University of Sao Paulo, Brazil	
11:20 am	**E2-3-11** Microstructure and Characterization of Ternary Sputtering Ni-Ru-P Coatings, **Y.-C. HSIAO**, F.-B. WU, National United University, Taiwan	
11:40 am	**E2-3-13** Adhesive Interlayers' Effect on the Entire Structure Strength of Glass Molding Tools" Pt-Ir Coatings by Nanotests Determined, F. KLOCKE, RWTH Aachen Univ, , CERTH, Greece & IPT, Germany, K.-D. BOUZAKIS, Aristoteles Univ of Thessaloniki, CERTH, Greece & IPT, Germany, **K. GEORGIADIS**, IPT, Germany, S. GERARDIS, G. SKORDARIS, M. PAPPA, Aristoteles Univ of Thessaloniki,CERTH, Greece & IPT, Germany	**Thank You & See You Next Year Party** **12:30 – 1:30 pm** **Trellises Courtyard near Pool**
12:00 pm	**E2-3-9** A Study on the Microstructures and Mechanical Properties of Ti-Al-Cr-Si-N Nanocomposite Thin Films Prepared by Pulsed DC Reactive Magnetron Sputtering System, **P.-C. HUANG**, Tungnan University, J.-W. LEE, Mingchi University of Technology, Taiwan, H.-P. CHEN, Tungnan University, Taiwan, Y.-C. CHAN, H.-W. CHEN, J.-G. DUH, National Tsing Hua University, Taiwan	**Award Nominations Deadline** **October 1, 2011**

	Applications, Manufacturing, and Equipment Room: Royal Palm 4-6 - Session G5 Coatings, Pre-Treatment, Post-Treatment and Duplex Technology **Moderators:** N. Bagcivan, RWTH Aachen University, E. Kusano, Kanazawa Institute of Technology	NOTES
8:00 am	**G5-1** The Growth of Single Fe_2B Phase on Low Carbon Steel via Phase Homogenization in Electrochemical Boriding (PHEB), **G. KARTAL**, S. TIMUR, Istanbul Technical University, Turkey, O.L. ERYILMAZ, A. ERDEMIR, Argonne National Laboratory	
8:20 am	**G5-2 Invited** Duplex Treatment for Forming Tools, **A. REITER**, Oerlikon Balzers, Germany	
8:40 am	Invited talk continued.	
9:00 am	**G5-4** Development of rf/dc Plasma Systems for Nitriding of Aluminum Alloys, **T. AIZAWA**, Y. SUGITA, Shibaura Institute of Technology, Japan	
9:20 am	**G5-5** Adherent Nanocrystalline Diamond Thin Films Grown on Surface-Modified Ti and Ti Alloys at Moderate Temperatures, **Y.-S. LI**, University of Saskatchewan, Canada	
9:40 am	**G5-6** Microstructure and Properties Thermally Sprayed and Laser Remelted of the Fe-Cr-Mo-W-Mn-C-B Coating, **A. IWANIAK**, G. MOSKAL, Silesian University of Technology, Poland	
10:00 am	**G5-7 Invited** Alumina Coatings Obtained by Thermal Spraying and Plasma-Anodizing - a Comparison, **T. LAMPKE**, D. MEYER, G. ALISCH, D. NICKEL, I. SCHARF, Chemnitz University of Technology, Germany	
10:20 am	Invited talk continued.	
10:40 am	**G5-9** Repair of Thermal Damage in Gate Dielectric for Germanium-Based Metal-Oxide-Semiconductor Device by Supercritical Fluid Technology, **C.-S. HUANG**, P.-T. LIU, National Chiao Tung University, Taiwan	
11:00 am	**G5-10** Improvements on the Cavitation Erosion Resistance of Austenitic Stainless Steels by Plasma Surface Alloying Processes with Carbon and Nitrogen Followed by PAPVD Cr-Al-N, **C. GODOY**, R. BORGES, Universidade Federal de Minas Gerais, Brazil, J.C. AVELAR-BATISTA WILSON, Tecvac Ltd, UK, R.G. MELO, Universidade Federal de Minas Gerais, Brazil	
11:20 am		
	Thank You & See You Next Year Party 12:30 – 1:30 pm Trellises Courtyard near Pool	**Thank You & See You Next Year Party 12:30 – 1:30 pm Trellises Courtyard near Pool**
	Award Nominations Deadline October 1, 2011	**Award Nominations Deadline October 1, 2011**

Authors Index

Bold page numbers indicate the presenter

— I —

— J —

— K —

— N —

— O —

— P —

— Q —

— R —

— S —

— Y —

— Z —

Hard Coatings and Vapor Deposition Technology
Room: Royal Palm 1-3 - Session B2-1

CVD Coatings and Technologies
Moderator: S. Ruppi, Walter AG, F. Maury, CIRIMAT CNRS-INPT-UPS ENSIACET

10:00am **B2-1-1 Mild Chemistry as a Strategy for the Preparation of Metal-Containing Films**, ***N. Bahlawane*** *(naoufal@pc1.uni-bielefeld.de)*, Bielefeld University, Germany & CRP-Gabriel Lippmann, Luxembourg **INVITED**

The deposition of metals using the thermal CVD process faces challenging issues regarding the purity and the nucleation kinetics on semiconducting surfaces. The use of adequate deposition chemistry is proposed as an alternative to overcome these limitations. In fact, transition-metal cations, which exhibit enhanced catalytic redox character, are able to induce the dehydrogenation reaction of alcohols under CVD conditions. Taking advantage of this intrinsic reactivity, a new method that enables the deposition of transition metal thin films through a self-catalyzed reaction pathway is developed. Hence, alcohols were used as powerful co-reactants to grow technologically relevant transition metals (i. e. Ni, Fe, Co, Cu, Ag, Pt and Ru) starting from commercially available, robust and cost-effective precursors.

Using this process, the precursors and the selected alcohol are admitted to the reactor as a single liquid feedstock, enabling the growth of device-quality metal thin films as well as a controlled growth of a large variety of alloys.

Since the driving force in the metals deposition is the intrinsic catalytic activity of the transition metal cations towards the alcohols, metal cations which do not possess a strong catalytic redox character, such as Zn, Al and Sn, grow as oxides under the same deposition conditions, which turns out to be an immense advantage. In fact, this process offers a unique chance for the CVD-growth of metal-metal oxide nano-composite thin films with the possibility to tune the composition of the metallic nano-particles and that of the oxide matrix as well. These composites can be considered as a ground for the development of innovative materials with tailored optical, electric and magnetic properties.

References:

- N. Bahlawane, P.A. Premkumar, Z. Tian, X. Hong, F. Qi, K. Kohse-Höinghaus, Chem. Mater. 22, 92-100, 2010

- N. Bahlawane, P.A. Premkumar, F. Reilmann, K. Kohse-Höinghaus, J. Wang, F. Qi, B. Gehl, M. Bäumer, J. Electrochem. Soc. 156(10), D452-D455, 2009

- P.A. Premkumar, A. Turchanin, N. Bahlawane, Chem. Mater. 19, 6206-6211, 2007

- N. Bahlawane, P.A. Premkumar, K. Onwuka, K. Kohse-Höinghaus, G. Reiss, Microelectron. Eng. 84, 2481-2485, 2007

- N. Bahlawane, P.A. Premkumar, K. Onwuka, K. Rott, G. Reiss, K. Kohse-Höinghaus, Surf. Coat. Technol. 201(22-23), 8914-8918, 2007

10:40am **B2-1-3 Deposition of Cobalt Oxide Thin Films by PECVD for Catalysis Application**, ***C. Guyon*** *(cedric-guyon@chimie-paristech.fr)*, Chimie ParisTech, France, *A. Barkallah*, UPMC, France, *F. Rousseau*, Chimie ParisTech, France, *K. Giffard*, UPMC, France, *D. Morvan, M. Tatoulian*, Chimie ParisTech, France

Plasma-enhanced chemical vapor deposition (PECVD) was used to prepare thin films of cobalt oxide. Cobalt oxide-based (CoO and Co_3O_4) catalysts were chosen for their efficiency during mineralisation of organic pollutants achieved by catalytic ozonation. Several authors have reported that Co_3O_4 spinel is the best active phase for the catalytic ozonation[1,2], and a very active component for hydrocarbons oxidation and combustion[3,4]. Moreover, the antibacterial properties of these products are not negligible[5]. In this paper, we used two types of PECVD processes for the production of cobalt thin films. In the first one, cobalt thin films were deposited using a parallel electrodes RF low-pressure plasma reactor (13.56 MHz, 100 Pa, 200 W) with cobalt carbonyl ($Co(CO)_8$) as precursor sprayed in gas carrier (argon and oxygen). In the second process, a solution of nitrate salt of cobalt is sprayed into a low pressure plasma discharge (600 Pa, 120 W) to obtain Co_xO_y layers.

The chemical composition and the microstructural evolution of the coating were studied by X-ray photo-electron spectroscopy (XPS), Fourier-transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD). To characterize the morphologies and the thicknesses of the studied films, scanning electron microscopy and EDX were used.

Considering thin films obtained from cobalt carbonyl precursor, analyses confirmed the presence of cobalt oxide (layer of 2 µm) on the surface of the substrate. XRD investigation showed the presence of crystalline phase of Co_3O_4 (crystallite size of about 42 nm) as shown in Figure 1. In the case of coatings produced from a solution of cobalt nitrate salt, a layer of 3 µm and an amorphous form of Co_xO_y oxides on surface was observed, as shown in Figure 2. Catalytic ozonation will be tested for oxidation of para-chlorobenzoic acid (pCBA) used as persistent organic pollutant.

[1] P.M. Alvarez et Al , Applied Catalysis B: Environmental 72 (2007) 322-330

[2] Hu, C., Xing, S., Qu, J., He, H., J. Phys. Chem. C 112, (2008),5978–5983

[3] T.-C. Xiao, S.-F. Ji, H.-T. Wang, K.S. Coleman, M.L.H. Green, J. Mol.Catal., A Chem. 175 (2001) 111.

[4] M.M. Zwinkels, S.G. Jaras, P.G. Menon, T.A. Griffin, Catal. Rev., Sci.Eng. 35 (1993) 319.

[5] Y-M. Jeong , J-K. Lee , S-C. Ha, S H. Kim; Thin Solid Films 517 (2009) 2855–2858

11:00am **B2-1-4 Polymeric Barrier Coatings via Initiated Chemical Vapor Deposition**, ***T. Parker*** *(thomas.c.parker1@us.army.mil), J.D. Demaree, D. Baechle*, U.S. Army Research Laboratory

Initiated chemical vapor deposition (iCVD) enables micron sized particles to be coated with conformal polymeric films. Unlike wet chemistries, particle agglomeration is mitigated due to the vapor phase deposition. A custom built iCVD with a rotary evaporator was used to coat a variety of particles with poly(glycidyl methacrylate) (PGMA). Glass beads with average diameters of 45 µm and 355 µm were coated with a ~1 µm PGMA film. Initially, it was found that the 45 µm particles stuck to the sides of the evaporator flask. To combat this, the flask was partially submerged in an ultrasonic bath which kept the particles free flowing during the deposition. Thermo gravimetric analysis (TGA) was used to assess if the beads were coated with PGMA. The TGA testing showed a 0.7 % mass loss at ~275˚C, which corresponds to the decomposition temperature of PGMA. In addition Sodium chloride (~355 µm) particles were coated in the iCVD system again with PGMA. The dissolution rate of these particles in an aqueous solution was found to be reduced by an order of magnitude (versus uncoated NaCl). Finally, particles with metallic coatings were coated with PGMA to help protect their optical properties.

Hard Coatings and Vapor Deposition Technology
Room: Golden West - Session B4-1

Properties and Characterization of Hard Coatings and Surfaces
Moderator: M. Fenker, FEM Research Institute, B. Zhao, Exxon Mobil

10:00am **B4-1-1 Comparative ab Initio and Experimental Study of Ti-Al-N, Zr-Al-N and Hf-Al-N**, ***P.H. Mayrhofer*** *(paul.mayrhofer@unileoben.ac.at), D. Holec, R. Rachbauer*, Montanuniversität Leoben, Austria

Hard coatings based on transition metal aluminum nitrides are well established and routinely used for various industrial applications due to their outstanding properties like high hardness, wear and corrosion resistance. However, the favourable phenomena are often strictly connected to their crystalline structure. While Ti-Al-N coatings are known to crystallize either in cubic or wurtzite structure (or a mixture of both) depending on the Al content, the crystallization behavior is more complicated for Zr-Al-N and Hf-Al-N, which can also form Zr_3N_4 and Hf_3N_4 based structures.

Here we present experimental and ab initio studies with emphasis on phase stability ranges and lattice structures of ternary $Ti_{1-x}Al_xN$, $Zr_{1-x}Al_xN_y$ and $Hf_{1-x}Al_xN_y$ alloys. The concept of special quasi-random structures to simulate more random-like alloys is compared with studies of ad hoc structures which can mimic also clustering of ions. Several crystallographic configurations (like cubic, wurtzite, hexagonal) are considered, as these are the stable and metastable phases of the binary constituents.

A strong dependence of the various phase-stability-ranges on the alloyed elements is obtained. In particular, the maximum metastable solubility limit for Al in the cubic structure decreases from ~0.7 for $Ti_{1-x}Al_xN$ to ~0.6 for $Zr_{1-x}Al_xN$ and to ~0.55 for $Hf_{1-x}Al_xN$. This result is rationalised by an analysis of the structural and electronic configurations and is confronted with experimental data showing a strong dependence of the evolving crystalline structure on the N_2 partial pressure during growth. We furthermore show that the Al-content of the films also strongly depends on the N_2/Ar partial pressure ratio when sputtering a powder metallurgically prepared alloy target.

10:20am **B4-1-3 The Effect of Elastic Anisotropy on the Spinodal Decomposition in TiAlN: a Phase Field Study**, ***J.M. Ullbrand*** *(jennifer@ifm.liu.se),* Linköping University, Sweden, *B. Jansson,* Seco Tools AB, Fagersta & Linköping University, Sweden, *F. Tasnádi, L. Hultman, M. Odén*, Linköping University, Sweden

TiAlN alloys are of interest for hard wear protective coatings, for example on metal machining cutting inserts. Arc evaporated TiAlN coatings can be grown as metastable solid solutions in the cubic (c) B1 structure over a wide range of Ti/Al ratios. This B1-structure possesses a broad miscibility gap and may decompose spinodally into c-TiN and c-AlN rich domains when heated. The evolving differences in lattice parameter and elastic constants during heat treatment affect the decomposition behavior and the final microstructure. Here the phase field approach is used to solve the Cahn-Hilliard equations including the elastic energy term to describe the microstructure evolution during decomposition. In order to appropriately address TiAlN alloys enthalpy of mixing and the elastic stiffness tensor, determined by first-principles density-functional theory (DFT) calculations, are also taken into account as input parameters.

The microstructure and local strain evolution is studied during spinodal decomposition. At compositions above 40 at.% AlN the microstructure reveals nanosized domains with preferred growth directions in the elastically compliant directions <100>. At AlN contents below 40 at.% where the elastic anisotropy is less pronounced spherical domains are instead formed. Hence, there is a strong correlation between the evolved microstructure and the elastic properties. The initiation of the spinodal decomposition is notably slower when the composition is displaced from the center of the miscibility gap towards lower amounts of AlN. In addition, the evolved modulation in elastic properties itself slows down the decomposition since it results in an increased amount of stored elastic energy. The origins of the observed kinetic differences are discussed and the simulated microstructure evolution is compared to experimental observations by small angle x-ray scattering, scanning transmission electron microscopy, and atom probe tomography.

10:40am **B4-1-4 Effect of Internal Stress on Cutting Performance of Coated Carbide Tools**, ***S. Imamura*** *(imamura-shinya@sei.co.jp), A. Shibata, H. Fukui, K. Tanaka*, Sumitomo Electric Hardmetal Corp., Japan

This study was intended to investigate the effect of internal stress on cutting performance of coated carbide tools.

In order to control the internal stress, PVD films were deposited under a lot of bias conditions. The depth profiles of internal stress measurement were carried out by using synchrotron radiation 'SPring-8' in Japan. In case of the PVD-TiAlN film, the bias voltage was changed linearly gradient from -50V up to -150V during the deposition, the compressive residual stress was increased to a maximum value of 5.5 GPa gradually from a substrate to a surface of film. Such a gradient stress film enhanced a balance between fracture property of cutting edge and adhesion of film. The film microstructure was evaluated by using Electron Backscatter Diffraction Pattern (EBSP) and Scanning Ion Microscopy (SIM). Furthermore, the cutting test was carried out with different stress condition films of TiAlN, TiSiN, AlCrN etc.

On the other hand, in order to control the internal stress of CVD-TiCN/Al_2O_3 film, shot-peening was treated from film surface. The internal stress of CVD-TiCN/Al_2O_3 film was changed from tensile stress (0.24GPa) to compressive stress (-0.17GPa) by shot-peening treatment. Such CVD film shows high chipping resistance in steel machining.

11:00am **B4-1-5 In-Situ Measurement of Residual Stresses Developed During Triode Magnetron Sputtering Film Depositions with Step-Variation of Substrate Bias**, ***C.F. Fernandes Lagatta*** *(cristiano.lagatta@usp.br),* University of Sao Paulo, Brazil, *A.A.C. Recco,* University of Santa Catarina, Brazil, *A.P. Tschiptschin, R.M. Souza*, University of Sao Paulo, Brazil

In this work, a series of depositions of titanium nitride thin films was conducted in a triode unbalanced magnetron sputtering chamber. Similar parameters were selected during each deposition, except for the substrate bias voltage, which was either step-increased or step-decreased. Depositions with constant substrate bias were also conducted. An in-situ measurement of film residual stresses was carried out as the depositions proceeded. This measurement was based on substrate curvature, which was assessed by a home-built capacitive sensor positioned inside the sputtering chamber. Results have indicated that the in-situ sensor was able to resolve differences between depositions in which the substrate bias was varied differently. Furthermore, the changes observed as the value of the substrate bias was step-increased or step-decreased were also described.

11:20am **B4-1-6 Low-Temperature Plasma Nitriding of Ti-6Al-4V: Microstructural Characterization and Mechanical Properties**, ***K. Farokhzadeh****, A. Edrisy (edrisy@uwindsor.ca),* University of Windsor, Canada, *G. Pigott, P.C. Lidster*, Exactatherm Ltd., Canada

Significant weight reduction occurs by using titanium alloys instead of steels for load bearing components. However, the application of Ti alloys has been restricted due to their poor tribological behaviour. Plasma nitriding has been successfully developed to improve load bearing capacity and wear resistance of Ti alloys, however, it had a detrimental side effect on fatigue properties. Grain growth, lack of good interfacial bonding and low fracture toughness of the hard deposited coatings have been identified to be responsible for coating failure under static and dynamic loadings.

In this investigation, plasma nitriding treatment parameters have been optimized to achieve a modified nitrided microstructure to deal with wear issues while maintaining other mechanical properties. For this purpose, the nitriding treatment was performed at low temperatures to minimize grain growth of the bulk material. Also, the active nitriding gas composition was diluted for minimal formation of hard, brittle nitride phases on the surface and enhanced diffusion of nitrogen atoms. Prior to the treatment, samples' surfaces were polished and possible sources of surface contamination like oxide scales were removed. The SEM, FIB and TEM examinations of the nitrided samples showed a thin compound layer (< 2μm) composed of TiN and Ti_2N formed on top of a relatively deep diffusion zone (~ 40μm). The surface-and depth-profiling chemical analysis was established by incorporating XRD, GDOES, and XPS results. Conventional metallographic preparation technique was used to prepare samples for nano-hardness versus depth measurements. Micro-scratch tests under progressive loading were performed to determine the resistance to surface deformation and the critical failure load of the compound layer to the diffusion zone as well as its friction behaviour. The results showed good interfacial bonding as well as load bearing capacity. The scratch paths were investigated using FIB, SEM and optical surface profilometry. The results showed that ductile β particles embedded at α-grain boundaries in the diffusion zone served as crack deflection sites. The hardened diffusion zone suppressed extensive plastic deformation of the substrate and provided good mechanical support for the compound layer, thus early spallation was inhibited and surface fracture toughness was increased.

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

Recent Advances in Optical Thin Films
Moderator: K. Khajurivala, Janos Technology, Inc., R. Sczupak, Reynard Corporation

10:00am **C1-1 Investigations of Diffusion Behaviour in Dielectric Coatings**, ***J. Kulczyk-Malecka*** *(justyna.kulczyk@stu.mmu.ac.uk), P. Kelly, G.T. West,* Manchester Metropolitan University, UK, *GCB. Clarke,* Pilkington Technology Management, UK, *I. Iordanova,* University of Sofia, Bulgaria, *V. Vishnyakov*, Manchester Metroplitan University, UK

Multi-layer dielectric/silver/dielectric coating systems have excellent proprieties as heat insulators and for solar energy reflection and electrical conductivity. The largest scale market is dominated by low-emissivity (low-E) coatings, which are applied to large area architectural glazing to reduce heat losses from buildings. They combine high visible transparency with high reflectance in the far-infrared region, where the thin (~10nm) silver layer reflects long wavelength IR back into the building and the dielectric layers both protect the silver and act as anti-reflectance layers.

In this study, a range of dielectric coatings have been deposited onto soda-lime glass substrates by reactive sputtering from metallic targets. The magnetron was driven in mid-frequency pulsed DC mode. Process variables investigated include operating pressure, oxygen flow rate and magnetron configuration. The as-deposited coatings were analyzed by micro Raman spectroscopy, X-ray diffraction (XRD) and scanning electron microscopy (SEM). Selected coatings were annealed at temperatures in the range 200-600°C and re-analysed. The oxide samples were then over-coated with silver and annealed for a second time. These coatings were analysed by secondary ion mass spectroscopy (SIMS) and X-ray photoelectron spectroscopy (XPS) to determine the diffusion rates of silver and sodium (from the substrate) through the oxide coatings.

The results to date, presented here, indicate that the structure of the coating, particularly the degree of crystallinity, has a greater impact on the diffusion of sodium through the coating than the diffusion of silver. Preliminary attempts have been made to estimate diffusion coefficients for these coating systems and to relate these values to processing conditions and the structural variations observed.

10:20am **C1-2 Electrochromic Performance of Hybrid Tungsten Oxide Films with Multiwalled-CNTs Additions**, ***C.-K. Lin*** *(cklin@fcu.edu.tw), S.-C. Tseng, C.-H. Cheng, C.-Y. Chen,* Feng Chia University, Taiwan, *C.-C. Chen*, National United University, Taiwan

In this study, tungsten oxide films were prepared by sol-gel technique. Various amounts of multiwalled carbon nanotubes (MWCNTs) were added during sol gel process to obtain hybrid WO3/MWCNTs films. The original and hybrid films were characterized by thermogravimetric analysis, X-ray diffraction analysis, X-ray photoelectron spectroscopy and scanning electron microscopy analysis. While electrochromic performance was evaluated by potentiostat and UV-Visible spectroscopy. The influence on the structure and properties of tungsten oxide film due to MWCNTs addition were investigated. The results showed that all the films were amorphous and hybrid tungsten oxide films with 0.1wt% MWCNTs addition exhibited the best electrochromic performance.

10:40am **C1-3 Opto-Electronic Properties of Graphene Oxide Thin Films**, ***M. Chhowalla*** *(manish1@rci.rutgers.edu)*, Rutgers University **INVITED**

In this presentation, a solution based method that allows uniform and controllable deposition of reduced graphene oxide thin films with thicknesses ranging from a single monolayer up to several layers over large areas will be described. The oxidation treatment during synthesis of GO creates sp^3 C-O sites where oxygen atoms are bonded in the form of various functional groups. GO is therefore a two dimensional network of sp^2 and sp^3 bonded atoms, in contrast to an ideal graphene sheet which consists of 100% sp^2 carbon atoms. This unique atomic and electronic structure of GO, consisting of variable sp^2/sp^3 fraction, opens up possibilities for new functionalities. The most notable difference between GO and mechanically exfoliated graphene is the opto-electronic properties arising from the presence of finite band gap. In particular, the photoluminescence can be tuned from blue to red to IR emission. The atomic and electronic structure along with tunable photoluminescence of graphene oxide at various degrees of reduction will be described.

11:20am **C1-6 Effect of Crystallinity and Oxygen Vacancy on Photocatalytic Properties of TiO_2 Thin Films**, ***J.-H. Huang*** *(u9622008@ems.ndhu.edu.tw), M.-S. Wong*, National Dong Hwa University, Taiwan

The effect of crystallinity and oxygen vacancy on photocatalytic properties of TiO_2 thin films was systematically studied. The films were prepared by argon–oxygen plasma using reactive sputtering with a titanium metal target and subsequently annealed at various temperatures of 400~800°C in air, vacuum and H_2 atmosphere. The results indicate that at the same temperature, the TiO_2 films annealed in H_2 achieve better crystallinity and generate more oxygen vacancies than the films annealed in air and in vacuum. In all the three annealing atmosphere, the higher the temperature is, the better the film crystallinity and the more the oxygen vacancies. Oxygen vacancies in TiO_2 film not only facilitate phase transformation but lower the band gap of TiO_2, and make the film visible-light responsive. Photocatalytic properties of the TiO_2 films were characterized in UV and visible light irradiation by following the Ag reduction and degradation of methylene blue. The films annealed at 600~700°C in H_2, possess the best film crystallinity and proper concentration of oxygen vacancies and exhibit the best photocatalytic performance under both UV and visible light.

11:40am **C1-7 Structural and In-Depth Characterization of Variable Refractive Index Chromium-Silicon Mixed Oxides Produced by Reactive Ion Beam Mixing of the Cr/Si Interface**, ***R. Escobar Galindo*** *(rescobar@icmm.csic.es), L. Vergara, O. Sánchez,* Instituto de Ciencia de Materiales de Madrid, Spain, *G. Fuentes,* Asociación Industria Navarra (AIN), Spain, *D. Duday,* Centre de Recherche Public Gabriel Lippmann, Spain, *N. Benito,* Universidad Autónoma de Madrid, Spain, *N. Valle,* Centre de Recherche Public Gabriel Lippmann, Spain, *V. Joco, C. Palacio,* Universidad Autónoma de Madrid, Spain, *J.R. Rubio-Zuazo*, SpLine, European Synchrotron Radiation Facility, France

The interest on mixed metal-silicon oxides includes their application, among others, as optical coatings with an adjustable refractive index. Chemical vapour deposition of these coatings is commonly used, although it frequently causes the undesirable incorporation of chlorine, hydrogen or carboxyl groups to the films. In this paper we report the formation of chromium and silicon mixed oxides using a novel alternative method. We induce the formation of mixed oxides from a sputter-deposited chromium film on a silicon substrate by reactive ion beam mixing bombarding the Cr/Si interface with oxygen. We have varied both the ion dose (from $1x10^{17}$ up to $1x10^{18}$ ions cm^{-2}) and the implantation energy (40-100 keV) in order to modify the final composition of the coating. The composition profiles have been obtained by means of Rutherford backscattering spectrometry (RBS) with He ions at 3.035 MeV to make use of the resonance of alpha particles with oxygen at this specific energy. A more detailed analysis of the composition depth profiles was obtained by changing the He energy from 3.035 up to 3.105 MeV. Results have been compared with depth profiles obtained by secondary ion mass spectrometry (SIMS) and elastic recoil detection analysis using a time of flight station (ERDA-TOF) and by Monte Carlo TRIDYN simulations. X-ray photoelectron spectroscopy (XPS) depth profiles were carried out using a simultaneous Ar^+ bombardment at low energy. Additional chemical state in-depth distributions were obtained by hard X-ray photoelectron spectroscopy (HAXPES) using synchrotron radiation and angle-resolved (ARXPS). Data obtained by ARXPS show that the Cr-O-Si system does not display preferential sputtering phenomena during Ar^+ bombardment in depth profiling. X-ray diffraction (XRD) and scanning and transmission electron microscopy (SEM, TEM) assessed structural changes of the sample from polycrystalline to amorphous state upon increasing the implantation dose. We have determined how structural changes brought about by varying the ion beam implantation parameters are related to the optical properties of the coatings (mainly refractive index, extinction coefficient and reflectivity) as measured by spectroscopic ellipsometry and UV-VIS spectroscopy.

Biomedical Coatings
Room: Royal Palm 4-6 - Session D1-1

Bioactive and Biocompatible Coatings and Surface Functionalization of Biomaterials
Moderator: E. Saiz, Imperial College, S. Kumar, University of South Australia

10:00am **D1-1-1 Nanoscale Engineering of Biointerfaces via Parylene Coatings**, ***M. Demirel*** *(mdemirel@engr.psu.edu)*, Pennsylvania State University **INVITED**

Anisotropic textured surfaces is generated in the same way in both the plant and animal kingdoms, using dual micro/nanoscale features to tune roughness and surface energy on structures as diverse as plant leaves, animal fur, and bird feathers. For example, a closer look at complex structures in water walking arthropods and lizard toes reveal organized anisotropic textured features at the microscopic scale. These structures are composed of millions of aligned columns per square millimeter, which create novel anisotropic properties. We engineered the first unidirectional (anisotropic) nanoscale surface for precisely tuning surface wettability, friction and adhesion. The surfaces, which comprise an asymmetric array of tilted polymer nanorods, are smooth on the microscale. In this talk, we will describe unique anisotropic physicochemical properties (i.e. morphing/folding, wetting, and friction) of anisotropic nano-rods/tubes, which mimic biological structures at the microscopic scale. This technology will provide significant advances for producing new generations of coatings that will be of great value to the medical and energy industries.

10:40am **D1-1-3 Enhance Surface Reactivity of High Strength Biomedical Ceramics**, ***J.R. Piascik*** *(jpiascik@rti.org),* RTI International, *S.D. Wolter,* Duke University, *B.R. Stoner*, RTI International

High-density, high-purity ceramic materials (i.e. alumina and zirconia) have been investigated for load bearing prostheses and dental restorations because they exhibit excellent corrosion resistance, good biocompatibility, high wear resistance, and high strength. However, one inherent issue with using these high-strength oxides is their inert or non-reactive surface properties. Earlier research presented data of a promising surface pretreatment, whereby yttria-stabilized zirconia (YSZ) surfaces are converted to a more reactive oxyfluoride using gas-phase fluorination. It was shown that employing conventional silanation techniques displayed higher bond strengths when adhered to resin-based composites. The present investigation focuses on the surface modification, via the gas-phase fluorination process, of yttria-stabilized zirconia (YSZ) to increase its wettability and reactivity with arcylate-based resin cements. YSZ plates and cylinders, as-received and roughened, were pretreated in a fluorine-containing plasma and bonded with a commercially available resin cement for simple shear bond adhesion testing. Shear bond tests revealed that bond strength increased with treatment time. Moreover, the pretreated as-received specimen group displayed relatively high bond strengths suggesting surface reactivity and direct chemical bonding with the resin cement. Simple contact angle measurements revealed that a 2 minute exposure reduces the contact angle from ~56° to 6° suggesting that the surface energy has been altered creating a highly hydrophilic surface. X-ray photoelectron spectroscopy (XPS) analysis revealed the surface conversion layer to be a mixture of phases; zirconium oxyfluoride, zirconium fluoride, and yttrium fluoride. It is hypothesized that these new phases have the potential to increase hydroxylation at the surface, creating a more reactive surface, thus allowing for covalent bonding between surface and resin cement. It is believed that this surface treatment has broad reaching impact when using high strength ceramics in a multitude of bio-applications. This research was supported through RTI International research and development fund.

11:00am **D1-1-4 SiNWs-Stimulated Human Adipose Derived Stem Cell (hADSC) Growth Behavior**, ***H.-I. Lin***, National Tsing- Hua University, Taiwan, *S.-W. Kuo, K.-S. Lee,* National Yang-Ming University, Taiwan, *T.-J. Yen (tjyen@mx.nthu.edu.tw)*, National Tsing- Hua University, Taiwan

Embryonic stem cells enable pluripotency to replicate indefinitely, making themselves the most multifunctional stem cell than the other stem cells. However, it remains controversial due to ethic problem. Alternatively, human Adipose-derived stem cells (hADSCs) capable of differentiating into various lineages of osteoblast phenotype and adipocyte. It is therefore appealed a widespread attention in tissue engineering and life sciences.Recent researches indicated that the differentiation pathway of hADSCs can be determined by the stiffness (elasticity) of the cultured matrix. Therefore, in this study we evaluate the growth behavior and interaction of cultured hADSCs with various lengths of SiNWs chips fabricated by Electroless Metal Deposition (EMD) process.

Our experimental results showed that the length of SiNWs chips by EMD method are easily controlled due to its linear etch rate of 1.06 μm/min. After culturing ADSCs with various length SiNWs chips, the hADSC surface protrusion would be more active on short SiNWs (10 min treated); meanwhile, gene expression of ADSC shows positive results on short SiNWs, either. Therefore, it indicates that ADSCs prefer growing on short SiNWs chips which are strongly influenced by SiNWs stiffness (elasticity).

11:20am **D1-1-5 Vertically Aligned Carbon Nanotube Arrays and Their Application as Biological Scaffolds for Stem Cell Growth**, ***G. Kucukayan*** *(kgokce@bilkent.edu.tr), V. Bitirim, C. Akcali, D. Tuncel, E. Bengu*, Bilkent University, Turkey

Synthesis of vertically aligned carbon nanotube arrays (VANTAs) using chemical vapor deposition (CVD) method has been studied using various different gas precursors such as methane, ethylene, ethane, etc. There are few studies where alcohol precursors are used for their synthesis, as well. In this study, we have synthesized VANTAs through alcohol chemical vapor deposition (ACVD) method using methanol, ethanol, isopropanol and acetone as carbon sources. During the synthesis a range of growth temperatures were used between 625 – 750°C . The catalyst layers necessary for the nucleation of CNTs were prepared following the sandwich method through e-beam and thermal deposition of Al / Fe or Co / Al bilayers on a pre-oxidized Si (100) wafer. The change in the carbon source types and the growth temperatures resulted in a significant change in the length of CNTs. The highest array length (~200µm) was been achieved using acetone as the carbon source. TEM images of arrays indicated that arrays were consists of single, double or multi-walled CNTs with a diameter range of 5 to 7 nm. Besides the change of length with growth parameters, we have also observed a switch of contact angle of water measured on these arrays from super-hydrophobic to hydrophobic by synthesis temperature. At the high growth temperatures (> 750°C), the contact angle was almost 180° and even after 20 minutes the angle was kept at 160°. However, the behavior switched to a hydrophobic one (angle ~ 140°) for CNT arrays grown at lower temperature (< 625°C). These results indicated that hydrophobicity can be modified by optimizing the growth parameters. We have also patterned and functionalized CNT arrays using water soluble conjugate polymers with positively and negatively charged end groups. We used the 2-D patterns formed on the CNT arrays after wetting by water as an extracellular support matrix for cell attachment. Finally, we seeded stem cells and cancer cells on the CNT arrays functionalized by various end groups to investigate the possibility of using CNT arrays as scaffold materials for biomaterials applications. The results from these experiments indicated that cells were well-adhered to these surfaces and no-adverse effects of CNTs were observed on the cells. All these results showed that VANTAs would be used as extracellular matrix for tissue engineering in future.

11:40am **D1-1-6 Controlling the Bioavailability of Silver Ions with a Nanocomposite Gradient Coating Produced in a Continuous Low-Pressure Plasma Process**, ***E. Körner*** *(enrico.koerner@empa.ch), D. Hegemann*, Empa, Switzerland

A variety of products promising antibacterial effects are commercially available nowadays. Silver (Ag) containing textiles, household equipment or wound healing products are especially widely present. Next to the question whether all the proposed applications are meaningful, it is important to ask if the antibacterial effectiveness of the products is always correctly adapted to their intended application. Indeed, the antibacterial properties have to be adapted to the usage conditions (environment) and duration, an aspect which often appears to be overlooked.

The combination of radiofrequency plasma-enhanced chemical vapor deposition (PECVD) and a physical vapor deposition processes (PVD) under low pressure conditions enables the production of Ag containing plasma polymer coatings. These Ag nanocomposites consist of an oxygen functional hydrocarbon matrix with embedded Ag nanoparticles. The polymer matrix is deposited by using an carbon dioxide (CO_2)/ ethylene (C_2H_4) mixture and the Ag nanoparticles are produced by the simultaneous sputtering of a Ag cathode in a one-step process.

Different degrees of the polymer matrix functionality were obtained by varying the CO_2/C_2H_4 ratio from 2:1 up to 6:1, the higher ratio leading to a higher content of oxygen functional groups in the matrix and a better wettability of the surface. The Ag content as well as the Ag particle size was adjusted by means of the power input and the gas ratio. Increasing both the power input and CO_2/C_2H_4 ratio results in higher Ag content. The size of the particles behaves differently. A higher CO_2/C_2H_4 ratio leads to smaller and more homogenously distributed nanoparticles whereas an increasing power input favours the formation of agglomerates, as observed by TEM analysis. A strong dependence of the Ag^+ ion release on the incorporated Ag was measured in bi-destilled water with ICP-OES. These Ag nanocomposite thin films can be used for short term applications where an initial Ag release boost is required e.g. to avoid bacterial inflammation.

Controlling the Ag^+ ion release over longer periods of time could be done by covering the Ag nanocomposite thin films with an additional Ag-free layer or with a layer containing a lower Ag amount. This approach enables the build-up of Ag reservoirs in the deeper lying coating regions, which are covered by cytocompatible polymer coatings that still allow Ag^+ ion release. These gradients in the coatings can be produced by changing the gas mixture without interruption of the process. The coatings can be adjusted to be antibacterial over a broad range without losing their cytocompatible properties.

Tribology and Mechanical Behavior of Coatings and Thin Films
Room: California - Session E3-1

Tribology of Nanostructured and Amorphous Films
Moderator: V. Fridrici, Ecole Centrale de Lyon - LTDS, O.L. Eryilmaz, Argonne National Laboratory

10:00am **E3-1-1 Influence of Nanocrystalline Diamond Concentration on DLC Tribomechanical Characterizations**, ***V.J. Trava-Airoldi***, *F.R. Marciano (fernanda@las.inpe.br), P.A. Radi, D.A. Lima-Oliveira, E.J. Corat*, Instituto Nacional de Pesquisas Espaciais - INPE, Brazil

The production of diamond-like carbon (DLC) films with nanocrystalline diamond (NCD) particles incorporated in their structure was for the first time developed in our research group. Our previous studies showed NCD-DLC films improve DLC and stainless steel electrochemical corrosion resistance, preventing aggressive ions from attacking metallic surfaces and becoming a potential candidate for an anti-corrosion material in industrial applications. After, the tribological behavior of these films was investigated under environment air and aggressive solution (NaCl) . NCD particles demonstrated to reduce DLC friction and wear even in aggressive environment. In the present paper, the influence of nanocrystalline diamond concentration in DLC films was investigated regarding the tribomechanical properties. The NCD-DLC films with different NCD concentration were deposited on titanium alloy (Ti6Al4V) samples by DC-pulsed plasma enhanced chemical vapor deposition. The tribological tests were performed in high vaccum in a wide range load and sliding speed. The response surface methodology was used to develop a mathematical modeling of friction and wear of these films, by using the experimental results, in order to identify the parameters that control friction and wear and to obtain the equation that describes these parameters to construct tribologic maps. Scratching tests and nanohardness were also used to characterize the films.

10:20am **E3-1-2 Effect of Diamond Nanoparticles Addition and Test Conditions on Tribological DLC Films Properties for Space Applications**, ***P.A. Radi**, F.R. Marciano, D.A. Lima-Oliveira, E.J. Corat, V.J. Trava-Airoldi,* Instituto Nacional de Pesquisas Espaciais - INPE, Brazil, *L.V. Santos (santoslv@ita.br)*, Technological Institute of Aeronautics, Brazil

Nanoparticles addition in DLC films can improve tribomechanical properties and produce adaptive coatings that change their tribological behaviour according environmental atmosphere [1]. Usual experimental approach to study material behaviour to vary one parameter at time while keeping the others constant, thus measuring influence of each variable. This approach requires more experimentation, ignores the interactions between the parameters and can lead to wrong conclusions. Two level factorial design (2-LFD) was used to describe overall effect when you vary all parameters at the same time allows representing the parameters influence in a simple way[2]. This paper presents the use of 2-LFD to study the effect of diamond nanoparticles addition and test conditions (environment, sliding speed and applied load) on tribological behaviour of DLC thin films. Tribological tests were performed in high vacuum and in environment air on rotational mode and in a wide range of load and sliding speed. Scratching tests was also used to study the effect of diamond nanoparticles addition on DLC films. Raman spectroscopy and images of worn surfaces was also used to characterize the films and wear debris.

10:40am **E3-1-3 The Influence of Bilayer Period and Thickness Ratio on the Mechanical and Tribological Properties of CrSiN/TiAlN Multilayer Coatings**, ***M.-K. Wu***, Tungnan University, Taiwan, *J.-W. Lee (jefflee@mail.mcut.edu.tw)*, Mingchi University of Technology, Taiwan, *J.-C. Huang,* Tungnan University, Taiwan, *H.-W. Chen, Y.-C. Chan, J.-G. Duh*, National Tsing Hua University, Taiwan

Nanostructured CrSiN/TiAlN multilayer coatings were deposited periodically by a bipolar asymmetric reactive pulsed DC magnetron sputtering system. The thickness ratio of CrSiN to TiAlN layers was fixed at 1:1. The bilayer periods of coatings were controlled ranging from 6 to 40 nm. On the other hand, several CrSiN/TiAlN multilayer coatings with same bilayer period (20nm) and different CrSiN/TiAlN thickness ratios were also deposited to explore the influence of thickness ratio on the mechanical properties of multilayer coatings. The crystalline structures of coatings were determined by a glancing angle X-ray diffractometer. Microstructures of thin films were examined by scanning electron microscopy and transmission electron microscopy, respectively. A nanoindenter, micro Vickers hardness tester, scratch tester and pin-on-disk wear tester were used to evaluate the hardness, toughness, adhesion and tribological properties of thin films, respectively. It was concluded that the maximum hardness was obtained when the bilayer period was around 10~15 nm. Meanwhile, the thickness ratio of CrSiN to TiAlN layer had great influence on the hardness, toughness and tribological properties of multilayer coatings.

11:00am **E3-1-4 Microstructure, Scratch and Wear Behavior in Thick Ti-Si-C-N and Ti-Al-V-Si-C-N Nanocomposites**, ***Y.-C. Chan**, H.-W. Chen,* National Tsing Hua University, Taiwan, *R. Wei,* Southwest Research Institute, *J.-G. Duh (jgd@mx.nthu.edu.tw),* National Tsing Hua University, Taiwan, *J.-W. Lee*, Mingchi University of Technology, Taiwan

Thick Ti-Si-C-N and Ti-Al-V-Si-C-N nanocomposites were fabricated by plasma enhanced magnetron sputtering. Characterizations by EPMA, XRD, TEM and SEM revealed the dependence for films with various deposition conditions on the composition, texture and microstructure transformation in coatings. Nanocrystalline Ti(C, N) and Ti-Al-V(C, N) with B1 structure embedded in an amorphous SiC_xN_y matrix, and such spinodal phase segregation ameliorated the hardness, H/E ratio and tribological properties. It was found that the damage and failure resistance were greatly different in Ti-Si-C-N and Ti-Al-V-Si-C-N, depending on the gradients of loading curve in the nanoidentation. In the micro-scratch and ball-on-disc wear tests, the observation of friction coefficient, worn surfaces and cross-sectional worn scars verified that thick nanocomposites exhibited remarkable tribological resistance. Hybrid anti-wear mechanism on the basis of hardness variation, composition contribution and microstructure evolution was proposed to elucidate the favorable durability of these thick nanocomposites.

11:20am **E3-1-5 Design and Deposition of Amorphous Carbon Nanocomposite Coatings for Tribological Application**, *T. Takeno (takeno@wert.ifs.tohoku.ac.jp)*, Tohoku University, Japan, *J. Fontaine,* Ecole Centrale de Lyon - LTDS, France, ***M. Goto***, Ube National College of Technology, Japan, *K. Ito,* Nihon University, Japan, *H. Miki, K. Adachi,* Tohoku University, Japan, *M. Belin,* Ecole Centrale de Lyon - LTDS, France, *T. Takagi*, Tohoku University, Japan **INVITED**

Diamond-like Carbon (DLC) coatings show excellent properties such as high hardness, low friction and low wear, which expand the wide range of their applications. However, there are some disadvantages. Especially, tribological behavior of DLC coatings is highly sensitive to environment and strongly influenced by contact pressure. These materials also exhibit very poor electrical conductivity. These drawbacks can sometimes cause problems for industrial applications. To address such issues, we have focused our attention on nanocomposite DLC coatings, in order to modify surface properties and provide new functionalities. For instance, electrical conductivity can be drastically improved by inclusion of metallic elements/clusters into the DLC coating. We have developed a combined vacuum process composed of plasma enhanced chemical vapor deposition (PECVD) and DC magnetron sputtering devices. Main parameters for the deposition are: gas mixture ratio of the hydrocarbon precursor and argon (controlling the DLC phase growth); and DC sputtering power (controlling additional phase growth). Thanks to the independent and adjustable parameters of CVD and sputtering, various types of nanocomposite coatings with different micro/nano-structures can be fabricated. Based on electron micrographs, structural changes of the coatings are presented depending on the gas mixture ratio of hydrocarbon precursor and argon. Tribological behavior of such coatings is of high interest, since it appears to be quite insensitive to environment (ambient air or ultra-high vacuum) or to normal load. Such results can be discussed in a viewpoint of shearing force of the material transferred from the coating to the counterface. Finally, we discuss "how to design nanocomposite coatings" as a strategic concept to achieve a desired performance.

12:00pm **E3-1-7 Improvement in the Resistance to Corrosion and Tribo-Corrosion of 301 Stainless Steel and Ti-6Al-4V Substrates Induced by Silicon-Based Multilayer Coatings**, ***D. Li**, S. Guruvenket, S. Hassani, M. Azzi,* Ecole Polytechnique de Montreal, Canada, *J. Szpunar,* McGill University, Canada, *J. Klemberg-Sapieha (jsapieha@polymtl.ca), L. Martinu*, Ecole Polytechnique de Montreal, Canada

Amorphous hydrogenated silicon-based multilayer coatings were deposited on 301 stainless steel (SS301) and Ti-6Al-4V alloy substrates using plasma enhanced chemical vapor deposition (PECVD), in order to integrate the advantages of the respective layers. Corrosion and tribo-corrosion behavior of the complete coating/substrate system on different substrates was investigated. The SiN/SiC double layer coating substantially improved the corrosion resistance of the metals: For SS301, the corrosion current, i_{corr}, was reduced by more than three orders of magnitude, and the breakdown voltage was increased from 0.34 to 1.37 V. For Ti-6Al-4V, the i_{corr} was decreased by a factor of ~50. Particularly, the Ti-6Al-4V/SiN/SiC multilayer system exhibited excellent anti-corrosion properties according to potentiodynamic polarization measurements, due to the superior corrosion resistance of both the Ti-6Al-4V substrate and the silicon-based coatings. Further enhancement of the tribo-corrosion resistance has been achieved by applying an a-C coating as a top layer in the three-layer system. In the tribo-corrosion test in 1 wt.% NaCl solution, the SiN/SiC/a-C coating reduced the wear rate and the friction coefficient by a factor of ~175 and ~4, respectively, compared with the bare Ti-6Al-4V. The Ti-6Al-4V/SiN/SiC/a-C multilayer system integrates in synergy the advantages of the respective layers, and its versatility makes it a particularly attractive candidate for applications in different harsh working environments.

New Horizons in Coatings and Thin Films
Room: Sunrise - Session F6

Coatings for Compliant Substrates
Moderator: B. Beake, Micro Materials Ltd, R.M. Souza, University of Sao Paulo

10:00am **F6-1 Comparisons of the Mechanical and Tribological Properties of Ceramic Coatings on Glass and Polymeric Substrates**, ***P. Kelly** (peter.kelly@mmu.ac.uk),* Manchester Metropolitan University, UK, *B. Beake,* Micro Materials Ltd, UK, *N. Renevier*, University of Central Lancashire, UK **INVITED**

Functional films underpin many electronic and opto-electronic devices, including flat panel displays, electrochromic coatings, OLED's, image sensors, thin film photovoltaic solar cells, etc. Increasingly, manufacturers of such devices are looking to move away from rigid glass substrates to flexible polymers to reduce the weight and cost of the devices and to increase their durability. Further substantial gains in productivity would be made, and new markets opened up, if the devices could be deposited directly onto polymeric web in very large throughput roll-to-roll coaters. In all cases, though, device performance depends on the quality of the individual layers and the coating/substrate system as a whole. Of the deposition techniques available, the newly introduced HIPIMS (high power impulse magnetron sputtering) technique is attracting attention for these types of applications due to the low thermal load at the substrate and highly ionised metal flux observed in this mode.

In recent years, significant advances have been made in the analysis of mechanical and tribological properties at the nano-scale. Widely used functional films, such as TiN, ZrN, TiO_2, Al_2O_3 and AZO (aluminium doped zinc oxide) deposited on rigid substrates (tool steel, glass, etc.) have been characterised using nano-indentation, nano-scratch and nano-impact testing. However, much less is known about the suitability of these techniques for analysing coatings deposited onto compliant substrates, and it is recognised that for 'hard' coatings deposited onto polymeric substrates the coating/substrate system is very different in nature and the mechanisms of failure may also be very different. In the work reported here we are, therefore, seeking to extend the analysis of the mechanical and tribological properties of functional ceramic coatings to include those deposited onto compliant substrates. We have investigated a range of metal nitride and oxide coatings deposited by HIPIMS (and other sputtering processes) onto commonly available polymer substrates. The effects of film thickness, elasto-plastic properties of the film and the substrate, etc. on failure mechanisms are considered and comparisons are made with the same coating materials deposited onto rigid substrates.

10:40am **F6-3 X-Ray Mechanical Properties of Metallic Thin Films Supported by Polyimide Substrates Studied under Controlled Biaxial Loading**, ***P.-O. Renault*** *(porenaul@univ-poitiers.fr), S. Djaziri, E. Le Bourhis, P. Goudeau,* University of Poitiers, France*, D. Thiaudière,* Synchrotron Soleil, France*, D. Faurie,* CNRS, Lpmtm Upr9001, France*, F. Hild*, LMT Cachan, 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 structures and the relationship with the microstructure still required for further understanding both from 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 of the sample. Metallic thin films are produced using Physical Vapor Deposition technique onto the center of a cruciform-shaped polyimide substrate (Kapton ®). The film-substrate composites are then deformed in the Diffabs X-ray goniometer. The mechanical modeling using homogenization methods is specific for thin films; it has to take into account both the crystallographic texture and morphology of the metallic films. But grain interaction model is very simple in the case a perfect local elastic isotropy such as W. This thin film allows for directly comparing microstrains (measured at the microscopic scale by X-ray diffraction) to macrostrains (measured at the macroscopic scale by DIC). The first results concerning W thin films in situ deformed with this biaxial tensile modulus will be presented.

11:00am **F6-4 Film Compliance and Constrained Yielding Effects on Interfacial Failure in Polymer-Metal Thin Film Structures**, ***N.R. Moody*** *(nrmoody@sandia.gov),* Sandia National Laboratories*, M.D. Ong,* Whitworth College*, M.S. Kennedy,* Clemson University*, E.D. Reedy, Jr., E. Corona, D.P. Adams,* Sandia National Laboratories*, D.F. Bahr*, Washington State University

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 that varied markedly between each system studied and from model elastic behavior. In this presentation we will use crack growth simulations to show that film compliance provides a lower bound to behavior for all but the thinnest samples while constrained yielding accounts for the pronounced differences in behavior between samples. This work was supported by Sandia National Laboratories through USDOE NNSA under Contract DE-AC04 94AL85000.

11:20am **F6-5 *In situ* Synchrotron X-Ray Strains Measurement in Film/Compliant Substrate Composites During Continuous Mechanical Tests**, ***D. Faurie*** *(faurie@univ-paris13.fr),* Université Paris, France*, G. Geandier, P.-O. Renault, E. Le Bourhis, P. Goudeau*, University of Poitiers, France

The objective of the present work is to study the deformation of metallic thin films deposited on polyimide substrates. The mechanical characterization of such structures and the relationship with the microstructure are still required for further understanding both from fundamental and technological applications. Noticeably, it is important to know how deforms the film during continuous testing of the composite film/substrate. This behaviour depends on the adhesion between the film and the substrate.

Metallic thin films (Au, Ni) are produced using Physical Vapor Deposition technique on polyimide substrates (Kapton®). For a few years, we develop *in situ* tensile tests combined with synchrotron x-ray diffraction [1]. In this study, the film-substrate composites were deformed in the D2AM X-ray goniometer (European Synchrotron Radiation Facility (ESRF), Grenoble (FRANCE)). Strain analysis was achieved during continuous mechanical testing using a 2D detector that allows recording Debye rings every few seconds [2]. Moreover, the semi-crystalline structure of polyimide was probed during the mechanical testing.

First results show the co-deformation (in the elastic and elasto-plastic regime) of thin film and Kapton® substrate.

[1] D. Faurie, O. Castelnau, R. Brenner, P.-O. Renault, E.Le Bourhis, PH. Goudeau, Journal of Applied Crystallography 42, (2009)

[2] G. Geandier, P.-O. Renault,E. Le Bourhis, PH. Goudeau, D. Faurie, C. Le Bourlot, PH. Djemia, O. Castelnau, S. M. Cherif, Applied Physics Letters 96, 041905 (2010)

11:40am **F6-6 Paraffin Wax Passivation Layer Improvements in Electrical Characteristics of Bottom Gate Amorphous Indium-Gallium-Zinc Oxide Thin-Film Transistors**, ***G.-W. Chang*** *(b922030049@gmail.com)*, National Chiao Tung University, Taiwan

In this research, paraffin wax is employed in passivation layer of the bottom gate amorphous indium–gallium–zinc oxide thin-film transistors (a-IGZO TFTs), and it is formed by coating in the atmosphere. Comparing with passivation-free a-IGZO TFTs, the threshold voltage (Vth) and subthreshold swing (SS) of paraffin wax passivation a-IGZO TFTs are improved. In the generalized case, positive gate bias stress can induce hump characteristic phenomenon. The hump phenomenon can be relieved after device passivation with a paraffin wax layer. In addition, the effects of bias stress on the passivation-free and paraffin wax passivation layer a-IGZO TFTs are investigated by capacitance-voltage and current-voltage measure. The hump characteristic in transfer curve depends on the drain voltage after positive bias stress, inferring that the a-IGZO backchannel appears with the drain-induced depletion electrical field.

Characterization: Linking Synthesis, Microstructure, and Properties
Room: Tiki Pavilion - Session TS4-1

Characterization: Linking Synthesis, Microstructure, and Properties
Moderator: C. Scheu, University of Munich, P. Schaaf, TU Ilmenau, Institut für Werkstofftechnik, F. Giuliani, Imperial College London

10:00am **TS4-1-1 Strain Mapping in Nanostructures and Thin Films by Dark-Field Electron Holography**, *M. Hÿtch (martin.hytch@cemes.fr),* ***N. Cherkashin****, S. Reboh, E. Javon, F. Houdellier, E. Snoeck*, CEMES-CNRS, Université de Toulouse, France **INVITED**

Dark-field electron holography (DFEH) is a new technique for measuring strain in crystalline materials [1]. The experimental setup is similar to conventional off-axis electron holography except that diffracted beams are used to create the interference. The diffracted beam emanating from a strained region of crystal is interfered with the diffracted beam coming from an unstrained part of the sample, typically the substrate. The holographic fringes encode the information about the relative deformation of the two crystalline lattices, and can be recovered using geometric phase analysis - a technique first developed for the analysis of high-resolution electron microscopy images (HRTEM) [2]. By combining the information from two diffracted beams, the full strain tensor can be determined in two dimensions. The advantage of the new technique is that strains can be measured to high precision, with nanometre spatial resolution and for micron fields of view. In addition, the samples are relatively thick, about 100-200 nm, and can be prepared by standard focussed-ion beam (FIB) or tripod polishing.

Dark-field holography was first developed for mapping strains in strained-silicon MOSFET devices [1,3] but the technique is not limited to such cases. Strained layers grown epitaxially on a substrate also have the required geometry to apply the technique. Examples will be given of the measurement of strain in carbon-doped silicon and germanium layers grown on silicon substrates [4,5]. Results will be compared with modelling using the finite-element method (FEM). Indeed, we will show that local relaxation due to misfit dislocations can be studied and quantified in the course of the analysis. Finally, the limitations and experimental requirements will be discussed along with future developments.

[1] M.J. Hÿtch, F. Houdellier, F. Hüe, and E. Snoeck, Nature 453 (2008) 1086-1089.

[2] M.J. Hÿtch, E. Snoeck and R. Kilaas, Ultramicroscopy 74 (1998) 131–146.

[3] F. Hüe, M.J. Hÿtch, F. Houdellier, H. Bender, and A. Claverie, Appl. Phys. Lett. 95, 073103 (2009).

[4] N. Cherkashin, M. J. Hÿtch, F. Houdellier, F. Hüe, V. Paillard, A. Claverie, A. Gouyé, O. Kermarrec, D. Rouchon, M. Burdin, P. Holliger, Appl. Phys. Lett. 94 (2009) 141910.

[5] J. M. Hartmann, L. Sanchez, W. Van Den Daele, A. Abbadie, L. Baud, R. Truche, E. Augendre, L. Clavelier, N. Cherkashin, M. Hytch, and S. Cristoloveanu, Semiconductor Science and Technology 45 (2010) 075010.

10:40am **TS4-1-3 Electronic Structure Investigation of Amorphous CrC_x Films**, ***M. Magnuson*** *(marma@ifm.liu.se),* Linköping University, Sweden, *M. Hanson,* Uppsala University, Sweden, *J. Lu, L. Hultman,* Linköping University, Sweden, *U. Jansson*, Uppsala University, Sweden

Chromium-based carbides (CrC_x) with different compositions constitute an interesting class of materials to investigate. This is mainly due to the large potential of making improved corrosion resistant coatings combined with other desired properties for potential applications as wear-resistant coatings, low-friction films, and electrical contacts. Moreover, CrC_x carbides can be fabricated as amorphous materials that make them particularly interesting for electronic structure and mechanical property investigations. Detailed understanding of the chemical bonding is necessary to optimize their properties. In this work, the electronic structure of a series of amorphous-to-nanocrystalline CrC_x (x = 0.2-0.8) films have been investigated by soft x-ray absorption (SXA) and emission (SXE) spectroscopy. The Cr 2p SXA spectra exhibit a crystal-field splitting of ~1.2 eV where the intensity of the unoccupied Cr states systematically increases as the C content increases. Correspondingly, the Cr L3/L2 branching ratio of the occupied states observed in SXE decreases simultaneously as the observed σ/π ratio in C K SXE decreases. This is a signature of an increased Cr ionicity as the C content increases. The results will be discussed together with XRD, XPS, TEM, and EELS results. The radial distribution functions obtained from EELS indicate a C-C bond distance of ~1.5 Å and a Cr-C distance of ~2.2 Å. The measured spectra are compared and interpreted with ab initio calculations including core-to-valence dipole matrix elements. The calculated results are found to yield consistent spectral functions to the experimental data. By varying the composition, a change of the electron population is achieved causing a change of covalent/ionic bonding between the Cr and C atoms, that enables control of the macroscopic properties of the materials.

11:00am **TS4-1-4 Electrical and Structural Properties of Ultrathin Polycrystalline and Epitaxial TiN Films Grown by Reactive Magnetron Sputtering**, *F. Magnus, A.S. Ingason, S. Olafsson,* University of Iceland, ***JT. Gudmundsson*** *(tumi@raunvis.hi.is)*, Shanghai Jiao Tong University, China

Ultrathin TiN films were grown by reactive magnetron sputtering using both dc and high power impulse magnetron sputtering (HiPIMS) on amorphous SiO_2 substrates and single-crystalline MgO substrates at various growth temperatures. The resistance of the films was monitored in-situ during growth to determine the coalescence and continuity thicknesses. Structural characterization was carried out using X-ray diffraction and reflection methods. TiN films grown by dc magnetron sputtering on SiO_2 are polycrystalline and for a growth temperature of 600°C the nominal coalescence and continuity thicknesses are 0.8 and 1.9 nm, respectively [1]. TiN films grow epitaxially on the MgO substrates from temperatures of 200°C and upwards as shown by XRD measurements [2]. As the growth temperature is increased from room temperature to 600°C the coalescence thickness drops from 1.09 nm to 0.08 nm and the minimum thickness for a continuous film drops from 5.5 nm to 0.7 nm [3]. A large drop in resistivity is seen with increasing growth temperature and the resistivity reaches 16.6 μΩcm for growth temperature of 600°C. X-ray reflection measurements indicate a significantly higher density and lower roughness of the epitaxial TiN films.

[1] A. S. Ingason, F. Magnus, J. S. Agustsson, S. Olafsson, and J. T. Gudmundsson, In-situ electrical characterization of ultrathin TiN films grown by reactive dc magnetron sputtering on SiO_2, Thin Solid Films, 517 (24) (2009) 6731-6736

[2] A. S. Ingason, F. Magnus, S. Olafsson and J. T. Gudmundsson, Morphology of TiN thin films grown on MgO [100] by reactive dc magnetron sputtering, Journal of Vacuum Science and Technology A, 28(4) (2010) 912 - 915

[3] F. Magnus, A. S. Ingason, S. Olafsson and J. T. Gudmundsson, Growth and in-situ electrical characterization of ultrathin epitaxial TiN films on MgO, Thin Solid Films, submitted June 2010

11:20am **TS4-1-5 On X-Ray Diffraction Study of Stresses and Preferred Grain Orientations in Thin Films - Specific Non-Routine Cases**, ***R.K. Kužel*** *(kuzel@karlov.mff.cuni.cz),* Charles University in Prague, Faculty of Mathematics and Physics, Czech Republic, *Z. Matěj, L. Nichtová,* Charles University in Prague, Faculty of Mathematics and Physics, *J. Buršík,* Institute of Inorganic Chemistry of Academy of Sciences of the Czech Republic, *D. Šimek,* Technical University Bergakademie Freiberg, Germany, *J. Musil*, University of West Bohemia, Czech Republic

Stresses and preferred grain orientations play an important role in thin films of many types and applications. X-ray diffraction (XRD) is one of the most important methods of their characterization. Selected examples of specific non-routine cases are presented we met recently during the study of thin films of a high technological interest (hard coatings, photocatalytic films, films with interesting electrical properties).

In TiO_2 thin films crystallized from amorphous state into anatase phase, tensile stresses are generated during the crystallization and inhibit further crystallization. This process results in strong dependence of both stresses and crystallization rate on the film thickness. The measured strains were highly anisotropic and recently calculated single crystal elastic constants of anatase were used for the stress evaluation by the conventional $\sin^2\psi$ method and because of absence of texture simultaneously also by our newly developed software for total XRD powder pattern fitting.

In the studied cubic $KTAO_3$ thin films on Si substrate with Pt interlayer, rather unusual multicomponent textures were detected when each of the component had narrow orientation distribution. In this case, a set of the so-called ω-scans was collected for finding of all the components followed by the standard θ-2θ scans at specific pre-calculated sample inclinations. Then the so-called crystallite group method could be applied for the stress determination.

The most difficult task was the analysis of compact highly textured hexagonal TiB_2 hard coatings on steel. The (00*l*) texture was very sharp but of fiber type. None of the above methods could be applied since the range of possible inclinations ψ was very narrow and the ratio of lattice parameters *c/a* could not be determined independently. Therefore, full maps of reciprocal space had to be measured and calculated. Finally, the stress could be evaluated only from the deformation and/or inclination of the diffraction spot in the map by the reciprocal map fitting.

In the last example, thin films of hexagonal ferrite $SrFe_{12}O_{19}$ on $SrTiO_3$(111) substrate were analyzed. After routine scans (symmetric or asymmetric θ-2θ scan, ω-scan, φ-scan) it seemed that there is just a strong fiber texture. Only more complex study on asymmetric planes discovered well developed epitaxial growth as a main feature of the partially inhomogeneous film and shape of diffraction spots was analyzed.

The examples showed that XRD studies of stresses in thin films at certain cases require also specific methods of measurement and evaluation and important (even dominant) features can easily be overlooked when routine methods are applied only.

11:40am **TS4-1-6 Information Depth of Mono-Atomic and Poly-Atomic Primary Ions in Secondary Ion Mass Spectrometry (SIMS): Fundamentals and Applications**, *F. Kollmer (felix.kollmer@iontof.com),* ION-TOF GmbH, Germany, *D. Breitenstein,* Tascon GmbH, Germany, *N. Havercroft,* ION-TOF USA, Inc., *P. Bruener,* ION-TOF GmbH, Germany, *M. Fartmann, B. Hagenhoff,* Tascon GmbH, Germany, *E. Niehuis,* ION-TOF GmbH, Germany, ***A. Schnieders***, ION-TOF USA, Inc.

TOF-SIMS is a very sensitive surface analytical technique, covering a wide range of organic and inorganic applications. It provides detailed elemental and molecular information about surfaces, thin layers, interfaces, and full three-dimensional analysis of the sample. In recent years, the application of cluster primary ions has led to a major breakthrough in the analysis of molecular surfaces by TOF-SIMS. Compared to mono-atomic bombardment the accessible mass range has been considerably extended and the sensitivity has been increased by orders of magnitude. In particular the Bi LMIS cluster source combines the fundamental benefits of cluster ion bombardment with a high brightness source to give uncompromised lateral and mass resolution. Moreover, the Bi cluster source emits a large variety of singly and doubly charged clusters and is therefore well suited for fundamental studies.

The information depth is a key capability of every surface analytical technique. However, the influence of cluster bombardment on the information depth in SIMS has hardly been investigated. We determined the information depth for atomic Bi as well as for a large variety of Bi clusters (Bi_2 to Bi_7) at different primary ion energies. Additionally, we investigated the samples by LEIS (low energy ion scattering) which is known to be the most surface sensitive technique. The samples under investigation included different core shell nano-particles as well as special alloys which tend to form pure mono-layers of one metal component at the surface.

12:00pm **TS4-1-7 XPS on Ar Atoms to Determine Local Structures of Thin Films Prepared by Magnetron Sputtering and PECVD**, *A. Rastgoo Lahrood (atena.rastgoolahrood@rub.de),* ***T. de los Arcos****, M. Prenzel, J. Winter*, Ruhr-Universität Bochum, Germany

X-ray Photoelectron Spectroscopy (XPS) is commonly used technique for elemental near-surface analysis of the composition of materials and of their chemical binding. In this study we investigate the potential of XPS to gain structural information on thin films.

It has been observed by XPS studies on Ar atoms (Ar 2p), naturally trapped in Al_2O_3 films deposited by RF magnetron sputtering, that the line shape has to be described as a superposition of at least two doublets.

A doublet structure and the associated energy shift has been correlated in earlier work on pure metals with the existence of bubbles formed by coalescing noble gas atoms in the solid [1, 2].

In other works the shift of Ar 2p peaks has been used as a probe of residual stress in amorphous carbon ultrathin films [3].

In order to systematically study this effect we have implanted Ar atoms at various energies into different substrates: pure Al, Al_2O_3 deposited by RF magnetron sputtering, DLC (diamond-like carbon), Si single crystals and SiO_2. In the case of Al_2O_3 the naturally trapped Ar from the deposition process were also measured. The doublets of 2p transitions of Ar have been analyzed by XPS. The line shape shows that in many cases more than one doublet structure is needed to describe the data. The relative intensities of these doublets change as a function of implantation energy and annealing temperature.

There is evidence that a correlation of the local structure of the sample with the shape and shift of Ar 2p Peaks exists, making XPS on Ar a probe for the local structure of the dielectric thin films investigated in this study.

The work is funded by DFG within SFB-TR 87.

[1] C. Biswas, A. K. Shukla, S. Banik, S. R. Barman, Phys. Rev. Lett. 92 (2004) 115506.

[2] P.H. Citrin, D.R. Hamann, Phys. Rev. B 10 (1974) 4948.

[3] W. Lu, K. Komvopoulos, Appl. Phys. Lett. 76 (2000) 3206.

Hard Coatings and Vapor Deposition Technology
Room: Royal Palm 1-3 - Session B2-2

CVD Coatings and Technologies
Moderator: S. Ruppi, Walter AG, F. Maury, CIRIMAT CNRS-INPT-UPS ENSIACET

1:30pm **B2-2-1 High-Speed Coating of α-Al_2O_3 Film by Laser Chemical Vapor Deposition on Cutting Tools**, ***T. Goto*** *(goto@imr.tohoku.ac.jp)*, Tohoku University, Japan **INVITED**

WC-Co composite has been widely employed to cutting tools due to high hardness and ductility; however, W is a rare resource and localized on earth. Therefore, alternate material should be sought to substitute W. Since Ti is more abundant and Ti-based compounds have high hardness and strength, TiN-Ni cermet can be a promising cutting tool material having competitive performance of WC-Co composite. The surface of these cutting tools should be generally coated by thermally insulative and anti-abrasive α-Al_2O_3film, preventing temperature increase and degradation of mechanical properties of substrate material. α-Al_2O_3 film has been commonly prepared by chemical vapor deposition (CVD) on cutting tools using halide precursors, typically $AlCl_3$, at more than 1300K. Metalorganic CVD (MOCVD) is also applicable to prepare Al_2O_3; however amorphous or γ- Al_2O_3 has likely been formed even around 1300K. In order to prepare α-Al_2O_3 film on TiN-Ni cermets, a low temperature deposition of α-Al_2O_3 and a high deposition rate are key issues for practical application of TiN-based cermet cutting tools.

We have employed laser CVD (LCVD) using triacetyl-acetoanate-aluminum ($Al(acac)_3$) as Al source gas with two lasers, i.e., Nd:YAG and diode (InGaAlAs) lasers. In the case of Nd:YAG laser, the crystal phase changed from γ to α/γ mixture to α type with increasing deposition temperature (T_{dep}) and laser power. α-Al_2O_3 film was prepared at 1214K. The preferred orientation of α-Al_2O_3 film changed from non-orientation to (104) to (104)/(006) mixed orientation with increasing deposition temperature and laser power. (104) oriented α-Al_2O_3 film had well-developed facetted grains. The cross-section showed a columnar microstructure suggesting nanometer-sized pores contained in the film. The high energy laser, i.e., diode laser, was more effective to prepare well-oriented α-Al_2O_3 films at farther lower deposition temperature. At 795K, amorphous Al_2O_3 film was obtained, while at more than 893K, α-Al_2O_3 film was obtained. At 110 W and around 950K, significantly (006) oriented Al_2O_3 film was obtained. The (006) oriented α-Al_2O_3 films exhibited hexagonal grains about several µm in size. With increasing laser power and deposition temperature, (104)/(012) oriented α-Al_2O_3 films were prepared. The preferred orientation was also strongly dependent on total pressure, and (104) and (012) orientations showed maxima at 0.2-0.4kPa and 0.2-0.6kPa, respectively. The highest deposition rates of α-Al_2O_3 film by laser CVDs were 310-324 µm/h which were more than 100 times greater than that of common conventional thermal CVD.

2:10pm **B2-2-3 Protective Aluminum Oxide Coatings on Titanium Alloys from Al Metal-Organic Chemical Vapor Deposition**, *Y. Balcaen, N. Radutoiu,* Université de Toulouse, INPT/ENIT, LGP, France, *D. Samelor,* Université de Toulouse, CIRIMAT/INPT/CNRS, France, ***J. Alexis***, *L. Lacroix, J.D. Beguin,* Université de Toulouse, INPT/ENIT, LGP, France, *A. Gleizes, C. Valhas (constantin.valhas@ensiacet.fr)*, Université de Toulouse, CIRIMAT/INPT/CNRS, France

Alumina coatings present great technological interest in numerous application domains, such as microelectronics, catalysis or surface protection. This study focuses on the implementation of different aluminum oxide coatings processed by metal-organic chemical vapor deposition from aluminum tri-isopropoxide on commercial TA6V titanium alloy to improve its high temperature corrosion resistance. Previous work allowed establishing processing conditions – microstructure relationships for such coatings. Films grown at 350°C and at 480°C are amorphous coatings and correspond to the formulas AlOOH, and Al_2O_3, respectively. Those deposited at 700°C contain g- Al_2O_3 nanocrystals. Their mechanical properties and adhesion to the substrates were investigated by indentation, scratch and micro tensile tests. Hardness and stiffness of the films decrease with increasing the deposition temperature and reach a plateau corresponding to the onset temperature crystallization of their crystallization (700°C). The hardness of the coatings prepared at 350°C, 480°C and 700°C is 5.8 ± 0.7 GPa, 10.8 ± 0.8 GPa and 1.1 ± 0.4 GPa, respectively. Their stiffness is 92 ± 8 GPa (350°C), 155 ± 6 GPa (480°C), and 11.5 ± 2.8 GPa (700°C). Scratch tests cause adhesive failures on the films grown at 350 °C and 480°C whereas cohesive failure is observed for the nanocrystalline one, grown at 700°C. Micro tensile tests show a more progressive cracking on the latter films than on the amorphous ones. Similar micro tensile tests were performed for Al oxide coated and uncoated Ti alloy substrates after corrosion with NaCl deposit during 100 h at 450°C. The coated samples have a mechanical strength similar to that of the as processed uncoated samples not corroded. After corrosion test, the mechanical strength of the coated Ti alloys is higher than that of the uncoated alloys. It is concluded that the films allow maintaining the good mechanical properties in the targeted operating conditions. However, after corrosion test only the film deposited at 700°C yields an elongation at break comparable to that of the as processed samples without corrosion. The other coatings do not allow the fall of ductility recorded after corrosion test on TA6V. As a conclusion; the as established processing – structure – properties relation paves the way to engineer MOCVD aluminium oxide complex coatings which meet the specifications of the high temperature corrosion protection of titanium alloys with regard to the targeted applications.

2:30pm **B2-2-4 Thermal Stability and Cutting Performance of Ti or Zr-Doped κ-Al_2O_3 Coatings by CVD**, ***M. Okude*** *(okude@mmc.co.jp), K. Tomita, E. Nakamura, A. Osada*, Mitsubishi Materials Corporation, Japan

Al_2O_3 coatings have been one of the most important coatings for the cutting tools. Al_2O_3, which maintains high hardness and excellent oxidation resistance under such a severe cutting condition, is that dominate the tool-life. Al_2O_3 has a several different crystal system, metastable κ phase and stable α phase Al_2O_3 have been used for the cutting tool. A lot of researches have been done about the heat transformation of κ→α phase. Recently, reported that B- and Ti-B-doped κ-Al_2O_3 slowly phase transformed to α-Al_2O_3 than non-doped one, however, investigation into the heat transformation mechanism of κ→α phase on B- and Ti-B-doped κ-Al_2O_3 has yet been successful.

In this paper, Ti or Zr-doped κ-Al_2O_3 coatings were deposited using a hot wall CVD equipment, with $AlCl_3$-$ZrCl_4$ or $TiCl_4$-CO_2-HCl-H_2 gas mixture. After being heated these Al_2O_3 coatings at several heat-treatment processes, crystal system and morphology of these Al_2O_3 coatings were analyzed. Heat transformation mechanism of Ti or Zr-doped κ-Al_2O_3 will be discussed.

2:50pm **B2-2-5 Microstructure and Wear Characteristics of Texture Controlled CVD a -Al_2O_3 and MT-CVD Ti(C,N) Layers during Steel Machining**, *R. M'Saoubi (rachid.msaoubi@secotools.com), O. Alm, T. Larsson,* ***M. Johansson***, *S. Ruppi*, Seco Tools AB Fagersta, Sweden

The microstructure and wear properties of CVD α -Al_2O_3 layers with (10-12) and (0001) growth textures were compared with MTCVD Ti(C,N) layers in single point turning of AISI 4140 steel. The experimental coatings were investigated by FEG-SEM, EBSD and a combination of FIB and analytical TEM techniques prior to and after machining. Substantial texture effects on wear performance of the α -Al_2O_3 layers were observed. When compared to (10-12) textured layer, an enhanced ability of the (0001) textured layer to undergo plastic deformation was confirmed. The deformation was localised in the near surface region of the layer. In contrast to the α -Al_2O_3 layers, the Ti(C,N) layer exhibited a more uniform plastic deformation across the entire layer thickness. The wear characteristics of the layers are further interpreted in the light of thermal, mechanical and frictional conditions occurring at the tool–chip contact interface.

3:10pm **B2-2-6 Effect of the N/Al Ratio in the Gas Phase at Constant Supersaturation on AlN Epitaxy on Sapphire by HTCVD**, *N.E. Baccar (nour-elhouda.baccar@simap.grenoble-inp.fr),* Grenoble-INP, France, *R. Boichoit, E. Blanquet,* ***M. Pons***, SIMAP, France

Aluminum Nitride (AlN) is a III-V wide band gap semiconductor material with a high thermal conductivity and good chemical inertia. These properties make it suitable for several applications in the opto-electronic field, the most important is the fabrication of UV diodes. Thick AlN layers have been processed by HTCVD (High Temperature Chemical Vapor Deposition) using $AlCl_3$ and NH_3 diluted in H_2.

The thermodynamic and kinetic modeling of AlN growth on AlN templates at different temperatures and N/Al ratios have been made in previous studies [1-2]. The conclusion of (Boichot and al. [1]) was that experiments should be conducted at constant supersaturation and thickness to understand the actual influence of N/Al ratio on AlN layer quality. The relationship between temperature and supersaturation was established by (Claudel and al. [2]).

In the first part of the study, experiments were performed on graphite substrates to study the preferential orientation of AlN crystals by varying the temperature and N/Al ratio. It is demonstrated that low N/Al ratio allows the control of growth orientation of the AlN crystal facets along the c-axis.

In the second part, experiments were carried out on *c*-plane sapphire substrates to investigate the effect of supersaturation and N/Al ratio on the morphology of grown layers. The layers are characterized by SEM, XRD, XPS and SIMS to evaluate both crystal quality and O and Cl contamination.

The main conclusion is that the control of surface quality in term of epitaxial relationship between sapphire and h-AlN is possible through a precise setting of supersaturation and N/Al ratio in the gas phase. It is also concluded that epitaxial growth along c-axis is not thermodynamically favored in classical CVD conditions (low pressures, high temperature and N/Al up to 1).

References

[1] R. Boichot, A. Claudel, N. Baccar, A Milet, E. Blanquet, M. Pons, 2010, Epitaxial and pollycristalline growth of AlN by high temperature CVD: Experimental results and simulation, Surface and Coating Technology, article in press.

[2] A. Claudel, E. Blanquet, D. Chaussende, M.Audier, D.Pique, M.Pons, 2009, Thermodynamic and experimental investigations on the growth of thick aluminum nitride layers by high temperature CVD, Journal of Crystal Growth 311, 3371–3379.

3:30pm **B2-2-7 Doped CVD Coatings – Process, Properties and Machine Technology**, ***H. Strakov*** *(hristo.strakov@ionbond.com), R. Bonetti, A. Scott*, Ionbond AG, Switzerland

The requirements of chemically vapour deposited (CVD) coatings for protective application has increased enormously over the past 30 years. The progress from simple monolayer coatings to of today's complex coating systems were made possible through innovations in coating equipments and the continual optimization of the processes; this in parallel with improved substrate materials, and the progress in preparation periphery, such as pre- and post-treatment operations. A potential for further coating improvement in industrial applications lies with defined structures and new material combinations. One route to obtain better controlled structures is by adding small amounts of metallic or non-metallic elements combined with controlled nucleation for well known processes. This will be illustrated on the example of boron additions to high and moderate temperature Ti-based coatings. The influence of the concentrations of dopants in connection with coating architecture (e.g. multi- or nano-layers) on coating morphology, hardness, friction and wear behavior will be reported.

Application examples of doped coatings and combined coatings will also be presented. Particularities related to diffusion phenomena of the highly mobile boron atom will be discussed.

3:50pm **B2-2-8 CO Addition in Low-Pressure Chemical Vapor Deposition of Medium-Temperature TiCN Based Hard Coatings**, ***C. Czettl*** *(christoph.czettl@mcl.at),* Materials Center Leoben Forschung GmbH, Leoben, Austria*, C. Mitterer,* Montanuniversität Leoben, Austria*, D. Rafaja, U. Mühle,* TU Bergakademie Freiberg, Germany*, S. Puchner,* TU Vienna, Austria*, M. Penoy, C. Michotte,* CERATIZIT Luxembourg S. à. r. l. , Mamer, Luxembourg*, M. Kathrein,* CERATIZIT Austria GmbH, Austria*, H. Hutter*, TU Vienna, Austria

$TiCN/Al_2O_3$ hard coatings grown by chemical vapor deposion (CVD) are state-of-the-art in metal cutting applications using indexable cemented carbide inserts. A TiCN base layer grown by a medium-temperature (MT) CVD process is a crucial feature for wear resistance and toughness of the tools. In order to influence the structure and properties of this base layer, five different MT-TiCN coatings with increasing amounts of CO in the feed gas were deposited using an industrial-scale low-pressure CVD system. The coatings were deposited using a $TiCl_4$-CH_3CN-H_2-N_2-CO feed gas system with a total flux of 60 l/min. The deposition temperature was 900 °C, the deposition pressure 100 mbar. Phase composition, preferred orientation of crystallites and residual stresses were characterized by X-ray diffraction (XRD). Surface topography and fracture cross-sections were investigated by scanning electron microscopy (SEM). Surface roughness was measured using a white light profilometer. Indentation hardness and indentation modulus of the coatings were determined using nanoindentation with a Berkovich indentor. The oxygen content of the different coatings was analyzed by using electron probe microanalysis (EPMA) and Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS). The thickness of the coatings was measured by light optical microscopy (LOM) on polished cross-sections. EPMA and ToF-SIMS measurements confirmed a good correlation between the oxygen amount in the coatings and the CO flow. With increasing CO amount up to 2.2 vol. % in the gas supply, the originally equiaxed grains change to plate-like grains, while the grain size decreases to a few hundred nanometers. Furthermore, the addition of CO makes the preferred orientation of crystallites weaker until it nearly vanishes at 2.2 vol.-% CO in the feed gas. Also the surface roughness decreases with rising CO addition. TEM analyses showed that the incorporation of oxygen leads to a homogenous distribution of voids within the TiCN grains and to increasing density of twin boundaries. The residual stress shows a minimum while hardness and indentation modulus reach a maximum for CO amounts of 1.5 vol.-% in the feed gas.

4:10pm **B2-2-10 Snthesis and Sensitivity by UV Light of SnO_2-ZnO Core-Shell Nanowires***,* ***K.-Y. Pan****, H-C. Shih (hcshih@mx.nthu.edu.tw),* National Tsing Hua University, Taiwan*, M.-H. Chan*, Instrument Technology Research Center, Taiwan

Zinc oxides deposited on Tin dioxide nanowires were successfully synthesized by atomic layer deposition (ALD). The thicknesses of SnO_2-ZnO core-shell nanowires are 80, 88, 95, and 100 nm at different ALD cycles: 50, 100, 150, and 200, respectively. The result of electricity measurements shows that the resistance of SnO_2-ZnO core-shell nanowires (ALD: 200cycles) is 925Ω, which is much lower than pure SnO_2 nanowires ($3.6\times10^6\Omega$). The explanation of this phenomenon is: when electricity passes through SnO_2-ZnO core-shell nanowires, the SnO_2-ZnO core-shell wires might have a strain at interfaces to keep their shapes complete. Therefore, the energy gap of SnO_2-ZnO core-shell wires might decrease, and the electricity will be increased. The result of UV light test shows the recovery time of SnO_2-ZnO core-shell nanowires (ALD: 200cycles) is 1030 seconds, which is lower than pure SnO_2 nanowires (1827 seconds). SnO_2 and ZnO adsorb oxygen easily to form oxygen vacancies on surfaces. The reason of this phenomenon is: when UV light is off, two depletion regions of SnO_2-ZnO core-shell wires might produce an effect to cut recovery time down.

4:30pm **B2-2-11 Optical and NO Gas Sensing Properties of GaN/Ga_2O_3 Zigzag Nanowires**, ***L.-W. Chang*** *(liwei0509@gmail.com), J.-W. Yeh, H-C. Shih*, National Tsing Hua University, Taiwan

In this study, we report on the fabrication of GaN/Ga_2O_3 zigzag nanowires via a chemical vapor deposition system with different ratio of NH_3/Ar atmosphere. X-ray, SEM, and High-resolution TEM analyses confirmed that the GaN/Ga_2O_3 zigzag nanowires have a single-crystal hexagonal structure with axis [101] alignment. The optical properties of GaN/Ga_2O_3 zigzag nanowires from catholuminescence (CL) and UV-visible absorption spectra show that blue, green, and red emissions because of N-doped process and red-shifts on the band-gap. For application of NO gas sensor, GaN/Ga_2O_3 zigzag nanowires exhibit drift in their recovery characteristics and for sequential detection of NO gas in the range of 300-400 ppm.

4:50pm **B2-2-12 Equilibrium Segregation of Graphene on Polycrystalline Ni Surfaces by Chemical Vapor Deposition**, ***C.-J. Hsu****, P.-K. Nayak,* National Cheng Kung University, Taiwan*, J.-C. Sung,* KINIK Company, Taiwan*, S.-C. Wang,* Southern Taiwan University, Taiwan*, J.-L. Huang (jlh888@mail.ncku.edu.tw)*, National Cheng Kung University, Taiwan

Few-layer graphene sheets were prepared on polycrystalline nickel flakes by chemical vapor deposition using equilibrium segregation at a temperature of 800 °C with a very slow cooling rate. The properties of graphene sheets as a function of the hydrogen flow rate were investigated at a constant (CH_4 : Ar) flow. It was observed that equilibrium segregation and an optimum gas mixing ratio (CH_4/H_2 = 0.6/10) are required to synthesize highly crystalline few-layer graphene. The effect of recrystalline treatment of the poly-Ni substrate on the quality of the graphene sheets was investigated. Scanning and transmission electron microscopy and micro-Raman spectroscopy were used to characterize the properties of few-layer graphene. Observations of graphene samples with various recrystalization treatments of the nickel substrate indicate that the defect source on the graphene surface is carbon nanotubes embedded with carbon nanoparticles. The number of graphene layers was estimated based on microscopic observations. The proposed method of growing high-quality large-area graphene provides information on the growth mechanism of graphene and facilitates its controllable synthesis and applications.

Hard Coatings and Vapor Deposition Technology
Room: Golden West - Session B4-2

Properties and Characterization of Hard Coatings and Surfaces
Moderator: M. Fenker, FEM Research Institute, B. Zhao, Exxon Mobil

1:30pm **B4-2-2 Al- and Cr-Doped TiSiCN Coatings with High Thermal Stability and Oxidation Resistance**, ***D.V. Shtansky*** *(shtansky@shs.misis.ru), K.A. Kuptsov, P.V. Kiruykhantsev-Korneev, A.N. Sheveiko,* National University of Science and Technology "MISIS", Russia, *A. Fernandez*, Instituto de Ciencia de Materiales de Sevilla, Spain

Multicomponent coatings based on refractory transition metal carbides and nitrides attract a great attention as protective layers on the surface of cutting and stamping tools, as well as various mechanical components working under load-bearing conditions at evaluated temperatures. Important coating properties for such applications are high hardness, stiffness, wear-, corrosion-, and oxidation resistance, as well as high thermal stability and low friction. The desired properties can be achieved by complex alloying with other elements such as Al, Cr, Si, etc. The aim of this work was a comparative investigation of the structure and properties of Al- and Cr-doped TiSiCN coatings deposited by sputtering of composite TiAlSiCN and TiCrSiCN targets produced by self-propagating high-temperature synthesis method. Particular attention was paid to the investigation of thermal stability, high-temperature oxidation resistance and tribological characteristics. In addition, the comparison of lifetimes of coated and uncoated WC-Co end mills in dry milling of chromium steel (X12BF brand mark, 52-53 HRC) was fulfilled. The results obtained show that the Ti(Al,Si)SiCN coatings with hardness of 30 GPa showed thermal stability up to 1200ºC. The TiAlSiCN coating was more oxidation resistant than the TiCrSiCN coating. After 1 h exposure at 1000ºC the TiCrSiCN and TiAlSiCN coatings, 2.7 mm thick, were only partly oxidized with oxidation depth of 0.7 (TiAlSiCN) and 1.1 mm (TiCrSiCN). The end mills with TCrSiCN coatings showed superior dry cutting performance against high-chromium steel compared to the TiAlCN, Cr- and Si-doped TiAlCN coatings. This can be attributed to its better mechanical (high hardness and elasticity) and tribological (low friction and wear) properties.

1:50pm **B4-2-3 Transition Metal Oxynitride Coatings: Enhancing Performance by Adding Oxygen**, ***L. Castaldi*** *(lorenzo.castaldi@oerlikon.com)*, Oerlikon Balzers AG, Liechtenstein **INVITED**

The different way nitrogen and oxygen bond with transition metals often results in completely different crystallographic and electronic properties between nitrides and oxides. This translates in divergent functionalities for various technological applications. Interestingly, by varying the O/(N+O) atomic ratio in several transition metal oxynitride coatings, it is possible to tune their electronic, optical and crystallographic properties and also enhance their hardness, thermal stability and oxidation resistance. Therefore, the understanding of the role of oxygen and nitrogen in such compounds is of great interest for a wide range of applications such as microelectronics, heterogeneous catalysis, magnetism and protective coatings. As a model example, it will be shown how the crystal structure and electronic properties of Cr-O-N and Cr-Si-O-N thin films change by varying the oxygen content, and how this variation may result in an enhancement of their mechanical properties, phase stability and oxidation resistance. Although Cr-Si and Cr oxynitride coatings exhibit similar crystallographic, electronic structure and mechanical properties, the Cr-Si-O-N films are superior in terms of phase, nanocrystalline stability and oxidation resistance. The cubic/rhombohedral transition occurs in the O/(N+O) range between 70 and 80%. The oxygen is substitutionally incorporated into the nitride cubic structure resulting in a decrease of the lattice parameter and the development of a strong (002) crystallographic preferred orientation as the oxygen concentration increases. According to SEM, all the coatings have dense and smooth microstructure. The maximum hardness is obtained for a oxygen concentration of 97% (28 Gpa) and 44 % (27 Gpa) for the Cr-O-N and Cr-Si-O-N coatings, respectively. Both Cr-based oxynitride coatings with the cubic structure exhibit an excellent phase stability and oxidation resistance in vacuum and in air, which is higher than 1000 °C for the Cr-Si-O-N coatings with a O/(N+O) ratio of 44%.

2:30pm **B4-2-5 Impact of Nb and Ta on the Phase Stability of Ti-Al-N Thin Films**, ***R. Rachbauer*** *(richard.rachbauer@unileoben.ac.at), D. Holec, P.H. Mayrhofer*, University of Leoben, Austria

Due to their outstanding mechanical properties at temperatures < 1000°C, ternary $Ti_{1-x}Al_xN$ thin films attract a huge industrial interest. At temperatures around and above 900°C the thermally induced spinodal decomposition of metastable cubic $Ti_{1-x}Al_xN$ results in an age-hardening effect during the first stages of decomposition. The advent of the stable wurtzite AlN phase, after forming c-AlN-rich domains, goes along with reduced mechanical properties.

In the present study, we highlight the influence of two refractory elements, Nb and Ta, on the thermal stability of magnetron sputtered $Ti_{1-x}Al_xN$ thin films. We thereby investigate the development of structure and mechanical properties from a single phase cubic coating after deposition towards their stable constituents as a function of annealing temperature. It is shown, that apart from a solid solution hardening effect in the as-deposited state, vacuum annealing to 900°C initiates a decomposition of the c-$(Ti_{1-x}Al_x)_{1-y}Nb_yN$ coatings, akin to $Ti_{1-x}Al_xN$, to form a dual phase structure of w-AlN and c-$Ti_{1-y}Nb_yN$. However, the formation of w-AlN and c-$Ti_{1-y}Ta_yN$ during the thermally induced decomposition of quaternary c-$(Ti_{1-x}Al_x)_{1-y}Ta_yN$ thin films is effectively retarded to higher temperatures with increasing amount of Ta.

This combined approach, implementing structural information, mechanical properties and comparison to *ab initio* calculations emphasizes the underlying structure-property relationships in Nb and Ta alloyed quaternary $Ti_{1-x}Al_xN$ based thin films.

2:50pm **B4-2-6 Improved Thermal Stability of TiAlN Through Cr Additions**, ***R. Forsén*** *(rikfo@ifm.liu.se), H. Lind,* Linköping University, Sweden, *M. Johansson,* Seco Tools AB Fagersta, Sweden, *F. Tasnádi, I. Abrikosov, N. Ghafoor, M. Odén*, Linköping University, Sweden

Thermal stability of protective tool coatings is a crucial factor for high speed and dry cutting during which the temperature can exceed 1000°C. Coatings retaining their mechanical properties at elevated temperatures is therefore of interest. This study reports an improved thermal stability of TiAlN when Cr is added. Cubic $Ti_{(1-x-y)}Al_yCr_xN$ ($x<0.4$, $0.45<y<0.6$) PVD layers were deposited by cathodic arc evaporation using compound TiAlCr cathodes in a N_2 atmosphere onto WC-Co substrates. After post deposition annealing at temperatures up to 1400°C the phase evolution and the mechanical properties of the coatings were investigated using nanoindentation, X-ray diffraction and analytical transmission electron microscopy. *In-situ* investigations of the thermal response of the coatings were investigated with differential scanning calorimetry.

Additionally, first principle calculations are reported. The disorder problem is, on the basis of previous work [1], treated as a coherent potential approximation with local relaxation implemented by means of the independent sublattice model, yielding the mixing free energy of the cubic TiAlCrN system. The mixing enthalpies are positive, giving a driving force for decomposition, except for systems with high contents of Cr.

The crystal structure of the as deposited coatings is cubic (B1). The hardness of the TiAlCrN coatings is maintained or even increased up to annealing temperatures of 1000°C, indicating an age hardening process, which is affected by the Cr-content. This is supported by transmission electron microscopy observations showing compositional modulations similar to what have previously been reported for TiAlN [2], however strongly affected by the Cr-content in accordance with our theoretical predictions. Results from differential scanning calorimetry demonstrate that the thermal stability of TiAlN can be increased by several hundreds degrees through Cr alloying.

[1] B. Alling, et al., Phys. Rev. B 75, 045123 (2007)

[2] A. Knutsson, et al., Appl. Phys.Lett. 93 (2008) 143110

3:10pm **B4-2-7 Quantification of the Hydrogen Content of a-C and a-C:H-Coatings Produced at Various Bias Voltages and their Tribological Behavior under Different Humid Conditions**, *W. Tillmann (wolfgang.tillmann@udo.edu),* ***F. Hoffmann****, S. Momeni,* Technische Universität Dortmund, Germany, *R. Heller*, Forschungszentrum Dresden-Rossendorf (FDZ) e.V., Germany

DLC (diamond-like carbon)-coatings stand for excellent wear and friction properties. Due to their good tribological properties these coatings increase the tool life, reduce the power consumption and improve the surface finish of the work piece. However, under different humid conditions DLC-coatings react very differently. Hydrogen-free a-C-coatings show excellent frictions properties under wet conditions because of the thin water film which is formed between the coating surface and the counter part. Under dry conditions the free C-atoms at the surface bond to the counter body material which deteriorates the frictions coefficient. The hydrogenated a-C:H films act contrary to this and have extraordinary tribological properties under dry conditions since the C-atoms at the surface are hydratized and not available for any bonding with the oppositional material. Under wet conditions water molecules are weakly absorbed by the a-C:H-coatings so the interaction between the coating surface and the tribological counter part changes to a dipole-like interaction which is disadvantageous or the tribological performance. According to this, the hydrogen-content plays an important role for the wear and friction behavior of DLC coatings under different humid conditions. This work focuses on the quantification of the hydrogen content of differently bias a-C and a-C:H top layered coating systems and their influence on the tribological behavior under dry and wet conditions.

By means of a magnetron sputter device two different DLC-coating systems, one with an a-C-top layer and the other one with an a-C:H-top layer have been deposited . In order to quantify the hydrogen content within the layers GDOES (Glow Discharge Optical Emission Spectroscopy) was used. In combination with the results of the tribological tests under different humid conditions using a Ball-on-disc-tester, correlations between the hydrogen content, the bias voltage and the wear and friction performance were made.

3:30pm **B4-2-10 Bonding Structures and Mechanical Properties of Silicon Doped Carbon Nitride Films**, ***S.B. Wei*** *(wsb08@mails.tsinghua.edu.cn), T.M. Shao*, Tsinghua University, China

Silicon doped carbon nitride (CN_x-Si) films with various silicon contents were prepared by ion beam assisted deposition. X-ray photoelectron spectroscopy (XPS) was used to characterize the bonding structures of the films. Surface topography and nanohardness were investigated by using an atomic force microscope (AFM) and a nanoindenter, respectively. The results show that adequate dope of Si in CN_x films could significantly increase the nanohardness of the films. As the increase of silicon content in CN_x films, nanohardness of the films increased. The nanohardness reached to a maximum value of 66GPa when silicon content increased up to about 40 at.%, and then rapidly decreased as the silicon content further increased. XPS spectra indicated an increasing proportion of single bonds (N-Si, N-C, et al.) and a decreasing proportion of double and triple bonds (N=C, N≡C et al.) with increasing silicon content of the films. It is suggested that the formations of N-Si and N-C led to the strengthening of the sp^3 network, and increased nanohardness of the films. However, the formation of redundant Si-Si bonds due to the continuous increase of Si content in the films, caused the decrease of nanohardness of the films.

Fundamentals and Technology of Multifunctional Thin Films: Towards Optoelectronic Device Applications
Room: Sunset - Session C2/F4-1

Thin Films for Photovoltaics and Active Devices: Synthesis and Characterization
Moderator: T. Miyata, Kanazawa Institute of Technology, A.P. Ehiasarian, Sheffield Hallam University

1:30pm **C2/F4-1-1 Plasma Processing for Photovoltaics: Fundamentals and Applications**, ***R. van de Sanden*** *(m.c.m.v.d.Sanden@tue.nl)*, Eindhoven University of Technology, Netherlands **INVITED**

In this presentation I will address the different roles atomic hydrogen and ions play in the synthesis of thin amorphous and crystalline materials. In particular I will address the role of atomic H during the growth of amorphous and microcrystalline silicon as determined from in situ studies using optical emission spectroscopy (to monitor the hydrogen flux) and evanscent wave cavity ring down spectroscopy to measure the subsurface defect density. Controlled monoenergetic ion energy distribution functions, by means of pulsed biasing scheme, will be used to illustrate the different roles of ion flux and ion energy in the densification of hydrogenated amorphous silicon. Moreover during ion bombardment studies on thin film amorphous silicon films an ion induced Staebler-Wronski effect was observed. It will be demonstrated that defects in this case are created by UV photon generation as a result of electron-ion recombination on the surface and is not due to ion collision cascade effects as normally assumed. In addition the role of H in ZnO:Al electronic transport properties will be addressed.

2:10pm **C2/F4-1-3 Glancing Angle Deposited Sculptured Titania Films for Light Scattering Enhancement in Solar Cells**, ***K.-H. Hung*** *(kvn.hung@yahoo.com)*, Industrial Technology Research Institute, Taiwan, *G.-D. Chiou, M.-S. Wong,* National Dong Hwa University, Taiwan, *Y.C. Wang, W.-T. Kuo, I-.S. Chung, C.-M. Yeh*, Industrial Technology Research Institute, Taiwan

Light trapping is a crucial approach to eliminate optical losses and to capture solar radiation effectively in solar cells. By texturing surface of front transparent conductive electrodes in which the incident light is scattered, its energy conversion efficiency can be substantially enhanced. For example, textured fluorine-doped tin oxides (FTO, Asahi U-type) exhibit rough surface morphology with excellent light scattering ability, and they are widely used as conductive electrodes in silicon-based solar cells. However, FTO can't endure in high hydrogen plasma and generally needs protective layers such as titania (TiO_2) or zinc oxide films during silicon thin film growth. In specific, TiO_2 films have not only excellent resistance against hydrogen environments but also act as anti-reflective coatings at TCO/silicon interface. Nonetheless, previous studies do not investigate the light scattering ability of TiO_2 films and their application on conductive electrodes. In this study, a promising technique to enhance the hydrogen-radical durability of FTO and its light scattering ability are demonstrated. A series of TiO_2 films were evaporated by glancing angle deposition (GLAD) method. The sculptured TiO_2 films were deposited on FTO glass at a fixed oblique angle of 86° under various substrate rotation rates from 0.16 to 1 rpm. As a result, the optical transmittance of FTO films retained at 80% after coating porous TiO_2 films. More significantly, the optical haze, a measurable parameter of light scattering ability, was markedly enhanced from 33 to 52% (at wavelength=400 nm). This haze values increase up to 57% improvement. In addition, the sheet resistance of TiO_2/FTO films were slightly reduced from 8.4 to 5.7 Ω/□. Transmission electron microscopy depicts that the TiO_2/FTO films exhibited pyramid-like texture accompanied with sculptured nanoporous TiO_2 films. By covering of sculptured TiO_2 films, the electrical and optical scattering properties as well as hydrogen-radical durability of FTO films are enhanced simultaneously, and they still exhibit transparent conducting behavior. We suggest that the glancing angle deposited sculptured TiO_2 films are promising for light scattering enhancement, and the sculptured TiO_2/FTO films may utilize as transparent conductive electrodes.

2:30pm **C2/F4-1-4 Optical and Mechanical Characterisation of Nanostructured Antireflectance Coatings for Solar Cells**, ***J. Moghal*** *(jonathan.moghal@materials.ox.ac.uk)*, University of Oxford, UK, *J. Best, M. Gardener,* Oxford Advanced Surfaces Group plc, UK, *A.A.R. Watt,* Univeristy of Oxford, UK, *G. Wakefield*, Oxford Advanced Surfaces Group plc, UK

Anti-Reflection (AR) coatings can be applied to a wide range of optical elements to significantly reduce reflections caused by step changes in the refractive index at the window surface. For example, on typical solar cells glass windows and plastic lenses reflect approximately 5% of incident light per surface. Current anti-reflection technology relies primarily upon expensive vacuum deposition techniques of multilayer stacks. There is a growing need to develop low cost processes which can be scaled to a wide range of applications and substrates. We have previously demonstrated an AR coating that can achieve a tuneable reflection minimum between 400nm and 1900nm and also shown that the short circuit current (I_{sc}) and the power conversion efficiency (PCE) of a solar cell is increased by between4.5% and 5.0%. High optical performance is achieved by using a binder system in conjunction with the mesoporous silica nanoparticles. The ratio of nanoparticles to binder and the process conditions are used to optimise the optical and mechanical properties of the film. This paper discusses the mechanical properties of the anti reflection coatings on polymer substrates. We describe the elastic behaviour of the coatings using nano-indentation, nano-scratch tests and impact testing. Even though the AR coating consists of a high (>50%) loading of inorganic nanoparticles, they have been shown to flex with the underlying polymer substrate. The coating can flex and recover from deformations of up to 40 times the original thickness under mechanical load.

2:50pm **C2/F4-1-7 Polymeric Materials and Self-Assembled Interlayers for Printed Photovoltaic Cells**, ***A. Facchetti*** *(a-facchetti@northwestern.edu)*, Polyera Corporation and Northwestern University **INVITED**

Polymeric Materials and Self-Assembled Interlayers for Pritned Photovoltaic Cells Antonio Facchetti Polyera Corporation and Northwestern University In this presentation we will report the design, synthesis, and characterization of new molecular precursors for the fabrication of self-assembled (inter)layers on SiO_x, metal oxide, metals, and organic films. These building blocks are designed to strongly adhere to the surfaces of these conductors altering charge injection, charge trapping, and light absorption. Several photovoltaic cell device architectures based on these interlayers are fabricated and shows that these materials enable improved performance or new functions. Furthermore, I will report on the synthesis of new donor polymers for bulk-heterojuction solar cells achieving efficiencies > 7%.

3:30pm **C2/F4-1-9 Fabrication of Large Area TiO_2 NT Dye-Sensitized Solar Cell on Stainless-Steel by Thermal Spraying and Anodizing Methods**, ***C.-C. Chen***, National United University, Taiwan, *C.-K. Lin (cklin@fcu.edu.tw), C.-J. Chang,* Feng Chia University, Taiwan, *C.-H. Hsu,* Tatung University, Taiwan, *W.-D. Jheng*, National Chin-Yi University of Technology, Taiwan

This article is to provide large-scale dye-sensitized solar cells (DSSC) and methods for their manufacture by thermal spraying and anodizing. An DSSC device that containing a photosensitive dye (N3) adsorbing on a large area surfaces of anode, a transparent conductive cathode disposed to be opposite to the anode and wherein a platinum(Pt) nano-catalytic particles are adhered to its surfaces, and an electrolytic solution sealed between the anode and the transparent conductive cathode. A titania nanotube (TiO_2 NT) film was fabricated by thermo-sprayed titanium film which was on 304 stainless-steel substrate. The film of Ti was then through anodization, $TiCl_4$ treatment, and heat treatment to form anatase TiO_2 NT film which was as an anode of DSSC. An indium doped tin oxide (ITO) glass coated with platinum (Pt) particles by sputtering was used as a counter electrode. Electrolyte containing 0.5 M lithium iodide (LiI) and 0.05M iodine (I_2) in acetonitrile (CH_3CN, 99.9%) was introduced into the electrodes. The photo-current conversion efficiency was tested under an AM 1.5 Solar Simulator. The DSSC device has short current density (Jsc) of 9.32 mA cm^{-2}, open voltage (Voc) of 0.58V, fill factor (FF) of 0.59, and conversion efficiency (η) of 3.2%. The internal impedance of DSSC were detected and simulated using an electrical impedance spectra (EIS) technique with inductance, resistors, and capacitors characteristics. The impedance of the bulk materials was simulated by using $L_0+R_0+R_b$; the impedance of the working electrode was simulated by $(C_1//R_1)//(R_a+(C_2//R_2)$; the electrolyte was simulated by $C_3//R_3$; and the counter electrode was simulated by $C_4//R_4$. The equivalent circuit of DSSC was illustrated express as: $(L_0+R_0+R_b)+\{[(C_1//R_1)//(R_a+(C_2//R_2))\}+(C_3//R_3)+(C_4//R_4)$.

3:50pm **C2/F4-1-10 Effect of (poly)Phosphate Anion Structure on Characteristics of Pulsed DC PEO Coatings on Ti, for Dye Sensitised Solar Sell Applications**, ***P.-J. Chu***, *A. Yerokhin (a.yerokhin@shef.ac.uk),* University of Sheffield, UK, *J.-L. He,* Feng Chai University, Taiwan, *A. Matthews*, University of Sheffield, UK

Plasma electrolytic oxidation (PEO) of Ti can be used to prepare TiO_2-based coatings with useful functional properties, e.g. photocatalytic and biological activity. Of particular interest is development of PEO coatings for dye sensitised solar cell (DSSC) applications. Appropriate coatings are required to be porous and enriched with metastable anatase phase. Anatase stabilisation requires approaches that are substantially different from those dominated in development of protective PEO coatings. One possibility consists in incorporation into the coating structure of anatase stabilizers, such as Si and/or P.

In this study, the detailed investigation of microstructure, surface morphology and porosity of porous titania coatings was carried out. Aqueous solutions of tri-sodium orthophosphate (Na_3PO_4), sodium pyrophosphate ($Na_4P_2O_7$) and sodium hexametaphosphate (Na_2PO_4-$(NaPO_3)_x$-Na_2PO_3, x = 10…12) of 0.01 to 0.03 mol l^{-1} concentration were utilised. A pulsed DC PEO mode was employed with voltages, pulse frequencies and duty cycles varied between 200 V to 600 V, 100 Hz to 4000 Hz and 0.11 to 4, respectively. The oxidation was carried out for 10 minutes. The coating microstructure, surface morphology and porosity was analyzed by X-ray diffractometry, scanning electron microscopy and electrochemical impedance microscopy. Inverse-type ITO glass/Pt/electrolyte (I_2+LiI)/dye/TiO_2/Ti devices were assembled using the above PEO-treated specimens. The DSSC photovoltaic efficiency was evaluated by exposing it to a fixed output-power solar simulation.

Results show that the PEO titania coating growth rate varies from 0.08 to 1.5µm min^{-1} and 6 to 8 µm thick coatings can be produced in orthophosphate electrolytes, containing maximum amount of anatase phase. The uniformly rough surface morphology is featured by small pores (200 to 300 nm in diameter) and deep craters (1 to 2 µm in diameter). Such a porous morphology is deemed to be beneficial for dye penetration and associated increment in photovoltaic efficiency for DSSC application.

4:10pm **C2/F4-1-6 Effects of Additive in Cu Solution for Electrodeposition of $CuInSe_2$ Film**, ***T.-W. Chang*** *(n2897109@ncku.mail.edu.tw),* National Cheng Kung University, Taiwan, *W.-H. Lee,* National Cheng-Kung University, Taiwan, *Y.-H. Su, F.-I. Chih*, National Cheng Kung University, Taiwan

In this work, we discuss the development of inexpensive, high efficiency, large-area solar cells of the thin-film $CuInSe_2$(CIS) type. We show that it is possible to fabricate p-type CIS entirely by electrodeposition. CIS is considered to be one of the best absorber materials for use in polycrystalline thin-film photovoltaic solar cells. It is an inexpensive, non-vacuum deposition technology which is inherently scalable to large-area deposition. A smooth under layer will lead to better qualities of $CuInSe_2$ films. Large grain size, great crystallinity, and fine morphology were characterized in the $CuInSe_2$ films. We conclude that better qualities of $CuInSe_2$ films will be achieved on smoother Cu under layers, and the addition of CH_4N_2S leveler in the Cu solution will help the formation of smoother Cu layers. We electrodeposit CIS to control ratio, and to fabricate the superior structural properties of these selenized films were also clearly reflected by X-ray diffraction (XRD). Field-emission-scanning electron microscopy indicates that the ordered copper indium diselenide thin-films are entirely filled, and the structure of the molybdenum thin-film. X-ray diffraction result shows that the copper indium diselenide thin-films are crystalline and have the highly preferential orientation. Energy dispersive spectrometer analysis observation shows the composition atomic ratio of copper indium diselenide.

Biomedical Coatings
Room: Royal Palm 4-6 - Session D1-2

Bioactive and Biocompatible Coatings and Surface Functionalization of Biomaterials

Moderator: E. Saiz, Imperial College, S. Kumar, University of South Australia

1:30pm **D1-2-1 Fabrication of Superhydrophilic and Superhydrophobic Surfaces on Titanium Substrates**, ***R. Fleming***, *M. Zou (mzou@uark.edu)*, University of Arkansas

Superhydrophobic and superhydrophilic surfaces are benifical in many biomedical applications. Here, we report a method of producing both superhydrophilic and superhydrophobic surfaces on titanium substrates. Sandblasting the titanium surfaces with alumina particles, followed by dip-coating in a colloidal silica nanoparticle solution, produces a superhydrophilic surface with a water contact angle (WCA) of less than 5°. Further chemical modification with a fluorinated-carbon film, deposited by introduction of C_4F_8 gas under the action of plasma in a deep reactive ion etcher, renders the surface superhydrophobic, with a WCA in excess of 150°. These surfaces are characterized by WCA measurements, scanning electron microscopy, energy-dispersive x-ray spectroscopy, x-ray diffraction, and surface profilometry. In addition, the hydrophilic and hydrophobic stability of these surfaces is discussed.

1:50pm **D1-2-2 Strontium as a Bioactive Agent in Magnetron-Sputtered Titanium Coatings**, ***M. Sillassen*** *(mbs@phys.au.dk), O.Z. Andersen,* Aarhus University, Denmark, *K.P. Almtoft, K. Rechendorff, L.P. Nielsen,* Danish Technological Institute, Tribology Centre, Denmark, *M. Foss, J. Bøttiger*, Aarhus University, Denmark

Titanium is a commonly used implant material because of its inertness and biocompatibility in e.g. orthopaedic applications. However, there is still a need for a faster healing process and improved fixation of implants. Strontium has demonstrated positive effects as a bioactive agent due to its anti-inflammatory and anti-osteoporotic properties.

Strontium-containing titanium films (thickness ~100 nm) were synthesized by magnetron co-sputtering from a pure 2-inch Ti target and a composite 2-inch Ti-Sr (80-20 at.%) target. The pure Ti target was run in DC mode, whereas the composite Ti-Sr target was run in pulsed DC mode in order to avoid target poisoning. Prior to deposition of Ti-Sr, an initial layer of pure titanium (thickness ~100 nm) was deposited onto the Si(001) substrates. During the depositions, the substrates were electrically floating. The amount of strontium in the coatings was varied by the relative power to the two targets by means of which strontium surface concentrations, as determined from XPS, ranging from 0 to 20 at.% were obtained. X-ray diffraction revealed a predominantly amorphous film structure, except in the case of pure titanium; high contents of strontium yielded completely amorphous Ti-Sr films. Furthermore, the effects of strontium concentration on the film morphology and surface topography were studied by cross-sectional SEM and AFM, respectively. Cell proliferation tests (1, 2, 4, 7 days) of the strontium-containing titanium surfaces were carried out with human dental pulp stem cells (hDPSCs), and the correlation between the proliferation of the hDPSCs and the strontium concentration was investigated.

2:10pm **D1-2-3 Bioactivity and Corrosion Resistance of Surface Treated F138 Stainless Steel**, ***V.H. Baggio-Scheid*** *(scheid@ieav.cta.br),* Institute of Advanced Studies, Brazil*, L. Marchini, R.F. da Rocha, C.P. de Deco*, State University of São Paulo - UNESP, Brazil

In this work we investigate the bioactivity (the ability of cells to bond with the surface material) and the corrosion resistance of plasma nitrided F138 stainless steel with different surface morphologies. Such structures were obtained by milling, sand blasting and acid etching pre-treatments. The samples were plasma nitrided for 3 h at temperatures varying from 698 up to 773 K. After nitriding, surfaces with different morphologies and hardness of 1100 HV have been obtained. The surface microstructures were studied using scanning electron microscopy, X-ray diffraction (XRD) and roughness measurements. Measurements of open circuit potential of samples immersed in simulated body fluid (SBF) shown that the treatments do not significantly affect the corrosion resistance of the treated surfaces. To evaluate the bioactivity, samples of treated steel were inserted into rat subcutaneous tissue. After intervals of 3 and 14 days, the tissue was removed and analyzed microscopically, using standard histological preparation. The results of these evaluations for the different surface treatments are presented and discussed.

2:30pm **D1-2-4 Mechanical, Tribological and Corrosion Behavior of Multilayer Coating of Ti/TiN/nc-TiN/a-Si_3N_4 Deposited by Sputtering on Stainless Steel M340 and Ti6Al4V Substrates for Biomedical Applications**, ***J. Garcia*** *(jegarcia@up.edu.mx),* Universidad Panamericana, Mexico*, M. Flores,* Universidad de Guadalajara, Mexico*, L. Pazos,* Instituto Nacional de Tecnologia Industrial, Argentina*, O. Jimenez*, Universidad de Guadalajara, Mexico

In this work a coating layer of Ti/TiN/nc-TiN/a-Si_3N_4, were deposited on Stainless steel M340 and Ti6Al4V substrates using DC and RF codeposition reactive magnetron sputtering technique. Characterization, mechanical and corrosive tests were conducted with the purpose of establish the possibilities to use it as a biomaterial in the body, including: XRD and XPS techniques to analyze the structure and composition of coatings, profilometry to analyze the topography of substrates, films and wore Surfaces (tribologicaly tested), scratch test to evaluate film adhesion to the substrate and electrochemical technique as well as a reciprocating tribocorrosion test in 1% NaCl water solution and artificial saliva solution, to evaluate the corrosion susceptibility under static and reciprocating conditions respectively. All the results are analyzed and discussed. The tests suggest that this multilayer is a promising biomaterial for biomedical applications.

2:50pm **D1-2-7 Development of Nanostructured Ternary Shape Memory Alloy Thin Films for Biomedical Applications**, ***N. Kaur****, N. Choudhary, D. Kaur (dkaurfph@iitr.ernet.in)*, Indian Institute of Technology Roorkee, India

Shape memory alloys (SMAs) offer a unique combination of novel properties, such as shape memory effect, super-elasticity, biocompatibility and high damping capacity. In the present study, NiTiCu and NiTiAg shape memory alloy thin films were successfully grown on Si(100) substrates by dc magnetron sputtering technique. Crystalline structure, hardness and phase transformation properties of NiTiCu and NiTiAg films were investigated using X-ray diffraction (XRD), nanoindentaion and four probe resistivity methods. Further, aim of the study was to deposit hard and adherent nanocrystalline NbN protective layer on NiTiCu and NiTiAg films to improve their surface, mechanical and corrosion properties without sacrificing the phase transformation and shape memory effect. The structural, electrical and mechanical studies were performed on both NbN/NiTiCu and NbN/NiTiAg films and the results were compared. Further the application of NbN/NiTiCu and NbN/NiTiAg films in the electrochemical sensing of dopamine, which has critical physiological importance in the Parkinson's disease has also been demonstrated.

Tribology and Mechanical Behavior of Coatings and Thin Films
Room: California - Session E3-2

Tribology of Nanostructured and Amorphous Films
Moderator: V. Fridrici, Ecole Centrale de Lyon - LTDS, O.L. Eryilmaz, Argonne National Laboratory

1:30pm **E3-2-1 Prediction of the Friction Behavior of Lubricated Tribological Systems Containing Amorphous Carbon Coatings using an Artificial Neural Network**, ***E. Schulz*** *(schulz@mfk.uni-erlangen.de), S. Roehner, S. Tremmel,* Friedrich-Alexander-University Erlangen-Nuremberg, Germany*, Y. Musayev, T. Hosenfeldt,* Schaeffler Technologies GmbH & Co. KG, Germany*, H. Meerkamm, S. Wartzack*, Friedrich-Alexander-University Erlangen-Nuremberg, Germany

Amorphous carbon coatings are more and more used in combustion engine applications to reduce friction and wear in highly stressed tribological systems to fulfill legislative guidelines concerning energy efficiency and CO_2 emissions. In oil-lubricated tribological systems working under mixed friction conditions, e.g. in the valve train, the performance of coated components like bucket tappets depends on the interaction between all elements of the tribological system. Engine lubricants and additives are actually still optimized for polar metal surfaces. In combination with non-polar and inert carbon surfaces, the effectiveness of these additives is reduced or prevented. Even undesirable effects may occur by the changed conversion of the additives. Up to now these interactions are not sufficiently understood. In literature, the impact of some additives on amorphous carbon coatings is described isolated. To handle the complexity of the tribological processes these works are always limited to the variation of a few influencing variables and the use of one specific tribological test. Therefore, the transferability of these results to applications is restricted. As well an analytical prediction of friction and wear is not possible since the friction and wear mechanisms are overlapping in the temporal and local undetectable real contact area. Thus always empirical studies are needed to determine the tribological behavior. In such studies as many influencing variables as possible should be varied to obtain a better understanding of the friction and wear behavior. Especially the high complexity of these systems and the large experimental effort show the need for a specific prediction of the friction and wear behavior. This article presents the development of a multilayer artificial neural network (ANN) to predict the friction behavior of such tribological systems. Using an ANN with its learning capability reduces the experimental effort significantly. Precondition for the modeling with such a network is the availability of empirical test data. In this article a total amount of 400 experiments were carried out by using various tribological test equipments, such as model, component and unit tests to assess the transferability between the different tests. Input parameters like type of coating, base oil, additives, temperature, pressure, etc. were varied systematically. The predictive capabilities of the ANN model were validated with experimental results. A satisfactory agreement between the predicted friction values and experimental observations was found. Furthermore the influence of the input parameters on the friction coefficient could be quantified.

1:50pm **E3-2-2 Fatigue Properties of a 21MnCr5 Steel Coated with an Amorphous Carbon Coating**, ***S. Tremmel*** *(tremmel@mfk.uni-erlangen.de),* Friedrich-Alexander-University Erlangen-Nuremberg, Germany*, B. von Großmann,* Georg Simon Ohm University of Applied Sciences Nuremberg, Germany*, S. Wartzack*, Friedrich-Alexander-University Erlangen-Nuremberg, Germany

A lot of components in technical applications, for example bucket tappets or piston pins, are both mechanical and tribological highly loaded. To enhance their tribological properties they often get coated with amorphous carbon by PVD or PACVD. Although it is known, that surface treatment may strongly influence the fatigue properties of steels, there are only a few investigations about the influence of amorphous carbon coatings up to now. Besides that, there is a lack of methods for dimensioning such coated parts, not least because there do not exist adequate stress limits for coatings. Motivated by the described situation this article presents results of fatigue tests of 21MnCr5 specimens similar to ASTM 606 and coated with an a-C:H:W coating under zero-to-tension cyclic loading. It is discussed, how strong the coating influences the fatigue properties of the substrate and if it is possible to identify fatigue limits of coatings under defined stress conditions using conventional fatigue tests on resonant testing machines. First results from a set of fatigue tests indicates, that the amorphous carbon coating does not influence the static strength, in particular the tensile strength, but decreases the fatigue limit with increasing cycle number. This effect is not understood up to now, although there are some presumptions, which should be discussed and compared to other works, which studies the influence of different hard coatings on the fatigue limits of different substrates, too. Furthermore, in this article a method is suggested, which allows in a quite simple way the detection of fatigue limits of the coating using microsections of the fatigue specimens and their investigation by light microscopy. Compared to other known methods, for example cyclic impact tests, the suggested method provides fatigue limits under quite well defined stress conditions.

2:10pm **E3-2-3 The Effect of Coating Properties on the Fracture Characteristics and Tribological Performance of a-C:H and ta-C Films**, ***H.A. Ronkainen*** *(helena.ronkainen@vtt.fi), K. Holmberg, A. Laukkanen, T. Andersson,* VTT Technical Research Centre of Finland*, M. Kumagai, M. Kano, T. Horiuchi,* Kanagawa Industrial Technology Center, Japan*, T. Suzuki,* Keio University, Japan*, M. Taki*, Onward Ceramic Coating Co, Ltd., Japan

DLC films cover a wide range of different carbon based coatings, starting from soft to extremely hard diamond-like carbon films. In this case two different types of DLC films have been studied in respect of their fracture characteristics and tribological performance. The coatings are a-C:H deposited by PECVD and ta-C coating deposited by filtered arc technique. In order to evaluate the stress and strain behaviour of the coatings under load, 3D FE modelling was carried out in combination with scratch testing. Also the tribological performance was evaluated with static load as well as with continuously increasing normal load pin-on-disc tests.

The 3D FEM model was developed for calculating the stress and strain distributions. The simulation model was applied to the scratch test contact conditions, when the spherical diamond tip was moving with increased load on a coated surface. The crack propagation during the empirical scratch testing was detected. It was observed that the first crack appeared for the both coatings as an angular crack representing the maximum stress experienced on the scratch groove edge. When combining the simulated stress values with empirical observation of coating fracture patterns the coating fracture toughness was determined. A major effect of the coating elastic modulus on the stress and fracture behaviour of the coatings was observed.

In the tribological testing the both coatings had a low friction performance. In the tribological testing with continuously increasing load, the critical load for coating delamination was higher for the a-C:H coating. This is in accordance with the results of FE modelling of stress accumulation and the fracture toughness evaluation of the coatings. The influence of coating characteristics on the performance properties in real applications will be discussed.

2:30pm **E3-2-4 Stress Reduction in Hard a-C:N DLC Coatings**, ***S. Louring*** *(sascha@inano.au.dk), N.D. Madsen, A.N. Berthelsen,* Aarhus University, Denmark*, B.H. Christensen, K.P. Almtoft, L.P. Nielsen,* Danish Technological Institute, Tribology Centre, Denmark*, J. Bøttiger*, Aarhus University, Denmark

Nitrogen-doped amorphous carbon (a-C:N) coatings were deposited by use of reactive DC magnetron sputtering with an industrial-scale deposition system. The reactive gas N_2 was used in combination with graphite targets, and the compositions of carbon, nitrogen and impurity atoms were measured by X-ray Photoelectron Spectroscopy (XPS). The mechanical properties of the coatings – hardness and elastic modulus – were extracted from nanoindentation data, and from the elastic modulus and the G-peak position measured by Raman-spectroscopy the compressive stress was calculated. High resolution XPS spectra were also recorded for the C 1s and N 1s spectra in attempt to link the microstructure of the coatings to their mechanical properties. The tribological performance of the films was investigated with a pin-on-disc setup using Al_2O_3 as counter-parts. The tests were carried out at room temperature in both ambient and controlled atmospheres and information about both wear rates and friction coefficients of the coatings were obtained. A number of process parameters – substrate bias, N_2 flow and deposition temperature - were systematically varied to optimize the mechanical and tribological performance of the coatings. An increased temperature during the deposition process led to a more than 50 % reduction in the compressive stress from above 3 GPa to 1.4 GPa. Increasing the deposition temperature caused a slight decrease in the N/C atomic ratio from 0.34 to 0.29, while the hardness was approximately constant at 15 GPa.

2:50pm **E3-2-5 2.5 nm Thick TiSiN Protection Layer for HDD Magnetic Media**, ***F. Rose*** *(franck.rose@hitachigst.com), D. Pocker, Q.-F. Xiao, B. Marchon*, Hitachi Global Storage Technologies Inc.

To achieve HDD areal densities of 1 Tb/sq.inch it is required that the magnetic spacing between the head sensor and the disk media is reduced to 6 nm. Especially, the overcoat (OC) film that protects the disk has to be as thin as 2.5 nm. Within this spacing budget the OC has to retain excellent tribological properties, lubricant compatibility, and anticorrosion protection of the Co-containing media.

TiSiN [1] and SiN_x [2] ultra-thin films are prospective materials for high density HDD disk OC. SiN_x films are denser than conventional diamond like carbon OC and can act as barriers that prevent migration and corrosion of Co. Unfortunately, SiN_x OC are unstable under high humidity and temperature. Water hydrolysis leads to SiO_x growth on the surface of SiNx OC resulting in HDD failures such as head crashes and irreversible disk damages.

Here, we show that adding Ti into SiN_x induces the formation of a TiO_x surface protection layer that allows reducing SiO_x growth and Co corrosion while concomitantly decreasing the OC surface energy. We present an extensive spectroscopy and microscopy study (XPS, XRR, FTIR, AFM, SEM, TEM, OSA) of 2.5 nm thick TiSiN OC, with focus on their composition and nanostructure, stability against hydrolysis, and anticorrosion protection.

OC were deposited by reactive magnetron sputtering on top of magnetic media on glass disks using different Ti_xSi_y targets to vary their content ratio R=Ti/(Ti+Si). These films were found to be different in nature than previously reported nanocomposite TiSiN [3]. They are completely amorphous with mass densities increasing with R (0 to 1) from 3.14 to 4.34 g/cc. These values are comprised between those of stoichiometric Si_3N_4 (3.2 g/cc) and TiN (5.4 g/cc). Moreover, angle-resolved XPS and FTIR showed that TiSiN OC are actually oxynitrides terminated with a native surface layer of TiO_x.

Overcoat stability against hydrolysis was studied in function of films Ti content. It was found that 4 at. % of Ti is enough to reduce SiO_x formation by half, and that higher Ti contents can block SiO_x surface growth. To reduce surface chemical reactivity and contaminant attraction it is desirable that disk OC have low surface energy. Surface energy of disks lubed with 1.2 nm of ZTMD, a perfluorinated lubricant, was measured by using the droplet contact angle method. TiSiN OC have much lower surface energy (16-19 mN/m) than SiN_x OC (31 mN/m). For comparison, we measured 17 mN/m for both TiN_x and TiO_x OC, which is consistent with TiSiN OC being capped with TiO_x.

[1] Q.Dai et al., US Pat. 6586070 B1 7/2003

[2] B.K.Yen et al., Vac. Sci. Technol. A 21(6), 1895, 2003

[3] S.Veprek et al., Surf. Coat. Technol. 202, 5063, 2008

3:10pm **E3-2-6 Tribology Behavior of Nanocrystallite Carbon Film Prepared by ECR Sputtering Method**, ***C. Wang*** *(venture.hit@stu.xjtu.edu.cn), D. Diao*, Xian Jiaotong University, China

Nanocrystallite carbon film has drawn much interests since it has not only high hardness and good wear performances comparable to those of diamond but also wonderful conductivity close to that of graphite. It has a brightly future as a new coating material in modern industry. Among the methods which are introduced to prepare carbon film, Electron Cyclotron Resonance (ECR) method has some exclusive advantages such as high energy efficiency, flexible working condition and simple facility. Therefore, ECR method is a very promising way to produce nanocrystallite carbon film in large scale.

In this study, we have prepared amorphous carbon films with different content of sp2 bonded nanocrystallite by ECR sputtering method. By controlling ECR plasma condition, either electron sheath or ion sheath was formed, and the film surface would be etched by either electron or ion during the film growth process, namely electron etching mode and ion etching mode. Carbon films with different nanocrystallite content were prepared under different etching mode and etching energy. The film's binding configurations and nano-structures were characterized by XPS spectrums and TEM pictures respectively. Friction coefficients and wear lives of the films were tested with a Pin-on-Disk tribometer, and super-low-friction phenomena were observed in certain films' wear tests.

3:30pm **E3-2-7 Tribological Behaviour of Aluminum Against Tungsten Doped DLC at Elevated Temperatures**, ***A. Abou Gharam*** *(abougha@uwindsor.ca),* University of Windsor, Canada*, M.J. Lukitsch,* General Motors Research and Development Center*, A.T. Alpas*, University of Windsor, Canada

Diamond-like carbon (DLC) coatings are particularly suited for applications that require minimum adhesion, low coefficient of frication (COF) and good wear properties against aluminum alloys. These properties however deteriorate rapidly at elevated temperatures. In this study, friction and wear behaviour of W doped DLC (W-DLC) was studied as a function of testing temperature to investigate the coating's surface and subsurface damage at temperatures up to 400ºC. Pin-on-disk tests of 319 Al ran against W-DLC showed that the lowest COF was observed at 25ºC (0.20). While at 100ºC, 200ºC and 300ºC, high average steady state COF values of 0.59 were recorded and as the temperature reached 400 ºC, the COF reduced again to

0.18. Cross sections of the wear tracks prepared by focused ion beam (FIB) milling showed that at 100ºC the coating was spalled and aluminum was adhered to the exposed substrate and hence resulting in the observed high COF. However, at 400ºC, FIB cross sections of the wear track showed no evidence of coating failure or aluminum adhesion. Additional analyses illustrated that at 25ºC and 400ºC, a transfer layer was formed on aluminum contact surface, which prevented aluminum/DLC interactions, and reduced the friction by eliminating aluminum adhesion. Further chemical investigations of the transfer layer using micro Raman, X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM) were conducted to elucidate details of the mechanisms responsible for the low COF at elevated temperatures.

3:50pm **E3-2-8 Identification of the Wear Mechanism on WC/C Nanostructured Coatings**, *S. El Mrabet, M.D. Abad,* ***J.C. Sanchez-Lopez*** *(jcslopez@icmse.csic.es)*, Instituto de Ciencia de Materiales de Sevilla, Spain

A series of WC/C nanostructured films with carbon contents ranging from 30 to 70 at.% was deposited on M2 steel substrates by magnetron sputtering of WC and graphite targets in argon. Depending on the amorphous carbon (a-C) incorporated in the coatings, nanocrystalline coatings (formed mainly by WC_{1-x} and W_2C phases) or nanocomposites (WC_{1-x}/a-C) were obtained with tunable mechanical and tribological properties. Ultrahardness values of 35-40 GPa were measured for the nanocrystalline samples whilst values between 16 to 23 GPa were obtained in the nanocomposite ones depending on the a-C content. The tribological properties were studied using a pin-on-disk tester versus steel (100Cr6) balls at 5N of applied load in dry sliding conditions. Three different zones were identified according to the observed tribological behaviour: I (μ>0.8; adhesive wear); II (μ:0.3-0.6; abrasive wear) and III (μ~0.2; self-lubricated). The wear tracks and the ball scars were observed by scanning electron microscopy (SEM) and Raman spectroscopy in order to elucidate the tribochemical reactions appearing at the contact and to determine the wear mechanism present in each type. A correlation among mechanical properties, crystal phases, a-C content and wear modes could be established for the series of WC/C coatings.

4:10pm **E3-2-9 Advanced Applied Technology of DLC Coatings**, ***M. Kano*** *(mkano@kanagawa-iri.go.jp)*, Kanagawa Industrial Technology Center, Japan **INVITED**

Reduction of the mechanical friction especially for automotive engine has been strongly required in recent years for improving fuel economy. Reducing the friction between the cam and follower is effective in this regard in the low engine speed range. A diamond-like carbon (DLC)-coated cam follower of the bucket type has been applied to the gasoline engines to reduce engine friction. This low friction property is obtained by the hydrogen free DLC, ta-C lubricated with the ester containing oil. The main experimental results of this applied technology are explained briefly. The recent topic of the applied DLC coating technology is the advanced technique of DLC coating on aluminum alloy with the high adhesive strength and wear resistance. The DLC coated aluminum engine piston showed the excellent wear resistance after the actual motor cycle 4h race. The second one is the potentiality of the super low friction property by DLC-DLC combination under the environmentally friendly fluid lubrication. The super low friction coefficient below 0.01 was obtained by the ta-C coating using the filtered arc deposition process under oleic acid lubrication. The material technology using DLC coating with the environmentally friendly lubricant has much potentiality to improve the environment problem in various kinds of the industries.

4:50pm **E3-2-11 Superlow Friction of SiO_x-Doped DLC Coatings under Oxygen and Hydrogen Ambients**, ***J. Fontaine*** *(julien.fontaine@ec-lyon.fr)*, Ecole Centrale de Lyon - LTDS, France*, R.W. Carpick,* University of Pennsylvania*, S.V. Prasad,* Sandia National Laboratories*, T. Le Mogne, S. Bec*, Ecole Centrale de Lyon - LTDS, France

Although diamond-like carbon films exhibit remarkable mechanical and tribological performance under a range of conditions, the addition of dopants is of interest for further improving properties, especially thermal stability. SiO_x-doped DLC's, also referred to as "diamond-like nanocomposite" films, exhibit lower surface energy, higher sp^3 bonding, higher hardness, and better thermal stability than typical hydrogenated DLC's. These properties are particularly advantageous for space applications of the coating. To investigate both the fundamental mechanisms of the tribological behavior of this material as well as to assess its behavior in environments with relevance to aerospace applications, the tribological behavior of a commercial SiO_x-doped DLC coating was investigated against a 52100 steel pin on an ultra-high vacuum tribometer. Linear reciprocating motion under a residual pressure lower than 10^{-7} Pa and a speed of 2 mm/s was used. The coefficient of friction increases very quickly from 0.2 to more than 0.7 within the first few cycles, exhibiting significant transfer of steel onto the coating surface, and then producing heavy coating damage. The tribological behavior under vacuum thus appears to be governed by adhesive phenomena. Experiments were also performed under different partial pressures of molecular oxygen and hydrogen. Under 1 kPa of O_2, or 6 kPa of H_2, coefficients of friction down to 0.005 were observed, with clear evidence of tribofilm build-up on the steel counterface. Investigations of the rubbed surfaces were then conducted by surface analysis (XPS, AES) and Atomic Force Microscopy. The involved solid lubrication processes will thus be discussed in light of tribochemical interactions as well as of surface topography evolution.

5:10pm **E3-2-12 Mechanical and Tribological Properties of a-C:H Thin Films Prepared by an Unbalanced Magnetron Sputtering System**, ***B. Feng*** *(feng_bao@cat.com), S.C. Taylor, L.V. Davies*, Caterpillar Inc

Hydrogenated amorphous carbon (a-C:H) thin films were deposited in an industrial scale unbalance magnetron sputtering (UBMS) system. Coating microstructure was studied with Raman spectroscopy. Nanoindentation tests were performed to characterize coating mechanical properties. Coating friction and wear behavior were evaluated using micro scale abrasion test (MSAT), high frequency reciprocating rig (HFRR) test, block on ring (BoR) test and impact test. BoR test was performed at different temperatures and in different fuels to simulate the operational condition of a diesel application. Comparison was made with tungsten containing hydrocarbon (W-C:H) and tetrahedral amorphous carbon (Ta-C) coatings. Coating selection considerations for potential industrial applications were discussed.

Characterization: Linking Synthesis, Microstructure, and Properties
Room: Tiki Pavilion - Session TS4-2

Characterization: Linking Synthesis, Microstructure, and Properties
Moderator: C. Scheu, University of Munich, P. Schaaf, TU Ilmenau, Institut für Werkstofftechnik, F. Giuliani, Imperial College London

1:30pm **TS4-2-3 Application of LEIS Static and Sputter Depth Profiling as a Novel Approach for Ultra-Thin Film Analysis**, *P. Bruener,* ***T. Grehl*** *(thomas.grehl@iontof.com), R. Moellers,* ION-TOF GmbH, Germany*, N. Havercroft,* ION-TOF USA, Inc.*, H.H. Brongersma, E. Niehuis*, ION-TOF GmbH, Germany

Scaling of ultra-thin films has reached dimensions where traditional analytical approaches start to struggle. Some lack surface sensitivity for separating layers in sputter depth profiling, others suffer from the transient regions at the surface and at interfaces, which are in the same depth range as the thickness of the film itself. The change in sputter rate prevents from establishing an accurate depth scale, while changing sensitivity factors especially in SIMS prevent accurate quantification in these transient regions. Furthermore, a variety of new and complex materials have been introduced such as new gate dielectrics, inducing additional complexity for the quantification.

An emerging technique in this field is high sensitivity high resolution Low Energy Ion Scattering (LEIS). It is the most surface sensitive elemental characterization technique and can provide quantitative information on the first atomic layer. Noble gas ions (He, Ne ...) of low energy (1 - 8 keV) are used as projectiles. The energy of the backscattered ions from elastic collisions depends on the masses of the target atoms and is measured by using electrostatic energy analyzers. In contrast to SIMS, the yields are not affected by the chemical environment. Compared to electron spectroscopic techniques, the surface sensitivity and therefore also the depth resolution are superior.

Ions scattered in deeper layers lose extra energy along the in- and outgoing trajectories. This allows obtaining "non-destructive" depth profiles in the range of 1 - 10 nm ("static mode"). In a dual beam configuration this can be combined with conventional depth profiling using low energy noble gas sputtering ("dynamic mode").

We studied a variety of sample systems by static and dynamic LEIS depth profiling and compared the results with depth profiles acquired by other techniques, especially TOF-SIMS and XPS. The combination of LEIS static and sputter depth profiling allows intrinsic depth scale calibration without using crater depth measurements, and even the continuous measurement of the sputter rate during the profile is possible. This is especially useful for multilayer systems, where the sputter rate changes between the different materials.

In addition we have established quantification procedures for a number of multilayer films that make use of the linear response of LEIS to the elemental concentration, allowing consistent quantification from the first monolayer of the sample with very good depth resolution.

1:50pm **TS4-2-4 Microstructure of Hot Dip Coated Fe-Si Steels***, **I. Infante Danzo** (ivonneeugenia.infantedanzo@ugent.be), K. Verbeken, Y. Houbaert*, Gent University, Belgium

Hot dipping is a coating technique pre-eminently used in industry to galvanize machine parts or steel sheet for constructional applications. However, other hot dipping applications have been developed and have a positive effect on specific material properties. For instance, in Fe-Si electrical steels, a Si/Al rich coating is applied to increase the electrical resistivity of the material and consequently, lower the power losses[1][2]. Hot dipped aluminised mild steels have been developed with increased corrosion resistance for high temperature applications by the formation of a dense Al_2O_3 layer [3]. Regardless of the type of steel coated and the intended application, after the interaction between the molten Al and the solid material, three constituents are formed: Fe_2Al_5, $FeAl_3$ and an Al-rich alloy. The structural morphology, which can negatively affect the wear resistance and the thermal stability [3], also appears to be highly dependent on the chemical composition of the base material [4]. To study thermo-mechanical and compositional effects on the coating behaviour after hot dipping, cold rolling with different reductions was performed in different Fe-Si materials. It was demonstrated that hardness differences between the layers caused crack formation inside the Fe_2Al_5 layer. The present work reports the results obtained on materials that were hot dipped in a hypo-eutectic Al + 1wt.%Si bath. The bath was used to coat Fe-Si steel substrates with variable silicon content with dipping times ranging from 1 to 20 seconds. Before dipping, the samples were heated to 700°C and subsequently immersed in the liquid bath at temperatures of 710°C, 720°C and 740°C. To further evaluate the interactions between Al, Si and Fe, a diffusion annealing treatment at 1000°C was performed. The main diffusing elements during this treatment are Al and Fe, although small variations of the composition are also observed for the alloying element Si. At a certain distance from the surface, voids were observed, which most probably can be related to the Kirkendall effect. A thorough characterization of the formed intermetallics was performed by Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDS) and X-Ray Diffraction (XRD) and Electron backscattered diffraction (EBSD).

References

[1] J. Barros, J. Schneider and Y. Houbaert, JMMM. 320 (2008) 389.

[2] I. Infante Danzo, K. Verbeken and Y. Houbaert, Defec. Diffu. Forum. 297 (2010) 370.

[3] Wei-Jen Cheng and Chaur-Jeng Wang, Surf. Coat. Technol. 204 (2009) 824.

[4] G. Hameed Awan and Faiz ul Hasan, Mater. Sci. Eng. A 472 (2008) 157.

2:10pm **TS4-2-5 High Supercapacitive Stability of ZnO-Added Manganese Oxide Coatings***, **C.-Y. Chen** (chencyi@fcu.edu.tw), H.-W. Chang,* Feng Chia University, Taiwan*, S.-J. Shih,* National Taiwan University of Science and Technology, Taiwan*, R.-B. Yang, C-.K. Lin*, Feng Chia University, Taiwan

Zinc oxide (ZnO) has been recently reported to exhibit electrochemical supercapacitive properties. We demonstrate, for the first time, a nanocrystalline (< 10 nm) composite powder of electrochemical supercapacitor in which ZnO-added manganese oxide was used as active electrode material. The ZnO-added (≤ 10 at.%) manganese oxide powders were prepared from their acetate-based salts by spray pyrolysis (SP) at 500 °C, and subsequently coated onto graphite substrates by electrophoretic deposition (EPD) to be supercapacitor electrodes. XRD data and TEM observation showed that the ZnO-added manganese oxide was identified as tetragonal Mn_3O_4 phase with a nanocrystalline structure. ZnO may dissolve in manganese oxide and inhibit the grain growth of the manganese oxide. The result of cyclic voltammetry indicated that specific capacitance of the manganese oxide coating in 1 M Na_2SO_4 electrolyte increased from 196 F/g to 230 F/g at 25 mV/s for 5 at.% ZnO-added manganese oxide. After activation, the cycling efficiency of the composite electrode was observed to exhibit a high value of > 90% up to 1200 cycles for all the compositions.

2:30pm **TS4-2-6 Spectroscopic Ellipsometry for Thin Film Characterization***, **H. Arwin** (han@ifm.liu.se)*, Linköping University, Sweden **INVITED**

Spectroscopic ellipsometry measures polarization changes due to reflection of a plane wave at a sample surface. These polarization changes carry information about the optical response functions of the sample constituents and the sample structure within the probe depth of the light. The spectral range of instruments commercially available is from the vacuum ultraviolet to the far infrared and expansion into the THz region is expected in the near future. Characterization possibilities include determination of refractive indices, layer thicknesses of single layers and multilayers, composition, anisotropy, chemical structure (IR) and more. From model parameters, it is possible to determine values on derived parameters like resistivity, color coordinates, Hamaker constants, porosity, surface mass density, etc.

Here a brief review of state of the art instrumentation and methodology is presented including discussion about features of standard, generalized as well as Mueller-matrix ellipsometry. Many different configurations can be employed such as ex situ, in situ (vacuum, liquids), imaging and real-time spectroscopy. A very important aspect of ellipsometry is modeling strategies and the use of model optical functions is emphasized.

Specific examples of basic thin film characterization are detailed like determination of thickness and refractive index and how color coordinates (L*a*b* and RGB) are derived (niobium oxide on niobium is used as an example). In a second example real-time spectral studies of optical properties of thin films of cellulose and swelling due to humidity are presented. Analysis of non-ideal effects like roughness, grading and thickness nonuniformities are addressed. Modern software includes possibilities to model not only permittivity using ellipsometric data but also permeability and gyrotropic effects, i.e. a full 6x6 constitutive matrix. Such effects can be found in metamaterials and analysis of artificial magnetism in nanosandwiches is presented. Finally some recent studies of complex chiral nanostructures in scarab beetles are used to exemplify the potential of Mueller-matrix ellipsometry.

3:10pm **TS4-2-8 *In Situ*, Elevated Temperature Micro-Compression of Silicon***, **J.M. Wheeler** (Jeffrey.Wheeler@empa.ch), R. Ghisleni, J. Michler*, Empa, Switzerland

The rapid miniaturisation of semiconductor components for microprocessors is the most successful example of nanotechnology. Fabrication of these structures increasingly requires knowledge of the nano-micromechanical behaviour of semiconductor materials. *In situ*, micro-pillar compression via an instrumented nanoindentation system installed within an SEM can allow direct observation into the deformation mechanisms of these materials.

Technical information will be presented on the modifications made to an *in situ* nanoindentation system for testing at elevated temperatures within an SEM. Thermal drift is managed by a combination of precision thermometry and resistance heating of both tip and sample. Procedures for the calibration of the tip temperature via Raman spectroscopy and precision thermocouple measurements will be discussed.

It has been observed that materials can undergo a brittle-ductile transition with increasing temperature [1]. A brittle-ductile transition has also been observed *in situ* in silicon micro-pillars at room temperature with pillar diameters of less than ~350nm yielding in a ductile fashion [2]. In this work, the ductile-brittle transition of silicon micro-pillars has been determined as a function of temperature and length-scale via *in situ*, elevated temperature micro-compression testing.

References

[1] S. Korte and W.J. Clegg, Scripta Mater., **60**, 807-810 (2009).

[2] F. Oestlund et al., Adv. Functional Mat., **19** 2439-2444 (2009).

3:30pm **TS4-2-9 Synthesis and Characterization of Complex Alloy Thin Films***, **A.M. Pagon** (arwen.pagon@rmit.edu.au), E.D. Doyle, D.G. McCulloch, K. Latham,* Royal Melbourne Institute of Technology University, Australia*, J.E. Bradby*, Australian National University

There has been considerable interest in the vapor deposition of metallic thin films in order to improve surface properties [1-4]. In addition, the reactive vapor deposition of multi element or more complex alloys such as austenitic stainless steel was recently reported [5-7]. This work showed that a range of interesting and novel phases can be synthesized. More recently, Pagon et al. [8] reported on the effect of deposition energy on the microstructure and mechanical properties of high speed steel (HSS) films prepared using a filtered cathodic vacuum arc. It was observed that the microstructure was critically dependent on the deposition energy. These previous works showed that it is possible to synthesis a wide range of microstructures in complex alloy thin films, which in turn, can lead to the development of a wide range of properties. Indeed, Leyland and Matthews [9] proposed the concept of exploiting predominantly metallic thin films with a nanograined and/or glassy microstructure for tribological applications where toughness in combination with hardness is required. The present study explores this concept further by investigating the effect of deposition energy and temperature on the evolution of microstructure and properties of reactively (with nitrogen gas) deposited HSS and stainless steel films using a filtered cathodic vacuum arc. The deposited films were characterized in terms of their stoichiometry using x-ray photoelectron spectroscopy, cross-sectional microstructure using transmission electron microscopy, crystal structure using x-ray diffraction and hardness using nanoindentation. These results will be discussed in terms of the evolution of microstructure and the effect on properties.

References

[1] I.I. Beilis, A. Shnaiderman, R.L. Boxman, Surf. Coat. Technol., 203 (5-7) (2008) 501-504.

[2] B.A. Movchan, Demchish.Av, Physics of Metals and Metallography-Ussr, 28 (4) (1969) 83-&.

[3] C. Li, S. Shang, P. Yang, L. Zhang, L. Qi, International Journal of Materials and Structural Integrity, 4 (1) 25-34.

[4] R.E. van de Leest, Corrosion Science, 29 (5) (1989) 507-515.

[5] S.R. Kappaganthu, Y. Sun, J. Cryst. Growth, 267 (2004) 385-393.

[6] S.R. Kappaganthu, Y. Sun, Appl. Phys. A: Mater. Sci. Process., 81 (2005) 737-744.

[7] S.R. Kappaganthu, Y. Sun, Surf. Coat. Technol., 198 (1-3) (2005) 59-63.

[8] A.M. Pagon, J.G. Partridge, P. Hubbard, M.B. Taylor, D.G. McCulloch, E.D. Doyle, K. Latham, J.E. Bradby, K.B. Borisenko, G. Li, Surf. Coat. Technol., 204 (21-22) (2010) 3552-3558.

[9] A. Leyland, A. Matthews, Surf. Coat. Technol., 177-178 (2004) 317-324.

3:50pm **TS4-2-11 Atomic-Scale Understanding of the Thermal Stability of 6H-SiC(0001): An *In Situ Scanning Tunneling Microscopy Study***, *Y. Murata,* University of California at Los Angels*, V. Petrova, I. Petrov,* University of Illinois at Urbana-Champaign*, **S. Kodambaka** (kodambaka@ucla.edu)*, University of California at Los Angels

SiC belongs to the special class of ultra-high temperature ceramics that are widely used in structural components such as airframe leading edges and reentry space vehicles due to their ultra-high melting temperatures, excellent high temperature strength, and oxidation resistance. Design and development of new refractory materials with improved properties for these applications requires a detailed atomic-scale understanding of the processes controlling high-temperature thermal and chemical stabilities of these materials. As a first step, we choose SiC(0001) as a model system and investigated its thermal stability in ultra-high vacuum environment.

Using high-temperature (~1400 K), UHV scanning tunneling microscopy (STM), we investigated the thermal stability of single-crystalline SiC(0001). We observe the formation of monolayer and bilayer graphene due to preferential evaporation of Si from the surface. STM images acquired as a function of annealing time indicate that graphene nucleates at the SiC surface step edges and grows inward at the expense of the SiC terraces. From the STM images, we measured time-dependent variation of areal coverages of SiC terraces and graphene. We find that the rate of disappearance of SiC is 3.15 × higher than the rate of growth of graphene. That is, for every layer of graphene formed, 3.15 layers of SiC are consumed. This result is consistent with the expected number of carbon atoms within each SiC layer. Our results provide atomic-scale insights into the factors influencing the thermal stability of SiC surfaces.

4:10pm **TS4-2-12 Swift Heavy Ion Induced Modifications of Nanostructured Ni-Mn-Sn Ferromagnetic Shape Memory Alloy Thin Films***,* ***R. Vishnoi****, R. Singhal,* ***D. Kaur*** *(dkaurfph@iitr.ernet.in)*, Indian Institute of Technology Roorkee, India

In recent years ferromagnetic shape memory alloys (FSMAs) have attracted increasing attention due to their large magnetic field induced strain and the possibility of using these materials as actuators and sensors. The martensitic transformation temperature in these alloys is an important parameter to enhance their applicability. Martensitic transformation temperature can be altered by irradiating thin films of FSMA using high energy heavy ions. In the present study, thin films of Ni-Mn-Sn ferromagnetic shape memory alloy were deposited on Si (100) substrate at substrate temperature of 400°C by DC magnetron sputtering using target prepared by solid state reaction of Ni, Mn and Sn powders. These films were irradiated by 200 MeV Ag ions at different fluences ranging from 1 x 10^{12} to 1 x 10^{14} ions/cm^2. X-ray diffraction (XRD) patterns at room temperature confirm the austenite phase $L2_1$ crystal structure of the as deposited films. Temperature dependent magnetization measurements reveal that the martensitic transition temperature varies with fluence. Four probe R-T measurements also support the variation of martensitic transformation temperature with fluence as obtained by temperature dependent magnetization data. Atomic force microscopy and scanning electron microscopy were used to observe the surface morphology of irradiated films at different fluences.

Energetic Materials and Micro-Structures for Nanomanufacturing
Room: Sunrise - Session TS5

Energetic Materials and Micro-Structures for Nanomanufacturing
Moderator: C. Rebholz, University of Cyprus, C.C. Doumanidis, University of Massachusetts Lowell, T. Ando, Northeastern University

1:30pm **TS5-1 Self-Propagating High Temperature Synthesis of B2-RuAl Thin Films***,* ***K. Woll*** *(k.woll@mx.uni-saarland.de), F. Mücklich*, Saarland University, Germany

Due to its favorable combination of properties the B2 intermetallic RuAl is superior to many other B2 aluminides. It combines an extraordinary high melting point of 2333 K, a high heat of formation and an unusual high room temperature toughness compared to other intermetallics. This property profile makes that intermetallic compound interesting for high as well as room temperature thin film applications. Among the room temperature applications, nanometric Ru/Al multilayers are very promising as a new kind of energetic material system. Typical applications may be e.g. the future use for reactive bonding purposes. These applications take advantage of the released exothermic reaction heat of a self-propagating reaction in a metallic multilayer. Hence, the fundamental understanding of self-propagating reactions in Ru/Al multilayers which are characterized by reaction front velocities up to several m/s is essential. High-speed methods are used to measure e.g. reaction velocities, temperatures as well as phase transformations in Ru/Al multilayers. Ignition thresholds are determined. Based on these results a reaction mechanism for the self-propagating reaction in Ru/Al multilayers to RuAl is proposed. Microstructural analysis of the final RuAl thin films is presented. Lastly, the findings for RuAl are compared to similar systems to discuss the potential of RuAl in the mentioned applications.

1:50pm **TS5-2 Effects of Environment on the Self-Propagating Synthesis of Reactive Multilayers Fabricated by Sputter Deposition***,* ***D.P. Adams*** *(dpadams@sandia.gov), J.P. McDonald, E.D. Jones, Jr., M.A. Rodriguez*, Sandia National Laboratories

Vapor-deposited, metal-metal multilayers are an ideal class of materials for systematic, detailed investigations of reactive material properties. Created in a pristine vacuum environment by sputter deposition, these high-purity materials have uniform reactant layer thicknesses between 1 and 1000 nm, minimal void density and intimate contact between layers. These key compositional and geometrical characteristics generally lead to reproducible reaction behaviors.

With this presentation, we describe the effects of test environment on the self-propagating synthesis of sputter-deposited, equiatomic Ni/Ti and Sc/Cu multilayers. By conducting reactions in air and at different vacuum pressures, we evaluate how surrounding gaseous environment affects (i) the propagating reaction wave dynamics and (ii) the final phase formation of these different multilayers. First, we show that the surrounding environment can affect the average propagation speed of a reactive multilayer with increased speeds observed at atmospheric pressure. For Ni/Ti multilayers the differences in speed manifest in the nucleation rate of transverse reaction bands that originate at the edge of specimens. For Sc/Cu we show evidence of a second propagating oxidation wave that trails the intermetallic reaction front when tested in air. High-speed microscopy demonstrates how this second oxidation wave can interfere with the intermetallic reaction front giving rise to a new form of oscillatory combustion. Reactions in air yield a mixture of intermetallic compounds and metal oxide for both Ni/Ti and Sc/Cu. As indicated by X-ray diffraction Ni/Ti multilayers reacted in air show evidence of both rutile and anatase forms of TiO_2 along with various Ni_xTi_y phases. Scandium/copper multilayers form Sc_2O_3 in addition to ScCu and $ScCu_2$ when reacted in air. Reaction of Ni/Ti and Sc/Cu in vacuum (1 mTorr) leads to the formation of intermetallic compounds with no evidence of crystalline oxide phases.

2:10pm **TS5-3 Rapid Formation Reactions in Nanolayered Foils and Particles: Scientific Studies and Commercial Applications***,* ***T.P. Weihs*** *(weihs@jhu.edu)*, Johns Hopkins University **INVITED**

Over the last 15 years we have investigated exothermic formation reactions that self-propagate in multilayer foils where the nanoscale layers alternate between materials with negative heats of mixing. These exothermic reactions can reach temperatures as high as 3000°C and can travel at velocities greater than 30 m/s. One common example of such a foil includes alternating layers of Ni and Al. With a pulse of electrical current at one end of the foil, ohmic heating provides sufficient thermal energy to initiate atomic diffusion between the Ni and Al layers and the formation of Ni-Al compounds, which then leads to energy release and propagation of the reaction away from the point of ignition. More recently we have developed similar reactions in microscale particles with nanoscale layers.

Using a combination of ignition experiments, velocity and temperature measurements, continuum modeling and molecular dynamic simulations we have identified many of the physical parameters that control ignition and the propagation of the reactions. We have also used *in situ* X-ray diffraction and *in situ* DTEM experiments to identify the phase transformations that appear in these foils under very rapid (~10^6 K/sec) heating conditions.

In addition to these scientific studies, we have also developed commercial applications for these reactive nanomaterials. In the most common example, the foils act as local heat sources that melt solder layers and bond two components without thermal damage. The lack of global heating has proven particularly beneficial when bonding temperature sensitive devices such as CPUs and LEDs. This presentation begins with a review of commercial applications for reactive foils and particles and then focuses on results from the scientific studies.

2:50pm **TS5-5 The Effect of Interface Quality on Self Propagating Exothermic Reactions (SPER) in Ni-Al Multilayer Foils**, ***K. Fadenberger*** *(konrad@ucy.ac.cy), I.E. Gunduz,* University of Cyprus*, F. Nahif,* RWTH Aachen University*, K.P. Giannakopoulos,* National Center for Scientific Research "Demokritos", Greece*, B. Schmitt,* Paul Scherrer Institut, Germany*, J.M. Schneider,* RWTH Aachen University, Germany*, P.H. Mayrhofer,* University of Leoben, Austria*, C.C. Doumanidis, C. Rebholz*, University of Cyprus

Reactive nanoscale multilayer foils represent a relatively new class of materials which have recently received considerable attention for use in joining applications. Other possible applications include targeted heat sources for micro scale manufacturing processes, biomedical applications, micro actuators and energy sources for autonomous micro devices. However, due to the fast reaction rates in these foils (between 1 and ~ 20 m/s for the Ni/Al system, depending on the individual bilayer thickness), much of the understanding of the reactions is derived from comparing before and after states of the samples. Only very recently different methods for analysis during reaction such as Dynamic Transmission Electron Microscopy (DTEM) [1] or fast X-Ray Diffraction (XRD) [2] have become available.

Here, we present a method for measuring the core temperature of multilayer foils during reaction based on lattice parameter measurements by fast high resolution *in-situ* XRD. Ni(V)/Al and Ni/Al multilayer foils have been analyzed using this method, allowing the identification of reaction stages during SPER on nanoscale structures, as well as Energy Filtered Transmission Electron Microscopy (EFTEM) Scanning Electron Microscopy (SEM), Electron Energy Loss Spectroscopy (EELS) and Differential Scanning Calorimetry (DSC). The results highlight the influence of intermixing and deposition parameters on the reaction kinetics, dictating the flame front velocity. Furthermore, it is shown that foils with different amounts of intermixing can reach the adiabatic formation temperature of B2-NiAl. These experimental results are important for further validation of numerical models regarding temperature and structure development in Ni–Al multilayer foils, as well as other metallic reactive systems. The new method significantly expands the characterization possibilities in this field.

[1] J. S. Kim, T. LaGrange, B. W. Reed, M. L. Taheri, M. R. Armstrong, W. E. King, N. D. Browning and G. H. Campbell, Science (2008) 321: 1472

[2] J. C. Trenkle, L. J. Koerner, M. W. Tate, S. M. Gruner, T. P. Weihs and T. C. Hufnagel, Appl. Phys. Lett. 93, 081903 (2008)

3:10pm **TS5-6 Streak Spectrograph Temperature Analysis from Electrically Forced Multilayered Ni/Al Formation Reactions**, ***C.J. Morris*** *(christopher.morris17@us.army.mil),* U.S. Army Research Laboratory*, P. Wilkins, C. May,* Lawrence Livermore National Laboratory*, E. Zakar,* U.S. Army Research Laboratory*, T.P. Weihs*, Johns Hopkins University

The nickel-aluminum (Ni/Al) intermetallic system is useful for a variety of reactive material applications, including the initiation of subsequent reactions, thermal batteries, and the localized heating required by many welding and joining applications. Reaction characteristics are well studied at the normal self-heating rates of 10^3–10^6 K/s. We recently reported on new experiments where we electrically heated patterned Ni/Al bridges at 10^{11}–10^{12} K/s, effectively forcing the reaction to occur at much higher rates. Such studies are important for future nanomanufacturing techniques, where it may be necessary to control spatial thermal distributions much more precisely by careful control of the timescales over which these reactions take place.

Here we report on rapid Ni/Al reactions observed by streak camera spectroscopy, with an optical resolution of 2.0 nm resolved temporally over 350 ns. We measured non-reactive Ni, Al, and reactive Ni/Al samples, and each exhibited both similar and distinct spectroscopic features. For example, both Al and Ni/Al samples produced peaks associated with atomic Al at 396 nm. However, peaks were not present at expected wavelengths for ionic Al, suggesting that Al atoms retained their electrons long enough to participate in intermetallic reactions with Ni. In separate experiments probing the kinetic energy of material ejected from the reaction zone, we measured a 10% increase in kinetic energy over non-reactive control samples, with the magnitude of this increase being equivalent to the energy expected from a Ni/Al reaction.

All samples exhibited an initial period of nearly broadband emission, with superimposed spectral peaks which grew more intense at later times. This emission was especially obvious in reactive Ni/Al samples, persisting much longer and at higher intensities than either the Al-only or Ni-only samples. By comparing this broadband emission to expected blackbody radiation curves given by Plank's Law, we deduced temperature values which peaked at 8180 K for Ni/Al and at 5230 K for Al, and which decayed initially with similar characteristic time constants of 198 and 175 ns, respectively. These higher Ni/Al temperatures validate our past measurements of increased kinetic energies.

The final paper will include temperatures calculated from other spectroscopic methods, as well as predicted temperatures based on measured electrical power delivered to each sample. These additions will help validate the significant result that Ni/Al formation reactions can proceed at much higher rates, leading to a variety of new reactive material applications.

3:30pm **TS5-8 Fully-Dense Reactive Nanocomposite Powders and their Reaction Mechanisms**, ***E.L. Dreizin*** *(dreizin@njit.edu)*, New Jersey Institute of Technology **INVITED**

This talk will present research efforts at NJ Institute of Technology aimed to develop new reactive materials for various applications. Specifically, a broad range of reactive nanocomposite powders is prepared using Arrested Reactive Milling, a ball-milling technique customized for work with material components capable of highly exothermic chemical reaction. Starting materials are mixed and ball milled with or without process control agents and the milling is interrupted just before the chemical reaction can be triggered mechanically. Produced powders typically comprise micron-sized particles with relatively broad particle size distribution while each particle has nanocomposite structure. Typically, a more ductile material component (such as Al for thermite compositions) forms a matrix while the second, more brittle material is contained as inclusions. The inclusion sizes vary from 10 to 1000 nm. The reactivity of such materials is defined by the interface area between the inclusions and matrix. Because of versatility of mechanical milling as a materials processing technique, there is practically no limitations on the compositions that can be prepared; the materials prepared to date include thermite (metal - metal oxide systems), metal-metalloid, and metal-metal composites. In addition to binary materials, more complex ternary compositions are also prepared.

Characterization of the new materials relies on a number of experimental methods, from thermo-analytical measurements, electron microscopy, and x-ray diffraction to custom ignition and combustion measurements for powder clouds and individual particles. The work focused on quantitative description of the thermal initiation mechanisms and reactions responsible for ignition of new materials at different heating rates. The role of oxidation reactions as well as various phase changes occurring in the prepared materials upon their heating is explored and will be discussed.

4:10pm **TS5-10 Ignitable Al/Ni Compacts Produced by Mechanical Alloying: Structural, Chemical and Thermal Characterization**, ***A. Hadjiafxenti*** *(hadjiafxenti.anastasia@ucy.ac.cy), I.E. Gunduz,* University of Cyprus*, S.M. Aouadi,* Southern Illinois University, Carbondale*, T. Kyratsi, C.C. Doumanidis, C. Rebholz*, University of Cyprus

Nanoscale materials that exhibit Self-Propagating Exothermic Reactions (SPER) are promising energy sources for thermal manufacturing, owing to their ability to provide intense localized heat. These materials are mainly manufactured in the form of bimetallic multilayer foils using magnetron sputtering. One alternative processing route is mechanical alloying in the form of ball milling (BM), in which powder mixtures are subjected to repeated plastic deformation. The idea is to generate lamellar structures within the powders to imitate sputtered multilayers, which have faster reaction rates owing to the high contact area between reactants. Although mechanical alloying has been carried out to produce materials with superior high-temperature mechanical properties, very little has been reported on synthesized powder mixtures that exhibit SPER. Most studies concentrate on reactions during processing, instead of external ignition of the milled powders to study the exothermic reactions and evaluate the heat released.

In this work, we show that BM is an alternative viable method for the generation of micro and nanoscale heat sources for thermal manufacturing. Al and Ni powders with a molar ratio of 1:3 were ball milled for different time durations in order to synthesize powder mixtures, which were then compacted into pellets and subsequently ignited using an external heat source. In order to evaluate the microstructure after powder mixing, Scanning- and Back Scatter Electron Microscopy images were studied, while X-Ray Diffraction analysis indicated potential formation of intermetallic phases during milling that may hinder ignition. Additionally, thermal evolution of ignited powder consolidates and the propagation speed of the heat wave-front were studied using high speed and infrared cameras. Finally, Differential Scanning Calorimetry analysis was used to characterize the thermal stability of the compacts.

Results revealed that after 7 h of interrupted and 3 h of continuous BM an aluminum/nickel lamellar structure forms at the particle boundaries for the selected parameters. The characteristic lamella dimension reduces with increasing milling time down to approximately 200 nm after 10 h and 4 h of interrupted and continuous BM, respectively. The ignition conditions for compacts of milled powders indicate that samples with a higher volume fraction of the lamellae possess the shortest ignition time.

4:30pm **TS5-7 Large-Scale Simulations of Nanoscale Ni/Al Multilayer Foils**, ***I.E. Gunduz*** *(emreth@yahoo.com), K. Fadenberger, M. Kokonou, C. Rebholz, C.C. Doumanidis*, University of Cyprus

Nanoscale multilayers (MF) of Ni/Al binary metallic system exhibit self-propagating exothermic reactions (SPER) due to the high formation enthalpy of the intermetallic compounds Ni2Al3, NiAl, Ni3Al. SPER in these MFs are receiving attention as heat sources due to their potential for joining temperature sensitive components such as microelectronics and amorphous metals, bulk synthesis and near-net in-situ forming of intermetallic parts. The high energy/weight ratio of this system makes it attractive as an energy source for micro-mesoscale robotics and self autonomous devices.

Previous modeling approaches on the reactions of this system rely on the use of a phenomenological diffusion coefficient representing NiAl growth, coupled with enthalpy or thermal fields. Recent work suggests that the reaction kinetics can be represented more satisfactorily with the sequential growth of Ni2Al3 followed by NiAl using the corresponding independently obtained diffusivities.

The paper presents simulation results from a new model that keeps track of not only temperatures, but also the phase information at each computation node over the whole MF geometry, which enables the investigation of heat loss effects, ignition characteristics and transient and final microstructures. The computational efficiency is improved by using a bimodal grid distribution in the radial direction in 3D cylindrical coordinates. This makes it possible to perform full scale simulations for large domains with a reasonable computational cost, which can be used to design heater elements.

Exhibitor Key Note Session
Room: Tiki Pavilion - Session A1

Exhibitor Keynote Session

8:00am **A1-1 Reactive Modulated Pulse Power Magnetron Sputtering**, ***W.D. Sproul*** *(bsproul@cox.net),* Reactive Sputtering, Inc., *J. Lin, J.J. Moore*, Colorado School of Mines

There are many reports of reactive sputtering using high power pulse magnetron sputtering (HPPMS). Films such as aluminum oxide, titanium dioxide, and chromium nitride have been successfully deposited. Depending on the deposition condition, hysteresis effects have been observed whereas in other cases they have not been observed. Helmersson and co-workers at Linköping University have shown that they can reactively deposit aluminum oxide using the HPPMS process without any hysteresis effects, whereas Audronis and co-workers at Gencoa Ltd. have observed hysteresis effect during the reactive HPPMS deposition of titanium dioxide films. Modulated pulse power (MPP), which is an alternative form of HPPMS, has also been used for the reactive deposition of aluminum oxide, aluminum nitride, and chromium nitride (both CrN and Cr_2N) coatings. In all of the work reported to date for MPP reactively deposited coatings, only flow control of the reactive gas has been used, and there have been no reports about hysteresis effects. In the current study, the reactive deposition of different coatings using MPP power has been performed, and the reactive plasmas have been characterized to determine ion mass and ion energy distributions. These characterizations show that there is a high degree of ionization of the reactive gas along with the sputtered species. The structure and selected properties of the deposited coatings have been characterized, and a correlation between the plasma properties and the structure and properties of the coatings will be presented.

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

PVD Coatings and Technologies
Moderator: P. Eklund, Linköping University, J. Vetter, Sulzer Metaplas GmbH, J.-H. Huang, National Tsing Hua University

8:00am **B1-1-1 Magnetron Sputtering, Past, Present and Future.**, ***V. Bellido-Gonzalez*** *(victor@gencoa.com), D. Monaghan, M. Audronis*, Gencoa Ltd, UK **INVITED**

Magnetron sputtering is a mature and well establish PVD deposition technique. Since the introduction of commercial planar magnetrons in the 1970s there are few vacuum coating sectors that haven't been touched by successful implementations of this deposition technique. In the 1970s the semiconductor industry was revolutinonized by the introduction of planar magnetron sputtering as an alternative to evaporation and diode sputtering. Even today more than a quarter of a century later, magnetron sputtering is at the heart of many of the advances in the new wave of the semiconductor revolution. In commercial terms we have seen very strong performances of magnetron sputtering technology in sectors like glass, web, thermal solar, photovoltaic thin film, display and decorative coatings., This presentation will give a historic overview of magnetron sputtering with its main breakthroughs, the current status of the technology in important PVD coating sectors and will look at the current and future challenges ahead.

8:40am **B1-1-3 Capability of Gas Flow Sputtering to Coat Non Line of Sight Areas**, ***S. Tang*** *(stanley.tang@dlr.de), U. Schulz*, German Aerospace Center, Germany

Physical vapour deposition techniques (PVD) such as magnetron sputtering and electron-beam vapour deposition operate in high vacuum. The mean free path of the sputtered or evaporated atoms is much larger than the source to substrate distance. The atoms arrive nearly without collision at the substrate. As a result, only areas are coated which are in line of sight to the deposition source. In contrast to these PVD techniques gas flow sputtering (GFS) is know for its capability to coat non line of sight areas (NLOS) without substrate manipulation. Atoms are sputtered from a hollow cathode by glow discharge. A high inert gas flow streams through the cathode and provides transportation of sputtered material to the substrate. The mixture of inert gas and sputtered atoms performs a circulation around the contour of the geometry and reaches NLOS areas. Coating thickness distribution depends on fluid dynamics.

In this investigation a basic understanding for the observed thickness distributions and a model for the mass transport was generated. Stripes, cylinders and turbine blades were coated with pure titanium. Thickness distributions and microstructure were examined by scanning electron microscopy. Some coating procedures were simulated by computational fluid dynamics to understand the correlation between gas flow and coating thickness distribution.

All substrates, especially their non line of sight areas, were completely covered with a coating. The coating thickness is inhomogeneously distributed along the substrate contour. This observation can be explained by the successfully adapted mass transport model. In general, the particles diffuse perpendicularly to the main flow direction out of the gas flow. Due to the wall friction, a boundary layer is formed near the substrate surface and increases in the downstream direction. The deposition rate and the coating thickness respectively decrease with increasing boundary layer thickness. This model and the gas flow simulation enable predicting and optimizing the coating thickness distribution for any kind of complex substrate geometry.

9:00am **B1-1-4 Influence of Inert Gas Species on Plasma Characteristics and Film Growth in a Magnetron Discharge**, ***G.T. West*** *(g.west@mmu.ac.uk), P. Kelly*, Manchester Metropolitan University, UK

Argon is the process gas of choice for most magnetron sputtering applications due to its large atomic mass, inert chemistry, and relatively low cost. Other inert gases are available for use in sputtering deposition that have varying mass and hence different momentum behaviour during ion bombardment of solid surfaces - affecting sputter yield, particle implantation and incorporation of process gas into deposited films. The plasma discharges generated from these gases vary in terms of the nature and energy of species incident at both target and substrate. In particular, the contribution from energetic neutrals varies as a consequence of the atomic mass of the process gas in comparison to the target material to be sputtered.

Magnetron plasma discharges were generated from neon, argon, krypton and xenon gases in DC and mid-frequency pulsed-DC modes with different transition metal cathode materials. The electrical characteristics, such as potential and current at the cathode, substrate and in the plasma bulk were measured and compared. Thin metallic films were then deposited and analysed in terms of structure, properties and process gas incorporation. The data generated is used to establish the relationship between process gas species, plasma discharge characteristics of those gases, and the subsequent growth and properties of deposited coatings.

9:20am **B1-1-5 Large Area EB-PVD and Plasma Activated EB Evaporation - Status and Prospects**, ***E. Reinhold*** *(reinhold.ekkehart@vonardenne.biz), J. Faber*, VON ARDENNE Anlagentechnik GmbH, Germany **INVITED**

Electron beam physical vapor deposition (EB-PVD) is an industrially well established large area PVD technology. Highly productive air-to-air coaters for metal strip, roll-to-roll coaters for plastic web or thin metal foils as well as inline carrier coaters for substrates or lots of substrates have been introduced into industrial production. Axial type high power EB guns having a nominal power of several 100 kW at 60 kV are available as technological key components in order to generate high vapor densities.

Great efforts have been made to combine high rate EB-PVD with plasma generation processes in order to activate the generated vapor. The industrial break through can be expected in the near future especially as result of current developments in the field of spotless arc activated deposition.

The paper presents solutions for long term stable processes meeting the demands of various applications. New customized coater concepts and prospective progress in technological details will be discussed. A forecast regarding challenges to be solved will be given.

10:00am **B1-1-7 High Power Discharge-Based EB Sources for PVD and Vacuum Metallurgy – PIC Simulation and Experimental Results**, ***P. Feinaeugle*** *(peter.feinaeugle@fep.fraunhofer.de), G. Mattausch, F.-H. Roegner*, Fraunhofer-Institut fur Elektronenstrahl- und Plasmatechnik (FEP), Germany

Electron beams are excellent tools for vacuum coating as well as for materials melting and refining purposes.

EB technology provides high power densities, fast and precise control of the beam spot combined with energy efficiency, and low contamination affinity.

High-voltage glow-discharge (HVGD)-based EB sources represent a compact and cost-efficient yet versatile variant of beam generation technologies. In the past, they have been used in fields as different as CRT or pumping of gas lasers for a long time. The high discharge voltage, compared to ordinary glow discharges, results in new effects, most importantly in runaway-electrons carrying the major part of the discharge power. Recently, significant progress has been achieved in understanding the underlying mechanisms of the discharge and of the beam generation as well as in enhancing the stability of operation by advanced technical means. This made it possible to design high-power cold-cathode EB guns of axial type capable of producing beam currents up to 15 A at accelerating voltages up to 45 kV and of focusing these beams into spots of 20 mm or less. These features brought applications such as PVD and vacuum metallurgy into the reach of cold-cathode EB technology.

Computer simulation appeared to be an important tool for gaining insight into the physics of high voltage glow discharges and for optimizing practical beam sources. Conventional ray-tracing codes can neither consider space charge effects of multiple species nor particle generation or loss by stochastic collisions despite these effects are essential in HVGD-based beam sources. Particle-in-cell (PIC) codes previously developed for simulating kinetic effects in plasma physics, however, proved to be able of correctly modeling HVGD. Congruence of the predictions of the simulation and of the experimental findings supports the plausibility of the numeric results. Additionally, new regimes of the HVGD might be able to overcome disadvantages of established designs. First experiences and explanations will be presented.

10:20am **B1-1-10 Modification of PVD TiN Coatings by Interrupting Film Growth**, ***T. Sinkovits***, *Y. Zhao (yue@uow.edu.au), D. Saini,* University of Wollongong, Australia, *S.J. Dowey*, Surface Technology Coatings Pty, Australia

TiN was deposited on tungsten carbide (WC) cutting inserts and high speed steel (HSS) test drills using the Innova deposition system from Oerlikon Balzers. The process was modified to interrupt film growth during deposition. The new coating was contrasted with an existing standard TiN coating architecture.

Microhardness of both TiN coatings was measured using a UMIS2000 microhardness tester. A significant increase in hardness was observed. The modified coating displayed a 25% increase in median values of hardness and Young's modulus when compared with the current TiN coating.

Coating performance was then compared by drill testing on a Haas vertical machining centre (VMC) using coated HSS test drills. Coatings were further analysed with scanning electron microscopy (SEM). Fracture cross-sections of the new coating revealed no distinct multilayer structure but continuous grain growth was observed. Transmission electron microscopy (TEM) of focussed ion beam (FIB) cross-sections revealed detailed grain features of the coating.

Glancing angle X-ray diffraction (XRD) was used to identify the coating phase structure across its thickness and showed fcc TiN with a predominant (111) orientation. Residual stress analysis was undertaken on a PANalytical X'Pert Pro materials research diffractometer (MRD), utilising the psi-tilt method and compared with standard TiN coatings. Additionally the X'Pert Pro MRD was used to examine the phase evolution of both TiN coatings at high temperatures.

10:40am **B1-1-11 Thick Nanocrystalline AlCr(Si)N/TiN Hardcoatings Deposited by DC Arc Evaporation**, ***F. Kaulfuss*** *(frank.kaulfuss@iws.fraunhofer.de),* Fraunhofer IWS, Germany, *C. Endter, P. Bogutzki, W. Siebert,* Dresden University of Technology, Germany, *O. Zimmer*, Fraunhofer-Institut für Werkstoff- und Strahltechnik IWS Dresden, Germany

The DC arc evaporation is a widely used PVD process for the thin film deposition, especially for wear protection. The used hard coatings extend the lifetime of machining tools and improve their performances. The film thickness is mostly limited to a few micrometers. But thicker films up to 50 micrometer and more are most desirable for many applications. The deposition of these films is challenging. They often show high level of intrinsic stress, which might end up in a total delamination of the film. On the other hand the sharp cutting edges of the machining tools become blunter with increasing film thickness. During the deposition more and more defects are growing. This leads to an increase of the roughness and a decrease of the film hardness.

Most of these problems could be solved by using a AlCr(Si)N/TiN nanolayered film on cemented carbide substrates. The single layer thickness is in the range of 20 nm with fluent interfaces which results in a nanocrystalline structure. The deposition process is very stable and deposition rates from 15 to 20 micrometer per hour with rotating substrates could be obtained. Very thick films (up to 50 microns) with a low level of intrinsic stress were deposited by using adapted process parameters. It could be shown, that a film thickness distribution on complexly shaped substrates and the suppression of film defects can be well controlled by process guiding.

The hardness measurements by nano-indentation show only a small decrease with increasing film thickness. Hardness values of 30 – 33 GPa at 5 µm thick films were obtained in comparison to 29 – 31 GPa at 50 µm thick films.

11:00am **B1-1-12 Study of CrN and NbC Interlayers for HFCVD Diamond Deposition onto WC-Co Substrates**, ***M. Fenker*** *(fenker@fem-online.de), K. Petrikowski,* FEM Research Institute, Germany, *J. Gäbler, S. Pleger, L. Schäfer*, Fraunhofer IST, Braunschweig, Germany

Chromium nitride (CrN) and niobium carbide (NbC) films were deposited by magnetron sputtering on Co-cemented tungsten carbide (WC–Co) substrates and diamond deposition was performed by using Hot-Filament Chemical Vapor Deposition (HFCVD) technique. The CrN and NbC interlayers have been deposited at different substrate temperatures (T_S = 400, 550 and 700°C). The stability of these interlayers for diamond deposition has been studied by a heat treatment in H_2 atmosphere for 60 h at a temperature of 765°C in the HFCVD reactor. X-Ray Diffraction (XRD), scanning electron microscopy (SEM) and glow discharge optical emission spectroscopy (GDOES) confirmed that due to this heat treatment the CrN films transformed into porous films composed of CrN_x, Cr_3C_2-, Cr_7C_3- und Co phases, accompanied by a dramatic loss of nitrogen which is replaced by carbon. It was observed that higher nitrogen contents in the CrN films reduce the Co diffusion through the CrN layer. For NbC films, deposited by non-reactive magnetron sputtering from an NbC compound target, the heat treatment in the HFCVD reactor revealed that the films are absolutely stable during the heat treatment with some relaxation of residual stresses up to a factor of 2. However, Co diffusion through the NbC films with a T_S-dependent accumulation on the NbC film surface was found. Stripping of NbC films from the WC-Co substrate in a commercial solution was possible, but after this treatment some edge outbreaks on the substrates were also visible. By HFCVD it was possible to deposit adherent diamond coatings on the CrN and NbC interlayers. However, a reasonable adhesion of diamond on NbC was only obtained after different pre-treatments of the WC-Co substrates. The adhesion seems to be mainly governed by the topography of the WC-Co substrates and not by a possible Co diffusion through the NbC interlayer.

11:20am **B1-1-9 Microstructure and Mechanical Properties of Hard Ceramic Coatings Deposited by Arc Plasma Acceleration Process**, ***V.N. Khominich*** *(vkhominich@phygen.com), D.C. Bell,* Phygen Coatings Inc, *N. Schwarzer,* Saxonian Institute of Surface Mechanics, Germany, *G. Favaro*, CSM Instruments, Switzerland

Intensity of ion bombardment plays a crucial role in coating structure development which in turn to a great extend defines resulting mechanical properties and coating performance in practical applications. Arc plasma acceleration process provides a potential for increased intensity of bombardment by low energy ions under controlled conditions to stimulate nano-crystalline growth, grain boundary adhesion, densification of coating structure and exceptional coating performance. Structural features of CrN and AlCrN films deposited by the arc plasma acceleration process were examined by using scanning electron microscopy and XRD. Instrumented nano-indentation technique was employed for true coating Young's modulus and yield strength measurements. This was achieved by new sophisticated analyzing technique taking the layered system structure fully into account. Physical scratch behavior and mixed load resistance were studied with a variety of different indenter geometries.

Hard Coatings and Vapor Deposition Technology
Room: Golden West - Session B4-3

Properties and Characterization of Hard Coatings and Surfaces

Moderator: M. Fenker, FEM Research Institute, B. Zhao, Exxon Mobil

8:00am **B4-3-2 Layer Structure and Interface Effects on Corrosion Behavior of Multilayer CrN/NiP Composite Coatings**, ***Y.-Y. Li***, *F.-B. Wu (fbwu@nuu.edu.tw)*, National United University, Taiwan

The Chromium Nitride/Nickel-Phosphorus (CrN/NiP) multilayer coatings were prepared on 420 stainless steels with a dual-gun magnetron sputtering system. The multilayer coating exhibited an alternating CrN/NiP configuration with a bilayer period from 10 to 500 nm and a total thickness of 1 µm. The layer-structure, morphology, interface and corrosion behavior of the CrN/NiP multilayer coatings were discussed. The microstructure evolution of the CrN/NiP multilayer coatings under various process temperatures was also considered. The NiP layer tended to be amorphous/nanocrystalline under lower deposition temperature at 450°C. The phase transformation and NiP precipitation were observed at 550°C according to the phase identification results. The composite coatings with NiP and CrN nanolayered configuration showed a superior corrosion resistance as compared to those with thicker bilayer periods. The corrosion mechanisms and related behaviors of the multilayer coatings were compared through AC impedance and equivalent electrical circuit results in the frequency range from 0.1 to 10 kHz. Through potentiodynamic scanning analysis, the improved corrosion resistance due to nanolayered feature was evident. The effects of the microstructure and interface on the corrosion resistance of the coatings were discussed.

8:20am **B4-3-3 In Situ Structural Characterization of TM-Si-N and TM-B-N Coatings During Air Oxidation**, ***J.-F. Pierson*** *(Jean-Francois.Pierson@mines.inpl-nancy.fr), A. Mège-Revil, D. Pilloud*, Ecole des Mines de Nancy, France **INVITED**

The addition of a third element in transition metal nitride coatings is widely used to improve their properties: high hardness is obtained by addition of silicon or boron and these elements also increase the high temperature oxidation resistance. Since machining technique evolution, i.e. high speed machining, imposes coatings protection to be more and more efficient, TM-Si-N and TM-B-N films are used to coat cutting tools operating in severe conditions. However, the literature is mainly focused on the characterization of such films at room temperature after an annealing step at high temperature. Although this procedure is the most convenient, it brings information about the films properties that may differ from those required for high temperature applications. This presentation is focused on the *in situ* structural characterization of TM-Si-N and TM-B-N coatings during air oxidation using XRD, Raman and FTIR methods.

Nb-Si-N and Fe-Si-N films were deposited on stainless steel and silicon substrates by reactive magnetron co-sputtering of elemental targets, while Cr-B-N films were synthesised by reactive magnetron sputtering of composite Cr/B targets with various compositions.

The characterization at room temperature of oxidized Nb-Si-N clearly highlights the formation of a niobium oxide top layer on the remaining Nb-Si-N films. On the other hand, *in situ* XRD analyses shows that the NbN diffraction peak intensity decreases while no diffraction peak of niobium oxide are observed, indicating that the low temperature NbN oxidation induces the formation of amorphous niobium oxide. The crystallization of the oxide top layer occurs at 525°C. A further increase of the annealing temperature induces the grain growth of the Nb_2O_5 phase but the coalescence step occurs at higher temperatures for higher values of silicon content. Concerning Fe-Si-N films, in situ XRD analyzes clearly highlight a progressive denitridation of the FeN grains and this phase is fully reduced in Fe_2N at 425°C. Then, hematite diffraction peaks are noticed at 450°C. This decomposition-oxidation mechanism is confirmed by *in situ* Raman analyses.

Since B-N and B-O bonds are evidenced by FTIR, this method is employed to characterize by *in situ* measurements the oxidation mechanism of films containing boron. Thin Cr-B-N films with high boron and nitrogen content exhibit at room temperature absorption bands of amorphous boron nitride phase. Their intensity decreases during air oxidation due to the formation of boron oxide. However, the intensity of the boron oxide bands decreases as a function of time due to the sublimation of this phase as confirmed by *ex situ* SIMS measurements.

9:00am **B4-3-5 Monitoring of Pitting Formation and Growth in TiN Film Deposited by Arc PVD Method as a Function of Time with Polarization Resistance and EIS**, ***I.K. KÜÇÜK***, Cumhuriyet University, Turkey, *C.S. Sarioglu (cevat.sarioglu@marmara.edu.tr)*, Marmara University, Turkey

The investigation concerned the corrosion behaviour of droplet and growth defects in PVD TiN coatings formed by cathodic arc physical vapour deposition (CAPVD) process on 4034 stainless steel. These coatings contain structural defects such as pores, pinholes, cracks and droplets. Thus, the substrate is not completely isolated from the corrosive environment. These growth defects in the coatings are detrimental to corrosion resistance of the coatings used in severe corrosion environments. In this study, the monitoring of pitting formation was studied in 3% (wt) NaCI solution using electrochemical techniques (polarization resistance and electrochemical impedance spectroscopy) as a function of time up to 24 hours. Coatings characteristics for instance, surface, defects and cross sections were examined by means of stereo optical microscopy, scanning electron microscopy (SEM) and EDS before and after corrosion. It was observed that the corrosion begins on the indicated droplet region during the corrosion tests and the results of electrochemical tests was closed the observations. Besides, EDS results pointed out that the corrosion region includes wastes of the corrosion after the tests. On the basis of the experimental findings and the pitting formation theory, the mechanisms of the growth pitting-related coating/substrate corrosion are finally proposed.

9:20am **B4-3-6 Microstructure and Mechanical Properties Evaluation of Pulsed DC Magnetron Sputtered Cr-B and Cr-B-N Films**, *C.-H. Cheng,* Tungnan University, Taiwan, *J.-W. Lee (jefflee@mail.mcut.edu.tw),* Mingchi University of Technology, Taiwan, *J.-C. Huang,* Tungnan University, Taiwan, *H.-W. Chen, Y.-C. Chan,* ***J.-G. Duh***, National Tsing Hua University, Taiwan

The pure CrB_2 and three Cr–B–N films with various nitrogen contents were deposited by a bipolar asymmetric pulsed DC reactive magnetron sputtering system. The structures of thin films were characterized by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS), respectively. The surface and cross sectional morphologies of thin films were examined by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The surface roughness of thin films was explored by atomic force microscopy (AFM). A nanoindenter, a scratch tester and pin-on-disk wear tests were used to evaluate the hardness, adhesion and tribological properties of thin films, respectively.

The phases of Cr-B-N coating transferred from CrB_2 into CrN and BN as the nitrogen content increased. It was found that a high hardness value was observed on the pure CrB_2 coating. The hardness and elastic modulus of Cr-B-N thin films decreased with increasing nitrogen content. The influences of nitrogen concentration on the mechanical and tribological properties of thin films were discussed.

9:40am **B4-3-8 Atomic and Electronic Structural Studies of Metal Nitrides (VN, CrN)/ MgO Interface by C_S-Corrected TEM**, ***Z. Zhang*** *(zaoli.zhang@oeaw.ac.at), B. Rashkova,* Austrian Academy of Sciences, Austria, *G. Dehm,* Montanuniversität Leoben, Austria, *P. Lazar, J. Redinger,* Vienna University of Technology, Austria, *R. Podloucky*, University of Vienna, Austria

Using aberration-corrected high resolution transmission electron microscopy (HRTEM), electron energy loss spectroscopy (EELS), and *ab-initio* density functional theory (DFT) the interface microstructures of VN (CrN)/MgO (001) are closely examined. By HRTEM, under the conditions of negative spherical aberration we show an atomic resolution structure of epitaxially grown VN (CrN) film on MgO with a clearly resolved oxygen and nitrogen sublattice across the interface. As revealed by DFT calculation, the (002) interplanar spacing oscillates in the first several VN layers across the interface. Quantitative EELS analysis across the interface was carried out. Interfacial chemistry determined by EELS analysis shows the preponderance of O and V atom at the interface of VN/MgO, and V-$L_{2,3}$ and O-K edges at the VN/MgO interface obtained by ELNES and the spatial difference analysis show slightly discrepancy from the bulk, a small detectable core-level shift as compared to the bulk. The fine structures of Cr-$L_{2,3}$ and O-K edges across the CrN/MgO interface were also revealed.

10:00am **B4-3-11 The Mechanical Properties of Ti-Si-N Nanocomposite Films Deposited by Magnetron Sputtering**, *W.-R. Chen,* ***G.-P. Yu****, J.-H. Huang (jhhuang@mx.nthu.edu.tw)*, National Tsing Hua University, Taiwan

Ti-Si-N is a newly developed superhard coating material. The common issue for the hard coating is the delamination due to high residual stress, especially as the coating thickness is larger than 1 µm. However, for the industrial application to deposit a superhard coating with a thickness larger than 1 µm is usually required. In addition, since the delamination is mostly caused by high residual stress, the measurement of residual stress on the Ti-Si-N coating is also important for understanding the adhesion issue. In this study, Ti-Si-N films were deposited on P-type (100) Si wafers using unbalanced magnetron sputtering (UBMS) at different deposition durations. The purposes of this study were to investigate the mechanical properties of Ti-Si-N films with different thickness, especially the hardness and residual stress, and to prepare Ti-Si-N films with high hardness and large thickness suitable for industrial applications. To study the intrinsic properties of the coating, no interlayer or buffer layer was inserted between the Ti-Si-N coating and Si substrate. The thickness of the thin films increased with increasing deposition time ranging from 281 to 2044 nm. The structure of the nanocomposite coatings characterized by X-ray diffraction (XRD) showed that the crystalline phase was TiN with (200) or (111) preferred orientation depending on thickness. The results of X-ray photoelectron spectroscopy (XPS) indicated the existence of Si_3N_4 bonding in the nanocomposites. Therefore, the Ti-Si-N films were TiN/SiN_x nanocomposite. Nanocomposite specimen with a good combination of hardness and thickness was obtained, where the hardness was 37 GPa with a thickness of 2 µm. Optical laser curvature method and XRD $\cos^2\alpha\sin^2\psi$ method were used to measure the average residual stress and stress of the

TiN phase in the nanocomposites, respectively. The results indicated that the amorphous SiN_x in the TiN/SiN_x nanocomposite could significantly relieve the average residual stress ranging from 19 to 68%. The degree of stress relief increased with increasing film thickness, which may be the reason that the thickness of nanocomposite can reach 2 μm. The critical stress of film delamination for each specimen can be estimated from fracture mechanics, and the stress decreased as film thickness increased.

10:20am **B4-3-12 Mechanical Properties of TaN-Cu Nanocomposite Thin Films After Multiple Annealing**, ***J.-H. Hsieh*** *(jhhsieh@mail.mcutedu.tw), Y.-J. Lin,* Ming Chi University of Technology, Taiwan, *S.I. Chang*, National Chung Hsing University, Taiwan

This study aims at understanding the structures, morphologies, and mechanical properties of TaN-Cu nanocomposite thin films after multiple aging and annealing. These films were deposited by reactive co-sputtering on Si and tool steel substrates. The films were then annealed using RTA (Rapid Thermal Annealing) at 400°C to induce the nucleation and growth of Cu particles in TaN matrix and on film surface. Cu nano-particles emerged on the surface of TaN-Cu thin films were then removed after the samples were tested for their structural and mechancial behaviors. The samples were then re-annealed (rejuvenated), and re-tested for their properties. This process was repeated for four times to investigate the annealing effect. The results reveal that the Cu particles would re-appear on film surface after each annealing cycle. The particle size appears to be smaller with the increase of the number of annealing cycles. The hardness of the samples would decrease gradually with the repeated annealing. This appears to be due to the increased porosity in the films. The wear rate and friction coefficient of these repeatedly annealed samples depends mainly on the formation of lubricious Cu films, not on the hardness values.

10:40am **B4-3-9 Investigation of Fundamental Deformation Parameters of Magnetron Sputtered TiAlN Films using High Temperature Nanoindentation from 300 K to 623 K**, ***M. Werchota***, Montanuniversität Leoben, Austria, *P.H. Mayrhofer (paul.mayrhofer@unileoben.ac.at)*, University of Leoben, Austria

Titanium aluminum nitride (TiAlN) films are one of the most common hard ceramic coatings in use today. Often out of lack of adequate measuring techniques, the characteristics of hard ceramic films are investigated at room temperature or after heat treatment. Although this approach is sometimes useful, it is sensible to test at temperatures, where dislocation activity is more significant. Using high temperature nanoindentation the typical hardness (H) and Young modulus (E) measurements were extended to calculate the fundamental deformation parameters, such as activation volumes (V*) and total activation energies (ΔG_{tot}).

Near-to epitaxial TiAlN films were grown on MgO single crystals (110) using a reactive magnetron sputtering system. The following chemical compositions were investigated: cubic(c)-$Ti_{0.44}Al_{0.\Delta56}N$, c-$Ti_{0.68}Al_{0.32}N$ and wurtzite(w)-$Ti_{0.36}Al_{0.64}N$. Additionally c-$Ti_{0.44}Al_{0.56}N$ was annealed at 600C for 24 hours. High temperature nanoindentation experiments were carried out in a temperature range from 298 to 673K at 3 loading rates of 0.5, 1 and 10 mN/s.

H values of the all cubic samples were stable in the measured temperature range, with a slight decrease at 673K. H for the wurtzite sample on the other hand decreased continuously from 19.8±0.9 GPa at 298K to 16.9±1.4 GPa at 673K. E values for all samples remained constant throughout the temperature range: 344 GPa±34 for $Ti_{0.68}Al_{0.32}N$, 336 GPa±23 for as-deposited- $Ti_{0.44}Al_{0.56}N$, 356 GPa±21 for annealed- $Ti_{0.44}Al_{0.56}N$ and 219 GPa±11 for w-$Ti_{0.36}Al_{0.64}N$. H of the films was found to be strain rate sensitive at all temperatures, leading to a percentual increase of up to 20% for the cubic films.

Fundamental deformation parameters were furthermore calculated. V* values ranged from 0.05-0.2 (burgers vectors)^3 (b^3) and 0.4-1.2 b^3 for cubic and wurtzite sample respectively. ΔG_{tot} for cubic samples were very close and ranged from 5.1-5.8 .10^{-3} μb^3. ΔG_{tot} values rose linearly with the temperate, whereby the mechanical work negligibly influenced the calculated values.

Summing up for the tested temperature range the crystallographic structure had the most notable influence on all parameters. The rate-controlling mechanism was determined to be lattice-resistance for the cubic films, as V* values were smaller than 1b^3 and ΔG_{tot} values of very low order. For wurtzite films a dislocation-dislocation interaction mechanism is assumed.

This investigation proved that high temperature nanoindentation can be used, to extract fundamental deformation parameters and to conclude, which rate-controlling deformation mechanism is taking place.

Fundamentals and Technology of Multifunctional Thin Films: Towards Optoelectronic Device Applications
Room: Sunset - Session C2/F4-2

Thin Films for Photovoltaics and Active Devices: Synthesis and Characterization
Moderator: T. Miyata, Kanazawa Institute of Technology, A.P. Ehiasarian, Sheffield Hallam University

8:00am **C2/F4-2-1 Influence of Sputtering Powers on the Characteristics of ZnO:B Thin Films**, *L.-H. Wong,* ***Y.-S. Lai*** *(yslai@nuu.edu.tw),* National United University, Taiwan, *D.-S. Wuu,* National Chung Hsing University, Taiwan, *J.-L. Wang*, Ming Chi University of Technology, Taiwan

ZnO:B thin films are deposited using ZnO-B_2O_3 (3 wt%) sputtering targets at rf powers ranging from 80 W to 180 W. It is found that the deposition rate and crystallinity increase with increasing rf powers. From θ-2θ XRD, it is found that the (002) diffraction peak shifts to low 2θ angle as the rf power increases. The transmittances of ZnO:B thin films are around 90% in the visible light region. The optical bandgap of ZnO:B thin film increases as the rf power increases. The ZnO:B films deposited at rf power of 180 W exhibit good electrical properties with resistivity of 4.46×10^{-3} Ωcm, carrier concentration of 1.15×10^{21} cm^{-3}, and carrier mobility of 15.03 cm^2/Vs, respectively.

8:20am **C2/F4-2-2 High Mobility Transparent Conducting Oxides: A Modulation Doping Approach**, ***S.H.N. Lim*** *(sunnielim@lbl.gov), R.J. Mendelsberg, A. Anders, K.M. Yu*, Lawrence Berkeley National Laboratory

Transparent conducting oxides (TCOs) are playing an important role in today's opto-electronic devices. However in recent years, there has been an increasing demand for high mobility TCO to satisfy the need of next generation technologies such as solar cells and low emissivity windows coating. The carrier mobilities of conventional single material metal oxides are physically limited by various scattering mechanisms. While most of these scattering events can be overcome by careful tailoring of the microstructure, the main limitation in the mobility of TCO is due to ionized impurity scattering. This scattering arises when charge carriers are deflected by the electrostatic field associated with the dopants.

In this presentation, we will describe the major scattering mechanisms governing the electron transport relevant to TCOs. We will introduce a technique of modulation doping which involves a multilayer thin film system which can overcome the limitations of ionized impurities scattering. We will present experimental results from electrical characterization and microstructure studies from TEM of modulation doping based on ZnO deposited by pulsed filtered cathodic arc deposition.

8:40am **C2/F4-2-3 Dominant Factors Determining Moisture Resistance of Highly Transparent Conductive Ga-Doped ZnO Films**, ***Y. Sato*** *(sato.yasushi@kochi-tech.ac.jp), T. Yamada, H. Makino, N. Yamamoto, T. Yamamoto*, Kochi University of Technology, Japan

Ga-doped ZnO (GZO) films have attracted attention for use in window layers of solar cells and transparent electrodes of liquid crystal display panels. We investigated the dominant factors determining moisture resistance of GZO films. GZO films with different Ga contents (1.5, 3.0 and 4.0 wt.%) were deposited on glass substrates at 200 °C by ion-plating deposition using dc-arc discharge.[1-3] To control the factors determining resistivity of the films; carrier density and Hall mobility, oxygen gas flow rate (fO_2) was changed in the range of 6 to 30 SCCM. The resistivity of 3.0 wt.% GZO films with a carrier density of 5.8×10^{20} cm^{-3} and Hall mobility of 31 $cm^2V^{-1}s^{-1}$ was 3.4×10^{-4} Ωcm and changed by less than 3% over a 500 h reliability test at a temperature of 60 °C and a relative humidity of 95%. Optical transmittance in the wave length from 450 to 1200 nm of the sample was above 80% . The resistivity of all the samples changed by less than 25% confirmed by the reliability test described above. On the basis of the analysis of the data obtained by Hall effect measurements, we concluded that the dominant factors determining moisture resistance of GZO films is carrier density, The maximum carrier density, n_{max}, needed for moisture resistant GZO films within the change of less than 10% is 7×10^{20} cm^{-3}. The resistivity of GZO films with a carrier density of 1.1×10^{21} cm^{-3} larger than n_{max} changes by about 20%. We will further discuss the difference in the contribution to the moisture resistant properties between extrinsic defects, Ga at Zn site, and intrinsic defects including Zn interstitial and oxygen vacancy.

This work was supported by New Energy and Industrial Technology Development Organization (NEDO) under the National Project of Rare Metal Indium In Substitute Materials Development.

[1] T. Yamada et al., *Appl. Phys. Lett.* 91, 051915 (2007)

[2] T. Yamada et al., *J. Appl. Phys.* 107, 123534 (2010)

[3] N. Yamamoto et al., *J. Electrochem. Soc.* 157, J13 (2010)

9:00am **C2/F4-2-4 Changes in Electrical and Optical Properties of Polycrystalline Ga-Doped ZnO Thin Films Due to Thermal Desorption of Zinc**, ***H. Makino*** *(makino.hisao@kochi-tech.ac.jp), Y. Sato, N. Yamamoto, T. Yamamoto*, Kochi University of Technology, Japan

Ga-doped ZnO (GZO) film is one of promising candidate as ITO substitute materials for transparent electrodes in optoelectronic applications, such as, flat panel displays and solar cells. In this paper, we studied changes in electrical and optical properties of transparent conductive GZO films due to thermal desorption of zinc. 150 nm thick GZO films were deposited on glass substrates by an ion-plating with DC-arc discharge at substrate temperature of 120°C. Resistivity of the as-deposited GZO film was 2.5 $x10^{-4}$ Wcm with carrier concentration of 1.2 x 10^{21} cm^{-3} and Hall mobility of 20 cm^2/Vs. Desorption of Zn from the GZO films was characterized by thermal desorption analysis (TDA). Amounts of desorbed Zn were evaluated by integral intensity of the TDA signals. In order to control amounts of desorbed Zn, the TDA measurements were interrupted at several temperatures. Although the resistivity showed little change after the TDA measurements, carrier concentration decreased and Hall mobility increased with increasing the interrupted temperature. It was found that the change in carrier concentration showed good correlation with the Zn desorption. The decrease in carrier concentration linearly increased with increasing the amount of desorbed Zn. It is suggested that the decrease in carrier concentration is due to desorption of interstitial zinc acting as native donors in ZnO. Optical absorption spectra showed a fundamental optical gap in ultra violet region and a free-carrier absorption in the mid-infrared region. In addition, we observed an optical absorption band in visible wavelength region due to some defects. After the TDA measurements, the intensity of optical absorption band linearly decreased with increasing the amount of desorbed Zn. It was suggested that the optical absorption band is most probably due to some Zn-related defects in the GZO films.

9:20am **C2/F4-2-6 Bending Properties of Transparent Conductive Ga-doped ZnO Films**, ***K. Nagamoto*** *(k-nagamoto@post.lintec.co.jp), K. Kato, S. Naganawa, T. Kondo,* LINTEC Corporation, Japan*, Y. Sato, H. Makino, N. Yamamoto, T. Yamamoto*, Kochi University of Technology, Japan

Transparent conductive oxides (TCO) on polymer substrates are prospected as a key material for next-generation devices such as flexible displays and photovoltaics. The advantages of polymer substrates include light-weight, low cost, a multiplicity of materials with tailored properties, shock absorption and highly flexibility. However, polymer substrates also have disadvantages such as low heat resistance and large thermal expansion coefficient compared with glass substrates. A main challenge for an efficient TCO on polymer substrate is not only to choose conductive oxide materials having capability of growing at low substrate temperature, but also to develop a deposition processes in order to obtain good electrical characteristics. Thus, in this study, we developed a multiple-deposition method to achieve deposit TCO on polymer substrates with lower than 100°C. The influences of process temperature on structural and electrical characteristics of 100 nm thickness Ga-doped ZnO (GZO) film on polymer substrates were investigated. In addition, the effects of bending strains on the characteristics were also discussed.

The structural, electrical, optical and bending properties of highly transparent conductive polycrystalline GZO films deposited on polyester substrates at various temperatures of less than 100 °C by ion plating with dc-arc discharge were investigated. We developed a multiple-deposition method to achieve controllable different polyester substrate temperatures. Analysis of data obtained from XRD measurements and cross-sectional SEM images show that polycrystalline GZO films with wurtzite structure exhibit highly (0002) orientation perpendicular to the substrate. The resistivity and average transmittance in the visible wavelength region of GZO films on polyester substrates were 5.0 x 10^{-4} ohm-cm and more than 80 %, respectively.

The mechanical bending properties of the GZO films were investigated on the basis of analysis of data obtained by comparing sheet resistance between before and after a bending test. The bending test was carried out for the GZO films deposited at various process temperatures. The GZO films deposited at lower substrate temperatures exhibit improved bending performance.

We have demonstrated that our multiple-deposition method to achieve controllable different polyester substrate temperatures works very well to control the bending properties of GZO films.

The financial support from the Japan Science and Technology Agency is gratefully acknowledged

9:40am **C2/F4-2-7 H-Bonded Effects and Properties of Novel Supramolecular Nanocomposites Containing Aryl-Imidazo-Phenanthroline -Based Metallo- Polymer H-Donors and Surface-Modified ZnO Nanoparticle H-Acceptors**, ***H.-P. Fang****, H.-C. Lin (linhc@cc.nctu.edu.tw)*, National Chiao Tung University, Taiwan

Abstract:

Four novel metallo-polymers (**P1**-**P4** as proton donors) were synthesized to study for the H-bonded effects on their nanocomposites to blend with pyridyl ZnO nanoparticles (**ZnOpy** as proton acceptors). In order to investigate the nanocomposites containing metallo-polymers **P1**-**P4** and surface-modified **ZnOpy** nanoparticles, nanocomposites **P3/ZnOpy** and **P4/ZnOpy** were characterized by Fourier transform infrared (**FT-IR**), X-ray diffraction (**XRD**), and Transmission electron microscopy (**TEM**) analyses. In the XRD measurements, the introduction of surface-modified **ZnOpy** nanoparticles to metallo-polymers **P3**-**P4** has induced higher crystallinities in their nanocomposites **P3/ZnOpy** and **P4/ZnOpy**. In the TEM studies, due to H-bonds formed between metallo-polymer **P3** and **ZnOpy** nanoparticles, **ZnOpy** nanoparticles were more homogeneously dispersed in metallo-polymer **P3**, which was not well dispersed in nanocomposite **P1/ZnOpy** (without H-bonds). Finally, it suggested that these nanocomposites might become useful materials for future photovoltaic applications.

10:00am **C2/F4-2-8 Non-vacuum Process of ZnO Thin Films Grown by Spray Pyrolysis Technique**, ***K. Yoshino*** *(t0b114u@cc.miyazaki-u.ac.jp),* University of Miyazaki, Japan*, Y. Takemoto, M. Shinmiya, M. Oshima,* University fof Miyazaki, Japan*, K. Toyoda, K. Inaba, K. Haga, K. Tokudome*, Tosoh-finechem Co. Ltd., Japan

Transparent conductive oxide (TCO) materials have attracted much attention for use in liquid crystal displays and photovoltaic devices. In particular, Sn-doped In_2O_3 (ITO) is known as a good transparent conductive oxide material. Recently, ZnO has also been studied as a TCO material because material (Zn) cost is very low in comparison to that of ITO (In). ZnO has shown promise for many applications including gas sensors, transport electrodes, piezoelectric devices, varistors and surface acoustic wave devices. Its direct optical band gap of 3.4 eV at room temperature is wide enough to transmit most of the useful solar radiation in ZnO/$CuInSe_2$ based solar cells. Furthermore, ZnO is a good candidate to substitute for ITO (In-doped In_2O_3) and FTO (F-doped SnO_2) in transparent conductive electrodes. Many techniques have been employed to produce the ZnO thin films including molecular beam epitaxy, metal organic chemical vapour deposition, radio frequency magnetron sputtering, spray pyrolysis and sol-gel methods.

Non-vacuum processes such as spray and sol-gel method are effective for thin film growth because damage to the surface due to plasma is avoided, high vacuum is not required, and equipment costs are low. Furthermore, low temperature growth of ZnO is important for compatibility with photovoltaic device fabrication processes.

In this work, undoped ZnO films on glass substrates were grown by a spray pyrolysis method at room temperature (RT, ~ 300˚C). Polycrystalline ZnO thin films were successfully grown at RT under an air atmosphere. Diethylzinc (DEZ) was used as the Zn source material. The DEZ solution was diluted by some solvent in order to use safely under an air atmosphere. X-ray diffraction indicates that (10-10) and (10-11) peaks are dominant. The lattice constants of the *a* and *c* axes are larger than that of ICDD data. The samples develop a *c* axis (0002) orientation with increasing substrate temperature. Furthermore, the lattice constants of the *a* and *c* axes become closer to those of ICDD data with increasing substrate temperatures.

10:20am **C2/F4-2-9 Electrical Conductivity Enhancement of Nb-Doped TiO_2 Sputtered Thin Films by a Post Hot-Wire Annealing in a H_2 Atmosphere**, ***C.J. Tavares*** *(ctavares@fisica.uminho.pt), M.V. Castro, P. Alpuim, E.S. Marins, A.S. Samantilleke, S. Ferdov, M. Benelmekki,* University of Minho, Portugal*, E. Xuriguera*, Universitat de Barcelona, Spain

In this work Nb-doped TiO_2 thin films were deposited by dc-pulsed reactive magnetron sputtering from a composite Ti:Nb target, using oxygen as reactive gas. In order to optimise the electrical conductivity of the as-deposited thin films, these were subsequently heat-treated by atomic hydrogen at 500ºC. The hydrogen flow was generated by a hot-wire filament, inside a high-vacuum CVD reactor, at a temperature of 1750ºC. The hydrogen pressure was varied between 10 and 500 mTorr, for different annealing times. A 2-orders of magnitude increase in conductivity was typically observed for optimised hydrogen treatments. Dark conductivity (σ_{dk}) and its activation energy were measured as a function of (inverse) temperature and the value of σ_{dk} at room temperature was used to assess the effect of the H_2 annealing on the transport properties. Carrier mobility and resistivity were also investigated using Hall effect measurements. Correlations between structural and electrical properties and the hydrogen

treatment conditions are discussed. The purpose of these coatings is to provide a transparent and conductive front contact layer for a-Si based photovoltaics, with a refractive index that better matches that of single and tandem solar cell structures.

10:40am **C2/F4-2-10 Structural and Electrical Properties of Sol-Gel Derived Yttrium Oxide Dielectric Films**, ***C.-Y. Tsay*** *(cytsay@fcu.edu.tw), C.-H. Cheng,* Feng Chia University, Taiwan*, Y.-W. Wang,* National Changhua University of Education, Taiwan*, C.-J. Chang, C-.K. Lin*, Feng Chia University, Taiwan

Metal oxide films are utilized as the gate dielectrics for ZnO-based thin film transistors (TFTs) can improve the characteristics of those devices. In this study, transparent dielectric films of yttrium oxide (Y_2O_3) were deposited onto alkali-free glass substrates (NEG OA-10) by a sol-gel spin coating process . The authors report on the effect of annealing temperature on the microstructural, optical and electrical properties of sol-gel derived Y_2O_3 dielectric films. Each as-coated film was preheated at 300ºC for 10 min, and then annealed at a temperature rage from 400 to 550ºC for 1 h under air ambiance. XRD results revealed that annealed Y_2O_3 films were polycrystalline with a cubic structure, exhibited preferential orientation along the (222) plane, and the crystallinity level of Y_2O_3 films enhanced with annealing temperature increased. Those as-coated films annealed at temperature above 450ºC had high optical transparency with average transmittance over 88.0% in the wavelength region of 400-1000 nm. Moreover, chemical compositions of sol-gel derived Y_2O_3 dielectric films were examined. The metal-insulator-metal (MIM) capacitor structure, $Al/Y_2O_3/ITO$/glass, were fabricated for examining film's electrical properties, namely dielectric constant, leakage current, and breakdown field, that were evaluated by capacitance-voltage (C-V) and current-voltage (I-V) measurements.

11:00am **C2/F4-2-11 Preparation, Synthesis Techniques and Some Properties on CdMnS Diluted Magnetic Semiconductor Thin Films**, ***J. Dargad*** *(jsdargad@rediffmail.com)*, Dayanand Science College, India

Highly oriented $Cd_{1-x}Mn_xS$ thin films were deposited onto the glass substrates by a chemical growth process. During deposition concentration of Mn^{2+} ($0 \leq x \leq 0.5$) was varied between 0 to 0.5. Layer thickness measurement, electrical and optical properties of these films were examined. Absorption spectra were used to investigate the optical band gap of $Cd_{1-x}Mn_xS$ films. An increase in the band gap of CdMnS films from that of the bulk CdS with increasing concentration of Mn^{2+} has been observed (2.34eV to 2.8eV). The growth mechanism and reaction kinetics have been suggested and discussed for these films. Chemical composition of the films was analysed by an EDS technique. The analysis showed that Mn^{2+} replaces Cd^{2+} from the lattice. No considerable removal of S^{2-} from the CdS lattice has been observed. The surface morphology studies showed polycrystalline nature of the samples and for lower concentration of Mn^{2+} in CdS (up to 0.01 mol %), the films become bit coarser whereas then become diffused and less crystalline at higher concentration of Mn^{2+} in CdS. The room temperature electrical conductivity decreased with an increase in Mn^{2+} concentration in CdS. The XRD studies showed structure of $Cd_{1-x}Mn_xS$ thin film exibits hexagonal wrutzit structure. A phtoelectrochemical cell formed with an active $Cd_{1-x}Mn_xS$ semiconductor photoelectrode and charectarised to determine various cell parameters.

11:20am **C2/F4-2-12 Structural, Electrical and Optical Properties of $AgInTe_2$ Films Grown by a Hot Wall Technique**, ***A. Singh*** *(singh_amarjit3@rediffmail.com), R.K. Bedi*, Guru Nanak dev University, Amritsar, India

Silver indium telluride ($AgInTe_2$) films have been deposited by hot wall technique onto a glass substrate kept at different temperatures in a vacuum of 10-5 torr. Experimental conditions were optimized to obtain better crystallinity in the films. The films so prepared were studied for their structural, electrical and optical properties. X-ray diffraction (XRD) pattern indicate that the prepared films are polycrystalline and are highly oriented in the (111) direction. Scanning electron micrographs (SEM) of the films show an increase in crystallite size with increasing substrate temperature. Observations reveal that the electrical conductivity of films increases with increase in substrate temperature. The band gap of the films was found to be lie in range 1.11- 1.14 eV and 1.64- 1.68 eV, which is due to the fundamental absorption edge and transition originating from crystal field splitting respectively.

Biomedical Coatings
Room: Royal Palm 4-6 - Session D2

Coatings for Biomedical Implants
Moderator: R. Hauert, Empa, J.R. Piascik, RTI International

8:00am **D2-1 Tribological Behavior of DLC Coated CoCrMo Alloys for Medical Joint Applications**, ***R. Hauert*** *(roland.hauert@empa.ch), U. Müller,* Empa, Switzerland*, G. Thorwarth,* Synthes GmbH, Switzerland*, K. Thorwarth, M. Parlinska-Wojtan, C.V. Falub,* Empa, Switzerland*, C. Voisard,* Synthes GmbH, Switzerland*, M. Stiefel*, Empa, Switzerland

In artificial joint replacements, especially in metal-on-metal articulating joints, an increasing number of patients is suffering from unwanted body reactions due to metallic wear debris. Therefore a very low wear coating is aimed at in medical applications. Diamond-like carbon (DLC) coatings have been proven to maintain low friction and low wear for billions of high load loading cycles in many technical applications. Attempts to obtain low wear in vivo by coating the articulating surfaces of artificial joints with DLC failed mostly after several years in vivo.

In an articulating joint simulator, we analyzed the wear behavior of DLC coated CoCrMo implant pairs up to 80 million loading cycles in simulated body fluid. The results indicate that low wear and lifetime performance may be obtained in-vivo, whenever the interfaces and interlayers between the coating and the implant are stable under biological conditions. Especially the only a few nm thick carbidic reaction layer between the DLC and the CoCrMo implant has a crucial influence on long term adhesion. We will show an XPS analysis of the stoichiometry of these reactively formed interfaces. The slow advancement of cracks in this carbidic interface layer was controlled by the laws of stress corrosion cracking, in highly stressed coatings when exposed to a corrosive liquid such as body fluid. We will also present analysis of in-vivo failed DLC coated implants and show that the primary cause of failure was mainly a slow corrosive attack of the interlayers by the body fluid.

8:20am **D2-2 *In Situ* Fabrication of TiN layer on the Nanostructured Surface of Orthopedic NiTi Alloy**, ***T. Hu****, S.L. Wu, J. Jiang,* City University of Hong Kong*, Y. Zhao,* The University of Hong Kong*, C.L. Chu,* Southeast University, China*, P.K. Chu (paul.chu@cityu.edu.hk), K.W.K. Yeung*, City University of Hong Kong

Because of the unique shape memory and super-elastic properties, orthopedic NiTi alloy are promising materials in surgical implants. In order to enhance the safety after surgery, the surface of the NiTi alloy is usually coated with a TiN film to enhance the anti-corrosion properties and biocompatibility. However, the film fabricated on NiTi is relatively thin and normally only about several hundred nanometers thick. The thin coating can deteriorate quite fast due to fretting inside the human body thus causing out-leaching of harmful nickel ions into human tissues. In this paper, we report the fabrication of a nanostructured layer on the surface of the NiTi alloy produced by plasma nitriding at 370°C. The experimental results show that nitrogen diffusion is enhanced significantly during this process and a thick TiN layer can be formed on the surface of the NiTi alloy. The corrosion resistance of the NiTi with the thick TiN layer is significantly improved. *Inductively-coupled plasma mass spectrometry* (ICPMS) reveals that the TiN layer can effectively impede the release of the harmful nickel ions into the simulated physiological solution. *In vitro* biological tests including MTT and cell spreading further disclose good cytocompatibility on the NiTi alloy with the thick TiN layer.

8:40am **D2-3 From DLC to Nanocrystalline Carbon Coating for Biomedical Applications**, ***S. Mitura*** *(stanislaw.mitura@gmail.com), K. Mitura,* Koszalin University of Technology, Poland*, P. Niedzielski, J. Grabarczyk*, Lodz University of Technology, Poland **INVITED**

In recent years there has been a great deal of research in many laboratories worldwide on the properties of carbon layers which have shown their potential usefulness in medicine. Various medical implants are covered by carbon coating which creates a barrier between the implant and the tissue environment. Studied of diamondlike (DLC) films have proved that such films show high biocompatibility. The biocompatibility of DLC is due to their chemical stability, biostability, and appropriate mechanical and adhesive characteristics of the implant/layer system.

However DLC are not specially applicable in the medical implants, with blood contact. DLC are generally thought to be chemically inert but their biological activity has also been reported.

So, better results has been reported with nanocrystalline diamond (NCD) coating. In this paper the results of experimental studies of nanocrystalline diamond coatings obtained by a method of RF plasma CVD are presented.

Nanocrystalline diamond coatings have a thickness of about micrometer and are composed of diamond. They are created from crystallites of the order of few nanometer in size, so they are referred to as nanocrystalline diamond.

They were reported to decrease the level of induced hemolysis and to inhibit lipid peroxidation in blood plasma. NCD Nanocrystalline Diamond Coating (NCD) was found to have positive effects on cells and tissues in the human organism with little adverse reactions. Antiinflammatory action of NCD has been reported.

At present examinations are assigned to acquiring new properties of NCD through their chemical modification which is creating covalent bond with organic moieties. Comparison of different functional groups obtained nanodiamonds depending on their origin causes their different behaviour in biological environment. Therefore examining functional groups of carbon powders coming from technological various processes, also will be recommended of the ones commercially available, next modifying through Fenton treatment, showing changes of functional groups after the reaction and of changes created after the application in the living cell.

9:20am **D2-5 Characterization of Drug Distribution in Model Polymer Films using XPS Sputter Depth Profiling**,
D. Surman *(dsurman@kratos.com),* Kratos Analytical Inc.*, S. Hutton,* Kratos Analytical Ltd., UK*, M. Alexander, A. Rafati*, University of Nottingham, UK

The chemistry of the surface and near surface region is well known to control the biocompatibility of materials intended for in-vitro use. The distribution of the active substance within polymer film coatings of drug eluting stents (DES) has been the focus of considerable research as the controlled release of the drug over extended periods is of great importance in the functioning of the device. This work presents x-ray photoelectron spectroscopy (XPS) concentration depth profiles using a cluster ion source of flat film models of DES devices containing a drug and poly(l-lactic acid) (PLA) spun cast onto cleaned silicon wafers. Samples were initially characterised using spectroscopic ellipsometry and determined to be ~100nm thick. XPS sputter profiling using a coronene ($C_{24}H_{12}^{+}$) primary ion source has provided quantitative elemental distribution as a function of depth through the polymer film whist retaining the chemical information. Results indicate that there is a depletion of codeine from the surface with segregation to the bulk of the sample rather than a uniform distribution of the bulk drug loading for these model systems. Parameters known to affect cluster ion depth profiles of DES model systems, including sample temperature and drug loading within the polymer matrix have been studied.

9:40am **D2-6 Strength and Fracture Behavior of Hydroxyapatite Coatings**,
H.S.T. Ahmed*, A.F. Jankowski (alan.jankowski@ttu.edu)*, Texas Tech University

Biocompatible coatings of hydroxyapatite must provide a strong interface between metal alloy implants and the porous surface overcoats required for successful in-growth of bone and tissue. The composite structure must transfer stress during loading that requires an adherent and robust base coating. In this study, hydroxyapatite coatings are sputter deposited onto titanium-coated silicon wafers for an evaluation of strength across a wide range of strain rates, and for assessing the initiation of fatigue fracture from high cycle loading. Our dynamic test procedures take advantage of a nanoanalyzer cantilever probe with a diamond stylus to initiate nanoscratch testing for measuring the change in hardness of the coating over a wide strain-rate range. The use of high strain rates may well simulate the loading conditions found at the interface between implants and hydroxyapatite coatings. Initial results indicate the hardness, hence strength, of the hydroxyapatite coating appear somewhat strain-rate insensitive. A second use of the nanoanalyzer provides a method for detecting the transition from elastic to plastic behavior. In the tapping mode, the vibrating cantilever probe is used to detect a linear elastic response when the probe tip contacts the surface and then resonates with deflection of the test surface. Plastic flow and material failure occur when the depth of the probe is progressed further into the surface. The high frequency of the tip-surface oscillation provides a new means of measuring fatigue failure through the loading-unloading cycles that accompany the resonant tip-surface displacement. Measurements are discussed for the fatigue crack growth rate that is especially useful to evaluate the longevity of the implant-coated component. This work was supported by the J.W. Wright Endowment for Mechanical Engineering at Texas Tech University.

10:00am **D2-7 Nanomechanical Characterization of Atomic Layer Deposition Coatings for Biomedical Applications**,
N. Bauer *(bauern@onid.orst.edu),* Oregon State University*, M. Wang,* Oregon Health and Science University*, S. Smith,* Oregon State University*, J. Mitchell,* Oregon Health and Science University*, J. Conley, Jr.*, Oregon State University

Atomic Layer Deposition (ALD) is a promising technique for the production of biologically safe, wear resistant and corrosion protective coatings for dental and orthopedic applications. In this work, we investigate the impact of coating thickness and surface preparation on the hardness (H), elastic modulus (E), wear resistance, and delamination of ALD Al_2O_3 films.

Al_2O_3 was deposited via ALD at 300°C using $Al(CH_3)_3$ and H_2O. 200 nm, 600 nm, and 1000 nm thick Al_2O_3 films were coated on polished 305 stainless steel (SS) substrates. Prior to deposition, SS substrates were cleaned using one of three methods: i) sonication in acetone, isopropyl alcohol and deionized water (AID), ii) AID followed by argon plasma treatment, iii) AID followed by oxygen plasma treatment. Nanowear, nanoscratch, and nanoindentation testing were performed using a Hysitron UBI-1 nanomechanical test system. A Berkovich diamond tip was used for nanoindentation testing to calculate the average H and E. A conical diamond tip was used to perform scratch testing in order to determine the delamination force and coefficient of friction values. The same conical diamond tip was also used for wear testing.

Nanoscratch testing and nanowear testing indicates excellent adhesion – Al_2O_3 films do not delaminate even when penetration depth is beyond the film thickness. Nanoindentation results indicate that the H and E of coated substrates are higher than that of the uncoated substrates. In addition, H and E exhibit a trend of modulus and hardness changing from bulk Al_2O_3 values to bulk stainless steel values with increasing penetration depth. Nanowear testing demonstrates that ALD Al_2O_3 films offer effective protection of the SS substrate. Although no distinguishable difference in the wear resistance was observed due to plasma treatment, films of increasing thickness exhibit greater resistance to wear due to reduced coefficient of friction.

In conclusion, we find that ALD exhibits great promise for protective coating of dental and orthopedic devices.

10:20am **D2-8 Ellipsometric Study of Protein Adsorption onto Biocompatible Coatings**,
P. Silva-Bermudez *(suriel21@yahoo.com), S.E. Rodil*, Universidad Nacional Autonoma de Mexico

Nowadays, medical implants are widely used to repair or replace damaged organs or parts of the human body, improving people's quality of life or even preserving life. In order to develop new medical implants and to improve the existing ones, it is necessary to develop novel biomaterials. One strategy to develop new biomaterials is to design the bulk material to fulfill the required properties for the implant's performance and then tailor its surface properties towards biocompatibility by coating it with an adequate thin film.

Whenever a material comes in contact with blood or physiological fluids, as it is upon implantation, a cascade of biological events is triggered; the right development of this cascade of events determines the material's biocompatibility. One of the first biological events to occur is the adsorption of a layer of proteins onto the material's surface. This protein layer mediates the subsequent biological events such as cell adhesion. Cells adhere preferentially to specific proteins in specific conformations; thus, the composition and the conformation of the protein layer is a key factor dictating whether the material is biocompatible or not. Due to the importance of protein adsorption to define the biocompatibility of a material, it is essential to develop a fundamental understanding of protein-surfaces interactions in order to design novel and successful biocompatible coatings. Transition metal oxide thin films can be considered as promising biocompatible coatings, based on the successful biocompatibility displayed by TiO_2 and the good mechanical, corrosion properties and bioinert response displayed by transition metal oxides.

To evaluate sputtered deposited TiO_x, TaO_x, NbO_x and ZrO_x thin films as biocompatible coatings, the *in-situ* adsorption of albumin, fibrinogen and collagen onto these films was studied by ellipsometry. Protein adsorption onto solid surfaces is affected by the physicochemical properties of the surface; therefore the chemical composition (X-ray photoelectron spectroscopy), wettability and surface energy (contact angle) and roughness and thickness (profilometry) of the thin films were characterized in order to identify any possible relation between these properties and the protein adsorption process. The results showed that for each protein, there is different adsorption kinetics depending on the material, clearly observed by the changes in the ellipsometer spectra. Moreover, the surface mass density of the protein layer, calculated from the fitting of the spectroscopic ellipsometer spectra, was observed to increase with both the average roughness (Rq) of the surface and the polar component of the surface energy.

10:40am **D2-9 Large-Scale Synthesis of Hierarchical Titanate Spheres as Cell Interface on Titanium Alloys for Bone Tissue Regeneration**, *S.L. Wu,* City University of Hong Kong, *X.M. LIU,* Hubei University, China, ***K.W.K. Yeung,*** City University of Hong Kong, *Z.F. Di,* Chinese Academy of Sciences (CAS), China, *T. Hu,* City University of Hong Kong, *Z.S. Xu,* Hubei University, China, *J.C.Y. Chung, P.K. Chu (paul.chu@cityu.edu.hk)*, City University of Hong Kong

Hierarchical titanate microspheres assembled by one-dimensional nanosheets grow naturally on titanium plate during a simple hydrothermal process. The effects of this new interface on the adhesion of endothelial and osteoblast cells are investigated systematically in this study. These hierarchical microspheres significantly promote endothelial cell adhesion and proliferation of osteoblasts. In addition, this new surface enables much faster mineralization of the adhered osteoblasts as well as formation of two types of major proteins in the bone matrix, namely osteocalcin (OC) and type I collagen (Col I). Our results show that these hierarchical titanate microspheres not only enhance the cytocompatibility for both endothelial and bone cells, but also support fast functionalization of bone cells. Therefore, the large-scale synthesis of hierarchical titanate microspheres which form a natural bone cell interface on titanium biomedical implants is very promising in clinical applications.

Tribology and Mechanical Behavior of Coatings and Thin Films
Room: California - Session E1-1

Friction and Wear of Coatings: Lubrication, Surface Effects, and Modeling
Moderator: J.C. Sanchez-Lopez, Instituto de Ciencia de Materiales de Sevilla (CSIC-US), R.D. Evans, The Timken Company, S.M. Aouadi, Southern Illinois University, Carbondale

8:00am **E1-1-1 Transition Metal Nitride Based Hard Coatings with Self-Lubricious Properties at Elevated Temperatures**, ***C. Mitterer*** *(christian.mitterer@unileoben.ac.at)*, Montanuniversität Leoben, Austria **INVITED**

Transition metal nitride based hard coatings deposited by plasma-assisted vapor deposition are widely used to reduce friction and wear of tools. Application temperatures may be extremely different ranging from low temperatures for deep drawing dies to above 1000°C for dry-cutting tools. These different loading conditions demand the specific development of coatings to meet the individual requirements of the given application. This contribution presents an overview on self-adaptation mechanisms available to reduce friction and wear in different temperature regimes.

Self-lubrication can be achieved by the in-situ formation of easily shearable tribo-layers on the coating surface in a sliding contact, to accommodate the velocity difference by interfacial sliding. $TiC_{1-x}N_x$ hard coatings have been studied as a model system because they present a time-dependent tribological behavior with an initial running-in period marked by an elevated friction coefficient, followed by a steady-state regime with low-friction and wear at room temperature in ambient air. Tribological tests performed at different relative humidity levels reveal that a minimum value between 15 and 25 % is needed to trigger the low-friction regime. By in-situ observations of tribo-layer film growth it could be observed that third body material is formed during this running-in period by plowing of the coating and shearing of the removed material. The appearance and thickening of the transfer film marks the beginning of the steady-state low-friction regime. At this stage in the tribological test, Raman spectra indicate the presence of C–H bonds in the wear track, being responsible for interfacial sliding and thus friction reduction.

Since humidity-based lubrication mechanisms as explained for $TiC_{1-x}N_x$ and other lubricant phases like diamond-like carbon or MoS_2 fail at elevated temperatures, the so-called Magnéli phase oxides have been studied as potential candidates for self-lubricious tribo-layers effective at high-temperatures. Among these Magnéli phase oxides, V_2O_5 formed in-situ by segregation and oxidation of V in elevated-temperature sliding contacts has been studied intensively for friction reduction due its low melting point of about 650°C, thus acting as low-melting oxide tribo-layer film on the V-depleted coating. This high-temperature lubrication mechanism is demonstrated for out-diffusion and oxidation of V in V-alloyed $Ti_{1-x}Al_xN$ and $Cr_{1-x}Al_xN$ coatings.

In summary, it can be concluded that the in-depth understanding of the coating behavior under particular loading conditions enables to tailor coatings with beneficial self-adaptive tribological properties.

8:40am **E1-1-3 Next Generation Temperature Adaptive Nanocomposite Coatings**, ***D. Stone,*** Southern Illinois University, Carbondale, *T. Smith, C. Muratore, A.A. Voevodin,* Air Force Research Laboratory, *S.M. Aouadi (saouadi@physics.siu.edu)*, Southern Illinois University, Carbondale

Nanocomposite thin films of niobium nitride, tantalum nitride, and vanadium nitride with silver nanoinclusions were created using unbalanced magnetron sputtering to investigate their potential as adaptive, friction reducing coatings. Our hypothesis is that in the low- to mid-temperature range, silver migrates via diffusion to the surface to reduce friction. At higher temperature, oxygen, silver and the transition metals react to form potentially lubricious double oxide phases at the counterface. The coatings were tribotested against Si_3N_4 at different temperatures between 22 and 1000°C while in-situ Raman measurements were performed during heating and wear testing at 750°C to identify the evolution of phases as the coating surface and in the wear track. The chemical and structural properties of the coatings were characterized before and after wear testing using x-ray diffraction and Raman spectroscopy. The post-wear testing investigations revealed the formation of silver niobate, silver tantalate, silver vanadate, and pure silver on the surface of the coatings. Tantalum and niobium-based coatings performed better than the vanadium-based ones throughout the entire range of temperatures. The NbN/Ag coating was then subsequently doped with MoS_2 to investigate if an increase in performance of the coating was attainable by introducing a low temperature lubricant. Friction coefficients were not reduced at low temperature, however, high temperature friction coefficients were lower. We speculate that the high temperature friction reduction may be the result of metal substitutions in the crystal lattice creating weaker chemical bonds, or different phases formed in the presence of sulfur.

9:00am **E1-1-4 Effect of Temperature on the Tribological Behavior of a MoS_2 Based Solid Lubricant Coating**, ***M. Bernard*** *(marine.bernard@ec-lyon.fr), V. Fridrici, Ph. Kapsa*, Ecole Centrale de Lyon - LTDS, France

The tribological mechanisms during friction interaction between stainless steel and steel at high temperature are very complex and can involve simultaneously different wear modes. The use of solid lubricants reduces these effects but their friction behavior at low and high temperatures have to be investigated, in order to optimize the coating nature and process used to protect the steel surface.

Cylinder-on-flat friction tests were conducted, using a linear reciprocating tribometer, to measure the friction coefficient of a molybdenum disulfide (MoS_2) based varnish coating and to quantify its durability. The varnish (5 microns thickness) was sprayed on a polished steel flat surface and then maintained fixed to the tribometer while a AISI-304L stainless steel cylinder (50 mm diameter, 15 mm width) was sliding on it. The conditions used during the tests were as follows: reciprocating motion (2.5 mm length, frequency 5 Hz), contact temperature between 20°C and 300°C, and normal load between 100 N and 400 N.

For each test, the evolution of friction coefficient versus time allowed us to determine the lifetime of the coating in the contact. The lifetime is defined as the number of cycles before elimination of the coating in the contact, corresponding to an increase of the friction coefficient. SEM and optical micrographs of the wear track (both on the cylinder and on the flat) were obtained to characterize the wear mechanisms of the coating and counterbody. The effects of test temperature and normal load on the durability of the coating and wear mechanisms are investigated.

The MoS_2 based varnish coating shows a high friction coefficient at high temperature. Determining the lifetime of a solid lubricant coating appears to be not easy. In general, it decreases with an increase in temperature or in normal load.

9:20am **E1-1-5 A Study of Mechanical and Tribological Properties of Self-Lubricating TiAlVN Coatings at Elevated Temperatures**, *W. Tillmann (wolfgang.tillmann@udo.edu),* ***S. Momeni****, F. Hoffmann*, Technische Universität Dortmund, Germany

In recent years, new solid lubricants, in form of metal, polymeric composite and ceramic, have been developed and widely employed in several tribological applications in order to increase the wear resistance and life-time of the forming tools. However, there are several manufacturing processes, in which the employment of solid lubricants is limited. In addition, ecological damage and higher production costs are further consequences of using such solid lubricants. This work aims at using the great potential of thin film technology to deposit adaptive, self-lubricating coatings as an alternative to conventional solid lubricants. Using magnetron sputtering process several titanium aluminum vanadium nitride coatings (TiAlVN) are developed in this study. These quaternary coatings possess the ability of forming lubricious oxides, known as Magnéli phases, at elevated temperatures, which significantly reduces the friction coefficient and surface wear. The process parameters like bias voltage, gas pressure and temperature are varied to deposit several TiAlVN coatings. The coatings are deposited on high-speed steel HS6-5-2C in plasma nitrided and non-nitrided form. The morphology and structure of the TiAlVN coatings are examined using scanning electron microscopy, energy dispersive scattering and X-ray diffractometry. Moreover, the mechanical and tribological properties of the coatings at different temperatures in the range of 25°C to 700°C are characterized using a nanoindenter and a ball-on-disc device to verify the concept of self-lubrication and to clarify the effect of process parameters on the self-lubricating behavior of TiAlVN coatings.

9:40am **E1-1-6 CrN-Ag and $Cr_{0.65}Al_{0.35}$N-Ag Nanocomposite Coatings for High-Temperature Adaptive Lubrication**, ***C.P. Mulligan***, Benet Laboratories, US Army ARDEC, *R. Deng, T.A. Blanchet, D. Gall (galld@rpi.edu)*, Rensselaer Polytechnic Institute

CrN-Ag and $Cr_{0.65}Al_{0.35}$N-Ag composite layers, 5-µm-thick and containing 2-20 at.% Ag, were deposited by reactive magnetron co-sputtering from Cr, Al, and Ag targets on Si(001) and 304 stainless steel substrates at growth temperatures T_s = 300-700°C. The composite microstructures consist of a transition-metal nitride matrix containing Ag segregates with an average size that increases from <25 nm for T_s < 500ºC to >200 nm for T_s > 700ºC. Vacuum annealing at T_a = 425-800°C, followed by quantitative microstructural analyses using surface and cross-sectional electron microscopy and Auger depth profiling, show that the lubricant mass transport is detachment limited and is a strong function of the microstructure and particularly the Ag aggregate size. The difference in operating and growth temperature, $\Delta T = T_a - T_s$, is the key parameter that determines lubricant transport and is therefore used to control the lubrication level. In addition, we demonstrate that the lubricant flow can be limited by a 200 nm thick dense CrN cap-layer, grown using ion-assisted densification. Friction and wear are measured in air at T_t = 25-700ºC, using ball-on-disk tests against alumina at both constant temperature and temperature ramping conditions. Samples designed for maximum lubrication, that is, grown without diffusion barrier and at low temperature to achieve finely dispersed Ag, exhibit very low friction coefficients <0.1 at T_t = 500ºC, but also a relatively high wear rate that leads to premature coating failure below 10,000 cycles due to premature Ag depletion. In contrast, carefully designed coating systems containing a composite and a diffusion barrier exhibit both a low friction of ~0.2 and a low average wear rate of $3x10^{-6}$ mm^3/Nm at T_t = 550ºC over 10,000 cycles.

10:00am **E1-1-7 Innovative High Temperature Nanotribology – to 800C**, ***B. Beake*** *(ben@micromaterials.co.uk), J.F. Smith*, Micro Materials Ltd, UK

Friction in every wear situation raises the temperature in the contact zone. For reliable modelling and coating optimisation for wear resistance it is essential to determine the actual mechanical and tribological behaviour at these high temperatures rather than infer from room temperature. Recently, elevated temperature nanoindentation has become a valuable addition to nanomechanical test capability, with the NanoTest capable of testing hardness, modulus and creep behaviour reliably to 750C and beyond.

Nevertheless, it can be more important to test other mechanical contact situations such as sliding, fretting or impact. Results of innovative nano- and micro-tribological experiments at high temperature will be presented for a range of hard coatings.

Friction results will be reported for both (heated probe + heated sample), and for a heated probe alone. The latter simulates a normal friction situation where heating takes place due to local heat generation, whereas the former allows diffusion and surface equilibration to occur before contact, for instance as in high temperature machining.

10:20am **E1-1-8 Tribology of Nanocrystalline Oxides and Adaptive Nanocomposite Coatings: Achieving Low Friction and Wear by Shear Accommodation**, ***T.W. Scharf*** *(scharf@unt.edu)*, The University of North Texas **INVITED**

Friction and wear mitigation is typically accomplished by introducing a shear accommodating layer (e.g., a thin film of liquid) between surfaces in sliding and/or rolling contacts. When the operating conditions are beyond the liquid realm, attention turns to solid coatings. The focus of this talk is how contacting surfaces change both structurally and chemically in order to control interfacial shear for two coating systems: nanocrystalline ZnO and nanocomposite MoS_2/Sb_2O_3/Au. It was determined that the coatings exhibit velocity accommodation modes (VAMs) of intrafilm shear and interfacial sliding, respectively, as characterized by advanced electron microscopy and spectroscopy techniques.

In the case of nanocrystalline ZnO, sliding and rolling contact fatigue (RCF) experiments and density functional theory (DFT) calculations revealed the atomistic origins of low friction and nanocrystalline plasticity when sliding along ZnO textured (0002) nanocolumnar grains. The atomic layer deposited (ALD) sub-stoichiometric ZnO film was structurally tailored to achieve low surface energy and low growth stacking fault energy basal planes. Sliding on this defective ZnO structure resulted in an increase in both partial dislocation and basal stacking fault densities through intrafilm shear/slip of partial dislocations on the (0002) planes via a dislocation glide mechanism. This shear accommodation mode mitigated friction and prevented brittle fracture classically observed in higher friction microcrystalline and single crystal ZnO, which has potential broad implications to other defective nanocrystalline ceramics.

In the case of amorphous-based MoS_2/Sb_2O_3/Au nanocomposite sputtered coatings, the main mechanism responsible for low friction and wear in both dry and humid environments is governed by the interfacial sliding between the wear track and the friction-induced transfer film on the counterface ball. In dry environments, the nanocomposite has the same low friction coefficient as that of pure MoS_2 (~0.007). But unlike pure MoS_2 coatings which wear through in air (50% RH), the composite coatings showed minimal amount of wear with wear factors of ~1.2-1.4 x 10^{-7} mm^3/Nm in both dry nitrogen and air. Cross-sectional TEM of wear surfaces revealed that frictional contact resulted in amorphous to crystalline transformation in MoS_2 with 2H-basal (0002) planes aligned parallel to the sliding direction. In air, the wear surface and subsurface regions exhibited islands of Au. The mating transfer films were also comprised of (0002)-orientated basal planes of MoS_2 resulting in predominantly self-mated 'basal-on-basal' interfacial sliding, and thus low friction and wear.

11:00am **E1-1-10 Simulations of Tribology in Nanocrystalline Metallic Films**, ***M. Chandross***, *S. Cheng (sncheng@sandia.gov)*, Sandia National Laboratories

Materials that perform well in electrical contacts usually exhibit high adhesion during frictional contacts. An excellent example of this phenomenon is pure gold, which has extremely low electrical contact resistance, but generally has a high friction coefficient. The exception to this, however, is nanocrystalline gold alloyed with minute amounts of Ni or Co, which in addition to its low contact resistance can also show low friction. The mechanism for this remains poorly understood. We will present the results of large scale molecular dynamics simulations that study the tribological response of both single crystal and nanocrystalline gold films in contact with curved probe tips under a variety of sliding conditions. Results from simulations of adhesion and friction in metallic alloys will also be presented.

11:20am **E1-1-11 Methodology of Selection of Coatings for Tribological Applications: Database Approach**, ***V. Fridrici*** *(vincent.fridrici@ec-lyon.fr)*, Ecole Centrale de Lyon - LTDS, France, *D.B. Luo*, Southwest Jiaotong University, China, *Ph. Kapsa*, Ecole Centrale de Lyon - LTDS, France

The use of coatings is more and more widely spread in contacts in order to reduce friction and protect surfaces from wear. Nevertheless, selecting an appropriate coating (from the very numerous available coatings) for given tribological conditions is always a complex process. The objective of this work is to develop a pre-selection tool of coatings, based on a coatings database and selection criteria.

The selection criteria (and consequently the characteristics of the coatings that are put in the database) are from diverse natures:

- Tribological behavior of the coating (wear resistance for different wear modes, friction coefficient in given conditions);

- Non tribological behavior (corrosion resistance, electrical, thermal or magnetic properties, biocompatibility, toxicity);

- Non functional characteristics (cost, deposition rate, color, pollution related to the deposition method);

- Limits coming from the running conditions (environment, temperature, relative humidity, loading, motion);

- Limits coming from the substrate (size, shape, material, substrate/coating adhesion, maximum temperature) and from the counterbody (hardness, roughness, chemistry…).

The initial version of the database contains 36 deposition methods and 156 coatings (with characteristics coming from the literature). It can be enlarged by the user.

The coatings in the database are ranked after a weighted search, with the requirements and selection criteria coming from the user.

Coatings are evaluated and compared by weight point and reliability. Weight point (W) is the sum of products of weight value (k_i) and weight factor (w_i) for each requirement (n_i). The values of k are linked to the coatings characteristics related to the selection criteria. They are between 0 and 10 and may come from quantitative or qualitative evaluation depending on the nature of the criterion. The values of w are chosen by the user (between 1 and 10) depending on the importance he wants to give to each research criterion in the selection. Reliability is used based on some presumption due to the incompletion of coating information. The total reliability (*R*) is the product of the reliability for each requirement (*r*).

Finally, all the remaining coatings are ranked according to the weight point considering all the requirements. The first 10 coatings are selected as candidates coatings, and their reliability are provided.

11:40am **E1-1-12 Analysis of Friction and Wear Mechanisms on Hard Coatings Deposited byReactive Magnetron Sputtering**, ***J.S. Restrepo*** *(johansrestrepo@hotmail.com),* Universidad Nacional Autonoma de Mexico, *M.F. Cano, F. Sequeda, J.M. Gonzalez, A. Ruden,* Universidad del valle, Colombia, *S.M. Saunders*, Universidad Nacional Autonoma de Mexico

Different Hard coatings have been deposited (ZrN, CrN, TiN, TiZrN, TiAlN, AlSiN and multilayers systems) by DC Reactive Magnetron Sputtering at different deposition parameters (substrate temperature, Nitrogen flow, Voltage bias), to evaluate tribological properties with a ball on disc technique using different loads and speeds parameters to know the influence of this, on the tribological behavior. The ball on disc test was stopped at different distances to identify the wear mechanisms using a profilometer, scanning electron microscopy (SEM) and optical microscopy. These techniques allowed observed differents transitions on friction coefficient associated with the wear mechanisms. The rugosity polishing showed a low friction coefficient that increases slowly, the ploughing and scratching wear mechanisms were observed, producing unstable high friction coefficient and wear rate. Also different kinds of debris particles were observed like angular and roll shape

Computational and Experimental Studies of Inorganic, Organic, and Hybrid Thin Films: An Atomistic View Room: Sunrise - Session TS1

Computational and Experimental Studies of Inorganic, Organic, and Hybrid Thin Films: An Atomistic View
Moderator: A. Amassian, KAUST, J. Rosén, Linköping University

8:00am **TS1-1 Semiconductor Nanostructures Direct-Write with an Atomic Force Microscope**, ***M. Rolandi*** *(rolandi@u.washington.edu)*, University of Washington **INVITED**

The integration of different solid-state semiconductors with nanoscale accuracy is a challenging pursuit essential for novel advances in electronics and photonics. Bottom-up approaches offer an unlimited materials choice. However, they often lack the precise placement and geometry control required for device fabrication. Here, we present a novel approach to semiconductor nanostructures that exploits the tip of an atomic force microscope (AFM) to precisely determine nanostructure growth. In this approach, the biased AFM tip (ca. -12 V) locally reacts a liquid precursor (diphenylgermane or dyphenylsilane) while it traces desired shapes on the sample. High quality, carbon free (SIMS, x-ray PEEM, TEM) Si, Ge, and SiGe heterostructures with deterministic placement, size, and composition control are produced in this fashion. Substrate dependent growth mechanisms and potential device geometries will be discussed.

8:40am **TS1-3 A Predictive Modeling Framework for Morphology Evolution in Thin Film Organic Photovoltaic Cells**, ***B. Ganapathysubramanian*** *(baskarg@iastate.edu)*, Iowa State University **INVITED**

Recent advances in organic photovoltaic technology have resulted in power conversion efficiencies reaching all time high values (~ 8:13%). These improvements have been possible through new materials development and new device designs. A key (often overlooked) aspect determining the power conversion efficiency of organic photovoltaics is the final morphological distribution of the electron-donor and electron-acceptor sub-regions. Recent experimental studies reveal that significant additional improvement in the power conversion efficiency is possible through better morphology control of the organic thin film layer during the manufacturing process. A set of computational tools that can predict the intermediate three dimensional snapshots of the material distribution within the active layer during the fabrication process as well as tools to relate the structure with device properties would strengthen the pursuit of this vision.

Driven by this goal, we develop a computational framework that effectively acts like a virtual "stereological microscope" to visualize morphology evolution from early stages of phase separation until the formation of the stable morphology. This multiscale framework is based on a continuum description of evaporation-induced phase-separation in ternary systems and is able to resolve nano-morphological features while simulating device scale domains. Comparison of predicted morphology with experimental measurements shows the validity of the developed framework. We will showcase the potential of such coupled computational and experimental analysis by investigating morphology evolution in a specific class of organic photovoltaics (P3HT:PCBM:solvent). The framework is used to characterize the organization of percolating networks within the active layer as a function of (a) blend ratio, (b) evaporation profile, (c) solvent type, and (d) substrate patterning. We finally establish process-structure-property relationships using tools developed based on recent advances in image processing and computational homology.

9:20am **TS1-5 Real-Time Observation of Thin Film Growth**, ***F. Schreiber*** *(frank.schreiber@uni-tuebingen.de)*, Universitaet Tuebingen, Germany **INVITED**

After a short general introduction to the concepts of thin film growth we will explain different approaches to real-time observations of growth using X-ray scattering and optical techniques.

Real-time techniques enable us to better study and understand the mechanisms of film growth, the evolution of structures and imperfections, as well as the possible appearance of transient structures and transformations, which can be crucial for the quality of the growing film and which would be missed in post-growth studies.

Particular emphasis is put on our experiments recording the scattered intensity in a broad range of q points simultaneously as a function of time as opposed to only one q point. We will explain how this can be used for an improved analysis of the data and the resulting structure.

We will also demonstrate how the optical properties of the films evolve and how they are related to the structure. Our experimental approach is quite general and applicable to many different materials, but examples will be mostly shown based on our work on organic semiconductors, which are applied in organic electronic and optoelectronic devices

(A. C. Dürr et al., Phys. Rev. Lett. 90 (2003) 016104; B. Krause et al., Europhys. Lett. 65 (2004) 372; S. Kowarik et al., Phys. Rev. Lett. 96 (2006) 125504; D. Zhang et al., Phys. Rev. Lett. 104 (2010), 056601; U. Heinemeyer et al., Phys. Rev. Lett. 104 (2010), 257401; A. Hinderhofer et al., Europhys. Lett., in print).

10:00am **TS1-8 Computational Study of Complex Oxide Thin Film Growth with Emphasis on Surface Diffusion During the Growth Process**, ***V. Georgieva*** *(violeta.georgieva@ua.ac.be),* University of Antwerp, Belgium, *M. Saraiva,* Ghent University, Belgium, *N. Jehanathan, G. Van Tendeloo,* University of Antwerp, Belgium, *D. Depla,* Ghent University, Belgium, *A. Bogaerts*, University of Antwerp, Belgium

The crystallinity of simulated $Mg_xM_yO_z$ (M=Al, Cr, or Y) thin films by a molecular dynamics (MD) model is studied with a variation in the stoichiometry of the thin films at operating conditions similar to the experimental conditions of a dual magnetron sputter-deposition system. The Mg metal content in the film ranges from 100% (i.e. MgO film) to 0%, (i.e. M_2O_3 film) [1, 2]. A classical ionic potential with formal charges describes the interactions between atoms. The structure of the simulated films was found to be in excellent agreement with the structure of the experimentally deposited films analyzed by X-ray diffraction (XRD) and transmission electron microscopy (TEM) techniques.

Both simulation and experimental results showed that the structure of the Mg-M-O film was varying from crystalline to amorphous when the Mg concentration decreases. The crystalline Mg-M-O films have a MgO structure (cubic, S.G. Fm3m) with M in solid solution.

The role of the surface diffusion in the growth process was studied by calculating the energy barriers for surface diffusion based on the classical potential used for the MD simulation. Some interesting results have been obtained about the mobility of species. For example, the energy barriers for surface diffusion are calculated to be lower in the Mg-Cr-O system compared to that in the Mg-Al-O system at the same Cr/Al content, which could explain the higher level of crystallinity observed in the Mg-Cr-O thin films compared to Mg-Al-O thin films with the same Mg-M metal ratio. In addition, increasing the other metal (Al, Cr, or Y) amount shifts the maximum of the energy barrier distribution to very low values (below 0.1 eV) which is a clear indication for a transition from an ordered to a disordered system.

[1] V Georgieva, M Saraiva, N Jehanathan, O I Lebedev, D Depla and A Bogaerts, J. Phys. D: Appl. Phys. **42** (2009) 065107.

[2] M. Saraiva, V. Georgieva, S. Mahieu, K. Van Aeken, A. Bogaerts and D. Depla, J. Appl. Phys. **107** (2010) 034902.

10:20am **TS1-9 Influence of Grain Boundary Chemistry in Mix-Mobility Thin Film Growth**, *B. Fu, W. An, C.H. Turner,* ***G.B. Thompson*** *(gthompson@eng.ua.edu)*, University of Alabama

Thin films exhibit compressive-tensile-compressive stress states during the nucleation of islands, coalescence of islands and post-coalescence stages of growth. Using an in situ wafer curvature measurement technique, the stress evolution in Fe-Pt and Fe-Cu alloy thin films has been investigated. The stresses were shown to be compositionally dependent. In general, the tensile or compressive stress for the various binary compositions was associated with whichever element enriched the grain boundaries. Under specific growth conditions, a 'zero-stress' state could be achieved. The as-deposited alloy stress states do not show significant stress recovery upon ceasing the deposition. For the FePt films, upon annealing, the magnitude of the compressive stress state was reduced with increasing order parameter and has been explained in terms of reduced adatom surface migration. The FeCu films showed phase separation and an increase in surface roughness. Density functional theory calculations were performed to quantify the possible diffusion pathways and binding energies for Fe and Pt on a {111} $L1_0$ surface. Upon ceasing deposition, the post-growth stress relaxation rate increased with FePt order parameter and is explained in terms of an increase in interfacial energy contribution at the grain boundaries formed by chemically ordered grains. XRD, TEM, and atom probe tomography have been employed to quantify the phase, grain size and grain boundary chemistries, respectively, as they relate to the preferential segregation and thin film stress measurements.

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

PVD Coatings and Technologies
Moderator: P. Eklund, Linköping University, J. Vetter, Sulzer Metaplas GmbH, J.-H. Huang, National Tsing Hua University

1:30pm **B1-2-1 Growth Morphology and Corrosion Resistance of Magnetron Sputtered Cr Films**, ***K.-T. Chiang*** *(kchiang@swri.org), R. Wei*, Southwest Research Institute

Chromium films are commonly used as corrosion resistant coatings because they form a passive, protective scale. The film morphology and microstructure are important aspects of corrosion resitance. In this paper, we presented grwoth mechanisms and morphologies of these films to provide insight into the microstructural properties of corrosion resistance. Thin films of Cr were deposited on silicon wafer, copper and carbon steel substrates using a plasma-enhanced magnetron sputtering technique. A filament was utilized to produce a plasma that effects an ion bombardment on the workpiece during the magnetron sputter deposition process. The deposited fims were characterized by x-ray diffraction, scanning electron microscopy and atomic force microscopy. The film growth morphology and microstructure are correlated with sample orientation (with respect to the magnetron) and the deposition parameters. On important deposition parameter affecting Cr film properties is the level of plasma ion bambardment. It has been demonstrated that at a low level of ion bombardment, a columnar structure is formed and film is discontiguous. As the level of ion bombardment increases, the film become denser and contiguous. Eventually the film becomes fully dense without indication of columnar structure. The corrosion behavior of the deposited films was studied using potentiodynamic polarization techniques. It has been demonstrated that adequate ion bombardment is necessary to achieve the required corrosion resistance.

1:50pm **B1-2-2 Fundamental Studies on the Deposition of Nanocrystalline Diamond (n-D) Films by Means of Pulsed Laser Deposition**, ***H. Grüttner*** *(hgruettn@hs-mittweida.de)*, Hochschule Mittweida - University of Applied Sciences, Germany

The results of fundamental studies on the deposition of nanocrystalline diamond (n-D) films by means of pulsed laser deposition (PLD) will be present. The n-D films were deposited on silicon (111) and hard metal by excimer laser ablation from a graphite target at elevated substrate temperatures and in hydrogen background gas. The variation of the microstructure and the properties of the films with temperature was investigated in the range of 100°C to 660°C and with hydrogen pressure in the range of 1 mbar to 7 mbar. With diamond and / or ion bombardment pretreated and non-pretreated substrates were used and the influence of the pretreatment process on the microstructure of the films was investigated. The films were produced at laser fluences between 10 J/cm² and 15 J/cm². The thickness of the films was varied from 100 nm up to 2 microns. The influence of deposition parameters on the n-D growth and the sp^2/sp^3 bonding ratio was determined by Raman spectroscopy and TEM / EELS analysis and it will be shown that n-D films of good quality can be prepared using proper parameters. The hardness and Young´s modulus were determined using nanoindentation and the optical properties in the UV / VIS range was measured by using photospectrometry. The variation of these properties with deposition parameters and their correlation with the microstructure of the n-D films will also be presented.

2:10pm **B1-2-3 Oxidation and Degradation of Nitride Thin Films at High Temperature under Controlled Atmosphere**, ***F.-H. Lu*** *(fhlu@dragon.nchu.edu.tw)*, National Chung Hsing University, Taiwan **INVITED**

Oxidation and degradation of nitride thin films, such as TiN, CrN, ZrN, AlN, prepared by magnetron sputtering were investigated over various temperatures in different atmospheres by analyzing changes in appearance and crystalline phases, as well as microstructures. The atmospheres contained air, nitrogen, and forming gas (N_2/H_2 = 9), which exhibited drastically different nitrogen and oxygen partial pressures. Oxidation of the nitride films was driven by the Gibbs free-energy changes between the nitrides and the formed oxides, and could be tailored by controlling the annealing temperature and nitrogen/oxygen partial pressures. Both internal stresses resulted from sputtering and thermally-induced stresses were responsible for many types of degradation in the films, which would be further discussed.

2:50pm **B1-2-5 Effects of Pulsed Laser Irradiation of As-Deposited c-BN-Films using Photons of 157 nm Wavelength**, ***R. Bertram*** *(rbertram@hs-mittweida.de)*, Hochschule Mittweida - University of Applied Sciences, Germany

We present the effects of pulsed laser irradiation of as-deposited c-BN-films using photons of 157 nm wavelength and 7.9 eV energy, respectively. The films were deposited by pulsed laser deposition (PLD) using a KrF excimer laser of 248 nm wavelength and up to 30 J/cm^2 laser fluence on the pyrolytic hexagonal boron nitride target with additional ion beam bombardment of the growing films using a mixture of nitrogen and argon ions produced in a r.f. ion source with 700 eV ion energy.

The irradiation of such coatings with a fluorine laser was found to influence the number and size of sp^2-bonded hBN particulates and thus the further cBN growth as well as the sp^3 / sp^2 ratio.

So, alternating deposition of sub-layers and irradiation directly affects the quality of the entire c-BN films.

Furthermore, calculations were done concerning the mean penetration depth of the photons in the c-BN films and, based on these evaluations of laser-induced temperature fields, experiments have been carried out using proper sub-layer thickness. The influence of the irradiation of the films with photons on the intrinsic shear stresses, which limited the film thickness so far, was investigated and will be presented.

3:10pm **B1-2-6 High Power Impulse Magnetron Sputtering of Niobium in Non-Reactive and Reactive Gas Environments**, ***R.J. Mendelsberg****, S.H.N. Lim, K.M. Yu, A. Anders (aanders@lbl.gov)*, Lawrence Berkeley National Laboratory

High power impulse magnetron sputtering (HIPIMS) is a young technology whose opportunities, advantages and limitations are currently intensely investigated by a number of groups. Here we selected niobium as one of the most interesting materials since thin films of niobium and niobium compounds are used in a diverse range of applications. Pure niobium films are needed for the next generation of superconducting radio-frequency cavities not made from solid niobium. Niobium nitride is a material sometimes incorporated in hard, wear-resistant coatings and multilayers for its added corrosion resistance benefit. Niobium oxide is an attractive high index material for optical and photonics applications. The complex refractive index can be tuned by going to niobium oxynitride. We report on the dramatic changes of the HIPIMS discharge behavior when going from pure metal mode to reactive deposition, and correlate some plasma and film properties. One could expect that HIPIMS with other transition metals exhibit similar features.

Work supported by the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

3:30pm **B1-2-7 Barrier Capability of Reactively Sputtered $Ta_xZr_{1-x}N$ Films with Slight Ta Addition Against Copper Diffusion**, ***J.-L. Ruan****, J.-L. Huang,* National Cheng Kung University, Taiwan*, H.-H. Lu,* National Chin-Yi University of Technology, Taiwan*, J.-S. Chen,* National Cheng Kung University, Taiwan*, D.-F. Lii (dflii888@csu.edu.tw)*, Cheng Shiu University, Taiwan

The $Ta_xZr_{1-x}N$ films were prepared by reactive magnetron sputtering and the concentration of zirconium and tantalum was regulated by controlling the power of the sputtering guns. A sputter-prepared Cu (100 nm)/$Ta_xZr_{1-x}N$ (5 nm)/SiO_2 (100 nm)/Si stacked structure was fabricated for the evaluation of diffusion barrier performance of $Ta_xZr_{1-x}N$ films. The composition, microstructure, resistivity and diffusion barrier properties of $Ta_xZr_{1-x}N$ films were studied by x-ray diffraction, electron probe microanalyzer, Auger electron spectroscopy, and four point probe method. Results indicated that the slight addition of Ta (3.5 at. %) could effectively further decrease the electrical resistivity of films to a value of 78 μΩ-cm compared with pure ZrN films due to the extra d valence electron of Ta comparing with Zr. Auger electron spectroscopy and sheet resistance measurements showed that the slight incorporation of Ta (3.5 at. %) into the ZrN films significantly improved the barrier performance against Cu diffusion. In addition, the $Ta_xZr_{1-x}N$ films with 3.5 at. % of Ta could be successfully used as a diffusion barrier layer between Cu and SiO_2 even up to the high temperature of 800°C for 5 minutes in a vacuum, while the ZrN films failed at the same temperature.

3:50pm **B1-2-8 The Influence of Substrate Biasing on the Crystal Orientation of γ-Al_2O_3 Films**, ***M. Prenzel*** *(Marina.Prenzel@rub.de), T. Baloniak, A. Kortmann, T. de los Arcos, A. von Keudell*, Ruhr-Universität Bochum, Germany

Substrate biasing is an established technique to control and adjust material properties during thin film deposition from a plasma. The external bias voltage manipulates the energy distribution function of the ions impinging on the substrate (IEDF). An optimized ion bombardment can significantly improve for example film hardness, adhesion, crystallinity, or wear resistance.

Here, we report on the influence of sinus RF biasing at 1 MHz on the crystallinity of aluminium oxide films. The films are prepared in a RF magnetron discharge, which is excited by 13.56 and 71 MHz frequencies and used for reactive sputtering of an aluminium target. The target is mounted on the powered electrode and the silicon substrate is placed on a biased electrode at the opposite side. The temperature of the substrate is varied and reaches up to 700°C. A feedback loop based on measurements of an Al-atom emission line is used to control the partial pressure of O_2 in the plasma.

The Al_2O_3 films are characterized by FTIR, XPS and XRD. During this study, a combination of arbitrary function biasing scheme and IEDF measurements with a retarding field analyzer has been performed. The results reveal a dependence of the orientation of the crystal structure in the film on the energy distribution of the ions. First results show that the orientation of the crystal structure can be manipulated by the variation of bias voltage. In future, these results are planned to optimize the Al_2O_3 deposition process and to reveal the role of the ion energy in the film growth. The work is funded by DFG within SFB-TR 87.

4:10pm **B1-2-9 Target Erosion Effects in Reactive Pulsed DC Magnetron Sputtering of Amorphous and Crystalline Alumina**, ***N.D. Madsen*** *(nisdam@phys.au.dk), S. Louring, A.N. Berthelsen,* Aarhus University, Denmark*, B.H. Christensen, K.P. Almtoft, L.P. Nielsen,* Danish Technological Institute, Tribology Centre, Denmark*, J. Bøttiger*, Aarhus University, Denmark

Alumina coatings were synthesized by reactive pulsed DC magnetron sputtering in an industrial-scale deposition system. The aim of this study was to investigate the influence of target erosion (racetrack depth) on the structural and mechanical properties of the alumina coatings. Hysteresis curves, showing the cathode voltage as function of oxygen flow, were mapped out for several target erosion depths. Each deposition was made with a fixed cathode voltage and the current was controlled by adjusting the oxygen flow in a feedback loop by means of which a constant power was maintained. Keeping the power constant, this procedure was repeated for various cathode voltages within the hysteresis transition region and at different deposition temperatures. The corresponding deposition rates were observed to depend mainly on the relative position of the cathode voltage on the hysteresis curve, and to a lesser degree the absolute cathode voltage. Coatings deposited at low temperatures (~200˚C) were amorphous, as evidenced by X-ray diffraction (XRD), but the films exhibited morphological changes with varying racetrack depth. Nanoindentation revealed hardness and reduced elastic-modulus values of 9 GPa and 160-165 GPa, respectively, regardless of the target erosion and the cathode voltage. However, at deposition temperatures around 550˚C, there were dramatic changes in the mechanical properties as a function of the cathode voltage within the hysteresis transition region but also due to changes in the racetrack depth. The changes in mechanical properties, e.g. hardness from 9 GPa to 20 GPa, was due to the deposited films changing from amorphous to crystalline.

4:30pm **B1-2-10 Thermal Stability of Magnetron Sputtered Alumina Coatings with Crystalline Metastable Structure**, ***P. Zeman*** *(zemanp@kfy.zcu.cz), S. Proksova, J. Blazek, R. Cerstvy, J. Musil*, University of West Bohemia, Czech Republic

Machining of materials with low thermal conductivity, such as stainless steel or nickel superalloys, demands to use cutting tools with an enhanced performance. Crystalline alumina coatings with high hot hardness and high chemical inertness are promising candidates. Present trends in the research of crystalline alumina coatings include two areas. One of them is the deposition of pure α-Al_2O_3 coatings at temperatures as low as possible (≤ 700°C) and another one is the deposition of metastable γ-Al_2O_3 coatings with thermal stability as high as possible. The present study extends knowledge in thermal stability of magnetron sputtered alumina coatings containing the crystalline γ-phase. Special attention is devoted not only to the effect of the temperature necessary for the γ-to-α transformation but also to the effect of the time during isothermal heating near the transformation temperature. Kinetic analysis of the γ-to-α transformation was also studied in detail. The crystalline alumina coatings sputtered in an argon-oxygen mixture at selected process parameters using a dual magnetron system equipped with two aluminum targets were investigated by means of differential scanning calorimetry and symmetrical high-resolution thermogravimetry. The structure of the coatings was characterized by X-ray diffraction and the surface morphology by light optical microscopy. It was found that the nanocrystalline γ-phase structure of the sputtered alumina coatings is thermally stable at least up to 1000°C Above this temperature the γ-to-α transformation occurs and is affected by the heating rate, the annealing temperature, the annealing time and the thickness of the coating. The γ-to-α transformation is accompanied by the cracking of the coating and by the formation of a metastable θ-Al_2O_3 phase. Its existence is, however, limited only to very narrow temperature and time range. Furthermore, kinetic data will be presented and the effect of additional elements on thermal stability of the metastable γ-phase structure will be discussed.

4:50pm **B1-2-11 Effect of Seed Layer Composition on the Structure of Arc-Evaporated High Al_2O_3 Containing $(Al,Cr)_2O_3$ Hard Coatings**, ***M. Pohler*** *(markus.pohler@unileoben.ac.at), R. Franz,* Montanuniversität Leoben, Austria*, J. Ramm,* OC Oerlikon Balzers AG, Liechtenstein*, C. Polzer,* PLANSEE Composite Materials GmbH, Germany*, C. Mitterer*, Montanuniversität Leoben, Austria

The nucleation of Al_2O_3 coatings in the corundum type crystal structure is strongly promoted by the addition of Cr_2O_3. Due to a rare combination of properties such as complete solid solution of Cr_2O_3 in Al_2O_3, low formation temperature, high melting point and good hardness, Cr_2O_3 is an ideal candidate to overcome the needs of high formation temperatures and to avoid the unfavorable polymorphism of Al_2O_3. Nevertheless, the cathodic arc deposition of crystalline corundum type $(Al,Cr)_2O_3$ coatings reaches its limit for Al_2O_3 concentrations higher than 70 mol-%. The use of thin seed layers seems to be a promising tool to control the growth of coatings having the corundum structure even at higher Al_2O_3 contents. The aim of this work was to investigate the influence of different $(Al_xCr_{1-x})_2O_3$ seed layers with x = 0.25, 0.5 and 0.6 on the morphology, microstructure and properties of corundum type $(Al_{0.7}Cr_{0.3})_2O_3$ and $(Al_{0.85}Cr_{0.15})_2O_3$ coatings. All coatings were synthesized in an industrial scale cathodic arc evaporation system using powder metallurgically produced AlCr compound targets with different Al/Cr ratio. The coatings were deposited in pure oxygen at 550°C. A dense and fine grained structure was obtained for all coatings, as observed by scanning electron microscopy. Investigations of the coating microstructure by glancing angle X-ray diffraction displayed a significantly increased crystallinity of the top-layer, e.g., $(Al_{0.7}Cr_{0.3})_2O_3$ on the $(Al_{0.25}Cr_{0.75})_2O_3$ seed layer compared to the coatings without seed layer. Biaxial stress measurements revealed a reduction of residual tensile stress from 200 to 65 MPa with decreasing Al_2O_3 content in the seed layer from 60 to 25 mol-%. Transmission electron microscopy shows pronounced columnar crystal growth of the top-layer in corundum type structure already in the very early growth stages. The experimental results however, showed that a minimal seed layer thickness seems to be necessary to stimulate columnar growth of the top-layer.

5:10pm **B1-2-12 Face-Centered Cubic $(Al_{1-x}Cr_x)_2O_3$ Thin Films: Deposition, Characterization, and Heat Treatment Studies**, ***A. Khatibi*** *(alikh@ifm.liu.se), J. Palisaitis, P.O.Å. Persson, J. Jensen, J. Birch, P. Eklund, L. Hultman*, Linköping University, Sweden

Face centered cubic $(Al_{1-x}Cr_x)_2O_3$ solid solution films, with x in the range 0.60<x<0.70, have been deposited using dual reactive RF magnetron sputtering from Al and Cr targets in mixed Ar/O_2 discharge at a substrate temperature of 500°C. The films have a strong <100> preferred orientation. The unit cell parameter is 4.04 Å determined by x-ray diffraction and high resolution transmission electron microscopy techniques. The $(Al_{1-x}Cr_x)_2O_3$ films are suggested to have a non-stoichiometric NaCl structure with 33% vacancy occupancy on Al/Cr sites. Nanoindentation shows that the films exhibit hardness values up to 26 Gpa and reduced modulus of 220-235 Gpa. In the present work, in-situ annealing studies were performed on as-deposited samples for a series of temperatures up to 1100°C and annealing time of 8 h. The results show that fcc structure remains intact up to 950°C. A gradual phase transformation from fcc to corundum at 1000°C is observed, where annealing for 1-3 h yields a partial transformation and annealing for > 4 h results in complete transformation to alpha-$(Al_{1-x}Cr_x)_2O_3$. There is no indication of any phase separation into alpha-Cr_2O_3 and alpha-Al_2O_3.

5:30pm **B1-2-13 Synthesis of Free Standing Al-Cu Intermetallics by Cathodic Arc Plasma Treatment**, ***E.A. Arpat****, M. Urgen (urgen@itu.edu.tr)*, Istanbul Technical University, Turkey

In this study; a new approach based on cathodic arc plasma treatment, introduced by Urgen and Çorlu[1,2], was utilized to produce free standing bulk alloys/ intermetallics in a cathodic arc PVD environment. Al-Cu binary couple was selected as an example, in which Al cathode as alloying material and Cu foil as substrate are used. Alloying was done by using cathodic arc plasma of Al and different deposition/ bombarding bias voltages which were applied to Cu foil substrate. Two different bias voltages were selected obtain adequate temperature that will allow maximum diffusion but securing the foil substrate from melting, (850°C nominal for the Cu-rich side of the Al-Cu phase diagram). Al-rich droplets and metastable phases at the surfaces within as processed materials were detected by standard characterization techniques. A second step of annealing at 700°C was also carried out to overcome heterogeneity. 25 µm thick Cu-rich γ-Al_4Cu_9, δ-Al_2Cu_3, ζ-Al_3Cu_4 intermetallics were produced. Mechanical, optical and conductance of these intermetallics were also determined.

Hard Coatings and Vapor Deposition Technology Room: Golden West - Session B3

Laser and Ion Beam Assisted Coatings and Technologies

Moderator: K. Sarakinos, Linköping University, S.B. Fairchild, Air Force Research Laboratory

1:30pm **B3-1 Growth of $Bi_5Fe_{0.5}Co_{0.5}Ti_3O_{15}$ Thin Films by Pulsed Laser Deposition**, ***Y. Lu***, U.S. Air Force Academy, *G.J. Brown (gail.brown@wpafb.af.mil),* Air Force Research Laboratory, *G. Kozlowski,* Air Force Research Laboratory/Wright State University, *K. Eyink,* Air Force Research Laboratory, *L. Grazulis,* Air Force Research Laboratory/UDRI, *K. Mahalingam*, Air Force Research Laboratory

Thin films of $Bi_5Fe_{0.5}Co_{0.5}Ti_3O_{15}$ (BFCTO) with potentially broad application in functional multiferroic devices were fabricated by using pulsed laser deposition (PLD) . In a search of optimal conditions to achieve epitaxially grown BFCTO thin films, different substrate temperatures (600°C, 650°C, 700°C and 760°C) and different partial pressures of oxygen (50 mTorr, 100 mTorr, 150 mTorr and 200 mTorr) in the PLD chamber were used during deposition of BFCTO films on $LaAlO_3$, LSAT, MgO and STO single crystal substrates with (100) surface orientations. Combination of 100 m Torr of oxygen partial pressure and substrate temperature of 650°C gives the best crystallinity of the thin films. Thorough structural and chemical studies of these BFCTO films were done by using SEM, HRTEM, AFM, XPS and Electron Probe Microanalyser measurements. Optical properties of these films were measured by using ellipsometry and their correlations with structural and chemical properties were established.

1:50pm **B3-3- Nanoparticle Fabrication by Through Thin Film Ablation**, ***P.T. Murray*** *(paul.murray@udri.udayton.edu), E. Shin, L. Petry*, University of Dayton

We have developed a process denoted Through Thin Film Ablation (TTFA), which entails ablating, from the backside, a thin film target. The TTFA process results in the deposition of nanoparticles on a substrate with little agglomeration and without the large micrometer-sized particles that are normally formed by standard pulsed laser ablation. The nanoparticles thus formed by TTFA typically have diameters ranging from 1 to 5 nm. We have done extensive characterization of the dynamics of the TTFA process and have determined the mass and speed distributions of the nanoparticles. In this presentation examples will be given for the formation of Fe and Pt nanoparticles.

2:10pm **B3-4 Laser-Deposition and Characterization of Amorphous Thermoelectric Films**, ***G. Wilks*** *(garth.wilks@wpafb.af.mil),* Air Force Research Laboratory, *P.T. Murray,* University of Dayton, *S.B. Fairchild, N. Gothard, J.E. Spowart*, Air Force Research Laboratory

From the Efficient Cluster Packing model describing the topology of metallic glasses, it is understood that certain compositions are favored for glass-formability based on the ratio of atomic sizes between constituents. In this regard, the half-Heusler composition $Zr_{0.5}Hf_{0.5}NiSn$ is nearly ideal. Although the crystallized form of this material has been widely studied because of its high thermoelectric power factor, it has been suggested that partial vitrification may enhance the thermoelectric figure of merit by preserving the favorable aspects of electronic structure while significantly disrupting thermal transport. Capitalizing on the high quench rates possible during pulsed laser deposition, a spectrum of thin films including amorphous and partially-amorphous duplex microstructures has been grown under various conditions. Transport characteristics relevant to the thermoelectric effect are rationalized in light of accompanying microstructure characterization.

2:30pm **B3-5 Multi-Beam, Multi-Target Pulsed Laser Deposition: Beyond Single Film Deposition**, ***R. Eason*** *(rwe@orc.soton.ac.uk)*, University of Southampton, UK **INVITED**

Many labs are currently using Pulsed Laser Deposition for rapid growth of a range of materials that would naturally includes metals, dielectrics, semiconductors, functional materials such as ferroelectrics or piezoelectrics, biomaterials, and more. Each PLD set-up will also have been designed around a particular interest or application area which might be the basic growth process itself, involving a range of on-line diagnostics, or the optimisation of a particular material, in terms of film quality, properties, thickness or size. However, while some labs may use multiple targets, via carrousels or specialist composite sector targets, one factor which is common to most facilities is that a single laser is used to ablate these targets and films are grown from a single laser plume/substrate interaction process.

We have chosen to extend the basic single beam/single target geometry to a new 3 laser/ 3 target deposition set-up, and we believe this offers unique new capabilities within PLD research. Three independent laser plumes allow either a sequential or coincident deposition capability. If sequential deposition is implemented, there is the added flexibility of adjusting the temporal delay so that plume-plume interactions can be either utilised or avoided. Use of multiple plumes means that oxide films for example can now be grown from their separate constituents, and dopants can be added to a growing film in a gradual or graded manner, for applications in lasing planar waveguides. Combinatorial growth can be explored in a manner equivalent to the RGB three colour palette. Films that incorporate lateral or horizontal variation such as donut structures can be fabricated and new materials such as quaternary or penternary oxide crystals can be grown from ternary targets. Finally, multilayers, superlattices and mixed films are readily grown, by rapid shuttering of the individual plumes or incident lasers.

Our work to date using multiple targets and laser beams will be described, for end applications that require low loss, single crystal films for lasing and amplifying end applications. I will describe what we now consider as routinely achievable and also our wish list for truly exotic fabrication strategies involving both horizontal and vertically integrated growth.

3:10pm **B3-7 Capacitive Properties of x $BaTiO_3$-(1-x) $BiScO_3$ Thin Films Fabricated by Pulsed Laser Deposition**, ***C.E. Stutz*** *(charles.stutz@wpafb.af.mil),* Air Force Research Laboratory, *G. Kozlowski,* Wright State University, *S. Smith,* Air Force Research Laboratory/UDRI, *A. Baker, C. Randall,* Penn State, *S. Trolier-McKinstry,* Pennsylvania State University, *G. Landis,* Air Force Research Laboratory/UDRI, *J.G. Jones,* Air Force Research Laboratory, *T.C. Back*, Air Force Research Laboratory/UTC

Thin films of x $BaTiO_3$-(1-x) $BiScO_3$ (BTBS) showing a high permittivity are useful both in capacitor applications and in piezoelectrics. BTBS thin films and $SrRuO_3$(SRO) or $La_{0.5}Sr_{0.5}CoO_3$(LSCO) conductive bottom electrodes were prepared by using pulsed laser deposition on <100> $La_{0.3}Sr_{0.7}Al_{0.65}Ta_{0.35}O_3$ (LSAT) single crystal substrates. In a search of optimal conditions to achieve epitaxially grown BTBS, SRO or LSCO thin films, different substrate temperatures (600°C, 650°C and 750°C) and different partial pressures of oxygen (100 mTorr, 200 mTorr and 300 mTorr) in the chamber were used during deposition on LSAT substrates. The best epitaxial films of BTBS strongly depend on composition (value of x). An example is if x is equal to 0.8, we have achieved the best quality film under 100 mT of oxygen partial pressure with a substrate temperature of 650°C. XRD diffraction pattern measurements show the high quality of these films. Also, a conductive buffer layer of SRO film requires 300 mT of oxygen partial pressure and substrate temperature of 750°C. The thorough structural and chemical studies of these BTBS films were done by using SEM, HRTEM, AFM and XPS measurements. The capacitance properties of these films were measured and their correlations with structural and chemical properties were established.

3:30pm **B3-8 Attempt to Synthesize a Ti_3SiC_2 Coating by Pulsed Laser Deposition of a Ti-Si-C Multilayer Structure**, *M. Hopfeld, T. Kups, E. Remdt, M. Wilke,* ***P. Schaaf*** *(peter.schaaf@tu-ilmenau.de)*, TU Ilmenau, Institut für Werkstofftechnik, Germany

The ternary compound Ti_3SiC_2 has a nanolaminated structure and belongs to the $M_{n+1}AX_n$ phases. In the last 20 years there were several attempts to reduce the formation temperature of MAX phases by different sputtering techniques. Eklund *et al.* mentioned that thin film processing and the growth of 312 MAX-phases like Ti_3SiC_2, Ti_3GeC_2 and Ti_3AlC_2 require high synthesis temperatures in the range from 800°C to 1000°C regarding the diffusion length of large unit cells [1].

In this work the pulsed laser deposition of Ti-, Si- and C multilayers and the formation of the MAX phase Ti_3SiC_2 are investigated in detail. The incoming ions and particles, generated by the Nd:YAG laser (λ = 1064 nm, τ = 6 ns) ablation, form dislocations and lattice vacancies in each layer at the substrate. These defects support the diffusion of the A element (Si) between the layers. First results from as-deposited films showed the formation of the $TiC_{0.95}$ phase at a substrate temperature of 25°C. With respect to the formation process of Ti_3SiC_2, the diffusion of the A element could be supported by increasing the substrate temperature. Thus, different sample-sets were prepared with a varied thickness of each layer at different substrate temperatures from 20°C to 800°C onto amorphous Si_3N_4 substrates. The thicknesses of the layers were calculated by "SRIM" software concerning the kinetic energy of the incoming ions and the recoiled atom distributions.

Afterwards, the diffusion profiles and elemental distributions of the as-deposited thin films were analyzed by glow discharge optical emission spectroscopy and electron energy loss spectroscopy. The structure and the phase formation of the as-deposited films were determined by X-ray diffraction using the Gracing Incidence method and transmission electron microscopy. Electrical properties as electrical conductivity were investigated by 4-point-probe. The indentation modulus and the Martens hardness were determined by nanoindentation.

[1] Eklund P, Beckers M, Jansson U, Hogberg H, Hultman L. The M(n+1)AX(n) phases: Materials science and thin-film processing. Thin Solid Films 2010;518:1851.

3:50pm **B3-9 Pusled Laser Deposition of Csl, TiC, and HfC Coatings for Field Emission Cathodes**, ***T.C. Back***, Air Force Research Laboratory/UTC, *M. Cahay,* University of Cincinnati, *P.T. Murray,* University of Dayton, *S.B. Fairchild (steven.fairchild@wpafb.af.mil), J. Boeckl*, Air Force Research Laboratory

Field emission cold cathodes continue to be an important area of research for uses such as electron microscopy, novel x-ray sources, vacuum electronic THZ sources, and high power microwave sources. Each of these applications typically requires high current densities with a high brightness electron beam. Fibers made from single walled carbon nanotubes (SWNTs) have demonstrated considerable promise as field emission cathodes. To further exploit the field emission properties of these fibers, uniform low work function coatings were applied to the SWNT fiber surface by pulsed laser deposition (PLD) and thermal evaporation. Low work function coatings have the potential for lowering the turn-on voltage required for emission as well as potentially protecting the fiber cathode from ion back bombardment from the anode. Cesium is commonly used in cathode coatings due to its low work function. For this study, CsI was used as starting material for both laser deposited and thermally evaporated thin films. XPS showed that CsI films deposited by PLD are cesium rich as compared to the thermally evaporated films and have a Cs:I ratio of 2:1. This result agreed well with UPS and in-situ Kelvin probe measurements which yielded work function values more typical of cesium, 2.0-2.4 eV. Carbide coatings were also studied since Cs is susceptible to depletion from the cathode surface which shortens the lifetime of the cathode and increases down time for repair. Hafnium carbide (HfC) and titanium carbide (TiC) were chosen due to their robust nature and stability at high temperatures. Although not as low as Cs, they still have the ability to lower the surface work function of the cathode by greater than 1eV. X-ray photoelectron (XPS) and Auger electron (AES) spectroscopy were used to characterize the chemistry of these coatings. Ultraviolet photoelectron spectroscopy (UPS) and in-situ Kelvin probe measurements were used to determine work functions. In-situ XPS, AES, and UPS were used to optimize the deposition process.

4:10pm **B3-10 Growth and Characterization of SBN60:Ce Thin Films**, ***H. Buller***, *D. Evans (dean.evans@wpafb.af.mil),* Air Force Research Laboratory, *G. Cook,* Air Force Research Laboratory/Azimuth, *S. Basun,* Air Force Research Laboratory/UTC, *G. Kozlowski*, Air Force Research Laboratory/Wright State University

Hybrid cell structures comprising a liquid crystal layer in between two photorefractive crystalline windows have been used for two beam coupling applications. They have shown absorption losses due to the thickness of the windows. Photorefractive thin films, that can replace the windows to minimize absorption loss. The Photorefractive thin films have been grown using Pulsed Laser Deposition (PLD) on substrates such as Lanthanum Aluminum Oxide (LAO), Magnesium Oxide (MgO), and undoped Strontium Barium Niobate (SBN). This method has been shown to grow very uniform films from 200 nm-1 µm of Strontium Barium Niobate doped with Cerium (SBN:Ce). Although these films are usually grown epitaxially with the c-axis normal to the surface, the growth of c-axis in the plane has been investigated. The direction of the c-axis is important for creating a space charge field on the surface of the film, which is used to control the liquid crystal layer. X-Ray Diffraction (XRD) has been used to study the lattice structure of the films. It was determined that films grown at 760°C and oxygen pressures of 200 mT give films with the c-axis normal to the surface independent of the substrate type and crystallographic orientation used. Results from the investigation of annealing and poling under electric fields to control the c-axis orientation will be discussed.

4:30pm **B3-11 Structural and Compositional Control of BCN Films in PLD-Based Deposition Processes**, ***M.A. Lange*** *(Matthew.Lange@WPAFB.AF.MIL),* AFRL/RXBT and UTC, *A. Reed, C. Muratore,* Air Force Research Laboratory, *J. Hu,* Air Force Research Laboratory/UDRI, *J.J. Gengler,* Air Force Research Laboratory/Spectral Energies, *J.E. Bultman,* Air Force Research Laboratory/UDRI, *J.G. Jones, A.A. Voevodin*, Air Force Research Laboratory

Carbon-based structures are well-known for pushing the limits of materials properties for important technological applications, such as thermal & electrical conductivity, mechanical elasticity, and strength. Sharing some similar physical and chemical properties of useful carbon-based structures, but with enhanced thermal stability, is boron carbon nitride, (BCN), which may be of interest for a range of advanced aerospace applications. BCN films have been grown using pulsed laser deposition, (PLD) in conjunction with other PVD techniques including magnetron sputtering with a choice of power coupling schemes (i.e., dc and HIPIMS). By selecting appropriate plasma sources, the flux of material at the substrate maybe changed which in turn allows manipulation of film structure and composition. For example, films with strong (100) orientations have been grown with pulsed laser deposition of a segmented boron nitride and graphite target in vacuum, as characterized with x-ray diffraction, while films with mixed (002)/(100) orientations have been grown using hybrid PLD/HIPIMS processes with a boron nitride PLD target, and graphite target on a HIPIMS magnetron. Using these PLD-based hybrid techniques, a broad range of compositions (measured by XPS) and structures (characterized with XRD, Raman spectroscopy and electron microscopy) have been explored, and correlated to thermal and mechanical properties, measured with time-domain thermoreflectance and nanoindentation techniques, respectively. Additionally, optical and electrostatic plasma characterization techniques have been used to correlate relative fluxes and characteristic energies of plasma species to the growth mechanisms of BCN films.

4:50pm **B3-12 Bonding Structures, Mechanical Properties and Biological Behaviors of CN_x Films Prepared by Ion Beam Assisted Deposition and Laser Induced Arc Deposition**, ***T.M. Shao*** *(shaotm@tsinghua.edu.cn), S.B. Wei, L. Yin*, The State Key Lab. of Tribology at Tsinghua University, China

We report some recent progresses in preparation and characterization of carbon nitride (CN_x) films. CNx films with different N contents were prepared by using laser induced arc deposition and ion beam assisted deposition, respectively. Bonding structures of the CN_x films were characterized by using X-ray photoelectron spectroscopy and Raman spectroscopy. Mechanical properties of the CN_x films were studied by using nanoindentation tester and tribo-tester. Influence of N content on the properties of CN_x films was investigated. Adsorption behavior of fibrinogen to the CN_x flms with different N content was investigated and comparison was made with the results of Ti and TiN films. The results show that CN_x film with adequate N content exhibited smallest fibrinogen absorption among the films tested. Frictional behavior of CN_x films deposited on stainless steel, under the lubrication of artificial saliva, was studied on a standard tribo-tester and a home made apparatus which simulates the friction between archwire and bracket in orthodontic application. Corrosion test was also performed for the CN_x films. The results show that both frictional behavior and corrosion resistance of the arch wire (stainless steel) were evidently improved after deposited with CN_x film.

Fundamentals and Technology of Multifunctional Thin Films: Towards Optoelectronic Device Applications
Room: Sunset - Session C2/F4-3

Thin Films for Photovoltaics and Active Devices: Synthesis and Characterization
Moderator: T. Miyata, Kanazawa Institute of Technology, A.P. Ehiasarian, Sheffield Hallam University

1:30pm **C2/F4-3-1 Ultrathin Metals – a New Approach for Transparent Conductive Films**, ***O. Zimmer*** *(otmar.zimmer@iws.fraunhofer.de), M. Schwach,* Fraunhofer-Institut für Werkstoff- und Strahltechnik IWS Dresden, Germany, *S. Schädlich*, IWS Dresden, Fraunhofer Institute for Material and Beam Technology, Germany

Transparent conductive oxides (TCO´s) are well established materials for transparent electrodes in various applications. By using TCO´s a good combination of transparence and conductivity can be obtained. However, the conductivity of TCO´s is lower by a factor 100…1000 in comparison to metals. On the other hand side, the deposition of thin, transparent metal films is state of the art, for example on architectural glass. These films are transparent but non-conductive.

The aim of the recent study is to create transparent silver films with high electrical conductivity.

The reason of the non conductivity of classical thin silver films is the island like structure of these films. The atoms tend to form separated islands during the growth of the first atomic layers. Within the thickness range of approximately 10 nm (percolation threshold) the film converts to a closed layer with high electrical conductivity and low transparence.

The way to obtain a high conductivity below 10 nm film thickness is to avoid the island-like film growth at the beginning. This can be realized by using highly energetic silver ions for the film deposition. The silver ions are implanted into the topmost atomic layers of the substrate surface. Thus the nucleation into clusters or islands is prevented, a uniform coverage of the surface is provided and an electrical conductivity at very low film thicknesses is obtained.

The filtered high current pulsed arc technology (F-HCA) can provide multiple charged metal ions. Thin silver films produced by F-HCA were deposited on glass substrates. It could be shown, that films with a few nm in thickness can provide optical and electrical properties comparable to TCO´s in the sub-micron range. It can be estimated that thin transparent conductive metallic films have a great potential for a lot of applications, such as for displays, solar cells and others.

1:50pm **C2/F4-3-2 Energy Band Lineup of Transparent Conducting Materials and High Efficient Electrodes for Organic Semiconductors**, ***H. Yanagi*** *(hyanagi@yamanashi.ac.jp),* University of Yamanashi, Japan*, T. Kamiya, H. Hosono*, Tokyo Institute of Technology, Japan

Transparent conducting oxides are attractive materials from a viewpoint of transparent electronics. One of the most promising applications is a transparent thin film transistor for next generation displays. When we apply these materials to an actual device, it is important to know energy positions of the valence band maxima (VBM) and the conduction band minima (CBM) with respect to the vacuum level. In this talk, the VBMs and the CBMs of transparent conducting oxides and related materials are determined by using ultraviolet photoelectron spectroscopy (UPS) and summarized in an energy band lineup. In addition, interfacial electronic structures between some of these materials and typical organic semiconductors measured by UPS will also be given as an application of the band lineup. High efficient carrier injection is an important issue to be solved to realize high performance heterojunction devices including OLEDs and the band lineup provide useful information to find out candidates of high efficient electrodes. We have examined RT-stable electride, C12A7:e^-, [1] and Cu^+ based p-type degenerated semiconductors, LaCuOSe [2] and Cu_xSe, [3] as candidates of high performance cathode and anode, respectively.

[1] S, Matsuishi et al., *Science*, **301**, (2003) 626.

[2] H. Hiramatsu et al., *Appl. Phys. Lett.* **91**, (2007) 012104.

[3] H. Hiramatsu et al., *J. Appl. Phys.* **104**, (2008) 113723.

2:10pm **C2/F4-3-3 Quality Improvement of Organic Thin Films Deposited on Vibrating Substrates**, *Y. Angulo, P.G. Caldas,* ***M. Cremona*** *(cremona@fis.puc-rio.br), R. Prioli*, PUC-Rio, Brazil

Most organic light-emitting diodes (OLEDs) have a multilayered structure composed of functional organic layers sandwiched between two electrodes. Thin films of small molecules are generally deposited by thermal evaporation onto glass or other rigid or flexible substrates. The interface state between two organic layers in OLED device depends on the surface morphology of the layers and affects deeply the OLED performance. The variation in the morphology of an organic thin film depends on the substrate, the contamination of the substrate, the deposition rate and the substrate temperature. For organic films substrate temperature cannot be increased too much due to their thermal stability. However, studies in inorganic thin film indicate that it is possible modify the morphology a film by using substrate ultrasonic vibration in the kHz range without increasing the substrate temperature.

In this work, the effect of the resonance vibration of glass and silicon substrates during thermal deposition in high vacuum environment of organic thin films with different deposition rates was investigated. The vibration used was in the range of hundreds of Hz and the substrates were kept at room temperature during the process. The nucleation and subsequent growth of the organic films on the substrates have been studied by atomic force microscopy (AFM). In the case of films grown with 1 Å/s as deposition rate and using a frequency of 100 Hz with an oscillation amplitude of some micrometers the results indicate a reduction in the island density and a decrease of 0,26 nm in the roughness. Moreover, the OLED devices fabricated with organic films deposited under these conditions showed an improved efficiency and an increase in their luminance of about 350 cd/m^2

2:30pm **C2/F4-3-5 Investigation of the Gate-Bias Induced Instability for InGaZnO TFTs Under Dark and Light Illumination**, ***T.-C. Chen*** *(d972030010@student.nsysu.edu.tw), Y.-K. Yang*, National Sun Yat-sen University, Taiwan

Mechanism of the instability for indium-gallium-zinc oxide thin film transistors caused by gate-bias stress performed in the dark and light illumination was investigated in this paper. The parallel V_t shift with no degradation of subthreshold swing (*S.S*) and the fine fitting to the stretched-exponential equation indicate that charge trapping model dominates the degradation behavior under positive gate-bias stress. In addition, the significant gate-bias dependence of V_t shift demonstrates that electron trapping effect easily occurs under large gate-bias since the average effective energy barrier of electron injection decreases with increasing gate bias. Moreover, the noticeable decrease of threshold voltage (V_t) shift under illuminated positive gate-bias stress and the accelerated recovery rate in the light indicate the charge detrapping mechanism occur under light illumination. Finally, the apparent negative V_t shift under illuminated negative gate-bias stress was investigated in this paper. The average effectively energy barrier of electron and hole injection were extracted to clarify that the serious V_t degradation behavior comparing with positive gate-bias stress was attributed to the lower energy barrier for hole injection.

2:50pm **C2/F4-3-6 Effect of N_2O Plasma Treatment on the Improvement of Instability Under Light Illumination for InGaZnO Thin-Film Transistors**, ***T.-Y. Hsieh*** *(m982030004@student.nsysu.edu.tw)*, National Sun Yat-Sen University, Taiwan

This paper investigates the impact of N_2O plasma treatment on the light-induced instability of InGaZnO thin film transistors with SiO_2 passivation layer deposited by plasma-enhanced-chemical-vapor-deposition (PECVD). For untreated device, because the SiO_2 passivation layer deposited by PECVD would cause extra trap states, thus, the anomalous subthreshold leakage current is attributed to the source side barrier lowering effect induced by trap-assisted photogenerated hole. Contrarily, the device treated by N_2O plasma both on gate insulator and active layer could effectively suppress the instability under illumination. In order to clarify the influence of N_2O plasma treatment, device with N_2O plasma treatment only on gate insulator was investigated. The slight improvement of the light-induced subthreshold leakage current for N_2O plasma treatment on gate insulator demonstrates that post N_2O plasma treatment on active layer was critical to prevent the damage from the SiO_2 passivation process. On the other hand, the instability of threshold voltage (V_t) under illuminated negative bias stress (NBIS) was significantly improved by N_2O plasma treatment in contrast to the untreated device. Furthermore, the different dark recovery rate follows NBIS for untreated and N_2O plasma-treated device indicates different hole trapping levels in the energy band.

3:10pm **C2/F4-3-7 Surface States Related the Bias Stability of Amorphous In-Ga-Zn-O Thin Film Transistors Under Different Ambient Gas**, ***Y.-C. Chen*** *(oa_ccc@hotmail.com)*, National Sun Yat-Sen University, Taiwan

This paper investigates the origin of the bias stability under ambient gas (oxygen moisture and vacuum) of In-Ga-Zn-O thin film transistors with different annealing condition. In Zn-based TFTs, the electrical characteristic of device is a strongly function with the ambient gas, the simultaneous gas ambient and bias stresses are applied on annealed devices, 150℃ or 330℃ in atmosphere ambient, to studies this issue. The result shows the 330℃ annealed device has worst relibility. We suppose that the sensitivity of gas ambient depending the surface state of back channel, which is associated to related to the annealing term.

3:30pm **C2/F4-3-8 Hot Carrier Effect on Gate-Induced Drain Leakage Current in n-MOSFETs with HfO2/Ti_xN_{1-x} Gate Stacks**, ***C.-H. Dai*** *(m953050006@student.nsysu.edu.tw)*, National Sun Yat-Sen University, Taiwan

This paper investigates the effects of hot carrier stress on gate-induced drain leakage (GIDL) current in n-type metal-oxide-semiconductor field effect transistor (n-MOSFETs) with HfO_2/Ti_xN_{1-x} gate stacks. The results indicate that GIDL current has a gradual decrease after the hot carrier stress. This phenomenon can be attributed to interface trap assisted band to band holes injection in high-k near the drain overlap region. The amount of holes injection is further related to the stress voltage across the gate and drain terminals. We also investigated the impact of different Ti_xN_{1-x} composition of metal-gate electrode on characteristics of hot carrier stress, and observed that the degradation of drain current decreases significantly with the increase of nitride ratio. In addition, the variation of GIDL current becomes insignificant due to the fact that nitride atoms fill up oxygen vacancies, reducing the concentration of traps in high-k dielectric.

3:50pm **C2/F4-3-10 Pulse Laser Deposition and Characterization of V_2O_5/Mn_3O_4 Composites Thin Films for Supercapacitor Application**, *C.-C. Chang, **C.-H. Hsu** (chhsu@phys.sinica.edu.tw), K.-W. Yeh, T.-W. Huang, M.-K. Wu*, Institute of Physics, Academia Sinica Taiwan, Taiwan, Republic of China

Supercapacitors based on various modified V_2O_5 or Mn_3O_4 thin films have been reported recently. In this letter we exhibit the effect of V_2O_5:Mn_3O_4 ratio on the performance of supercapacitor. A series of $(V_2O_5)_{1-x}(Mn_3O_4)_x$ (x = 0.05, 0.1, and 0.15) thin films have been prepared by KrF (λ = 248 nm) pulse laser deposition (PLD) on ITO/glass substrate at oxygen partial pressure of 200 mTorr and 250°C. The morphology, structure, optics and electrical characterizations of thin films have been investigated by means of X-ray diffraction (XRD), Scanning electron micrograph (SEM), optical absorption and cyclic voltammograms. The doped $(V_2O_5)_{1-x}(Mn_3O_4)_x$ thin films exhibit significantly improved capacity and charge/discharge rate in comparison with the undoped thin films. These results demonstrate that PLD doped $(V_2O_5)_{1-x}(Mn_3O_4)_x$ thin film is a promising candidate in supercapacitor application.

4:10pm **C2/F4-3-9 Chemiresistive Chlorine Gas Sensor Based on Spin Coated Copper(II) 1,4,8,11,15,18,22,25-Octabutoxy-29H,31H-Phthalocyanine Films**, ***R. Saini***, *A. Mahajan, R.K. Bedi (rkbedi2008@gmail.com)*, Guru nanak dev University, Amritsar, India

Hazardous effects of chlorine (Cl_2) gas on environment and biological system makes it one of the important pollution issues. Here, we report the fabrication and characterization of chemiresistive chlorine gas sensor based on copper(II) 1,4,8,11,15,18,22,25-octabutoxy-29H,31H-phthalocyanine ($CuPc(OBu)_8$) films, deposited by low cost spin coating technique. $CuPc(OBu)_8$ films of thickness 50 nm were chosen for the fabrication of chemiresistive gas sensor. This gas sensor shows a response of the order of 90 % to few parts per million level of chlorine with response time of 5 minutes at room temperature 25 °C. The interactions between sensor and analytes followed first order kinetics with rate constant $0.5 \leq k \leq 1$. The chemiresistive sensor showed very good stability at room temperature over a long period of time. The effect of gas sensing temperature and concentration of gas has also been observed.

Biomedical Coatings
Room: Royal Palm 4-6 - Session D3

Coatings for Mitigating Bio-Corrosion, Tribo-Corrosion and Bio-Fouling

Moderator: M.M. Stack, University of Strathclyde, M.T. Mathew, Rush University Medical Center

1:30pm **D3-1 Metal Oxide Coatings for Dental Implants: What is Important?**, *P.N. Rojas, G. Ramírez, A. Almaguer,* Universidad Nacional Autonoma de Mexico*, R. Olivares-Navarrete,* Georgia Institute of Technology*, P. Silva-Bermudez, S. Muhl, **S.E. Rodil** (ser42@iim.unam.mx)*, Universidad Nacional Autonoma de Mexico **INVITED**

Metal alloys are widely used in biomedical devices and components, especially as hard tissue replacements as well as in cardiac and cardiovascular applications, because of their desirable properties, such as relatively low modulus, good fatigue strength, toughness, formability and machinability and bioinertia. However, they are still far from the ideal biomaterial. Some of the issues that need to be improved are corrosion resistance in body fluids, improving the cell-surface interactions in order to promote a specific cell response (bioactivity instead of bioinertia), such as, bone-growth or antibacterial properties. Similarly, for some applications the tribological response needs to be improved, reducing friction coefficients and increasing the wear resistance. Remarkably, all these requirements are associated to surface-related-properties instead of bulk properties. Therefore a recent proposal has been the development of different surface treatments for the currently used metallic alloys. One popular method of surface modification involves the deposition of coatings or thin films, which allows the selective modification of the surface-mechanical and biological properties of conventional materials retaining their bulk properties. Obviously, the purpose of the coating material is to improve all the fails of the metallic implants, otherwise the costs will not be attractive. It means that the coatings have to be smartly engineered to fulfill the different requirements. The actual development of multilayered or nanocomposite coatings is an attractive method to obtain surfaces with multifunctional properties.

In this review, we present our research work on sputtering deposition of metal-transition oxide films on stainless steel substrates as candidates for dental implants. Titanium, zirconium, tantalum and niobium oxides were produced and their corrosion resistance has been evaluated using potentyodynamic polarization and electrochemical impedance spectroscopy using physiological solutions. Similarly, the oral bacterial attachment and biofilm formation on the different surfaces was studied, as well as the effect of the bacterial attachment on the electrochemical response. The biocompatibility of the coatings have also been evaluated directly in-vitro using osteoblast-like cells or indirectly by studying the protein adsorption on the surfaces, which dictates the later cell-surface interactions. Moreover, the effect of the film thickness, structure, surface energy and topography on the functional response has also been analyzed in order to determine what is important for the future development of biomedical coatings.

2:10pm **D3-3 Synthesis, Characterization and Performance of Silver Nanoparticle Coatings on Bioimplants**, ***C.G. Takoudis*** *(takoudis@uic.edu)*, University of Illinois at Chicago

In 2003, 220,000 Total Hip Replacements (THR) were performed and this figure is expected to rise. Of the surgeries performed, 8% of the THR's resulted in infections and required revisions. Biofilms are matrices of bacteria enveloped in proteins and polysaccharides which evade the immune system. The goal of this work is to inhibit bacterial colonization with a silver nanoparticle infused linseed oil coating on Ti90Al6V4 alloy which could prevent biofilm formation and avert infection.

Silver nanoparticles with diameters less than 30 nm are believed to be non-toxic to living tissues. In this project, silver nanoparticles are formed by means of the autoxidation process that occurs during the drying of the linseed oil rich in polyunsaturated fatty acids. The abstraction of hydrogen from the fatty acid chains creates free radicals that react with silver benzoate to release silver nanoparticles. The confirmation of nanoparticle formation and range of diameters are determined with transmission electron microscopy. Three groups consisting of coated Ti90Al6V4 pins, linseed oil-coated Ti90Al6V4 pins and a control group consisting of uncoated Ti90Al6V4 pins are exposed to Staphylococcus aureus and Escherichia coli, respectively. The bacterial growth in these three groups is quantified at 8, 24 and 48 hours by phase contrast microscopy. Furthermore, coated pins are stored and continually tested for long term stability during three weeks of experimentation. Our results seem to support the infection-free properties of the silver nanoparticle coating. Over the course of 48 hours exposure to bacterial growth, the silver nanoparticle coated pins are found to contain the least amount of bacteria out of the three groups proving the bactericidal effects of the silver nanoparticle coating.

2:30pm **D3-5 Tribo-Corrosion Mechanisms of Ti Based PVD Coatings on Y-TZP Dental Implants**, ***M.M. Stack*** *(margaret.stack@strath.ac.uk),* University of Strathclyde, UK, *W.-L. Li*, National Cheng Kung University, Taiwan

In studies of tribo-corrosion of dental replacement materials, there have been few evaluations of the performance of coatings. This is despite the fact that coatings may provide a significant opportunity to reduce wear in such environments. In addition, there have been few studies of the characterization of mechanisms of tribo-corrosion in such conditions for coated systems.

Recent work on Y-TZP materials (a dental replacement material) has shown that the effect of pH and exposure time may change the erosion-corrosion mechanism on the surface. Wear and phase transformation maps have been generated for the material. The results have identified that at low pH values, and longer exposure times, the wear rate significantly decreases in such conditions.

In this work, a range of Ti based PVD coatings on Y-TZP were evaluated under combined erosion-corrosion conditions. Wear maps were produced using the results. The maps indicate the mechanisms of wear and the conditions under which the coatings may modify the wear rate in such environments.

2:50pm **D3-7 Biotribolayer Formation in Metal-on-Metal Hip Prostheses- a Beneficial Coating Process?**, ***M.A. Wimmer*** *(markus_wimmer@rush.edu), M.T. Mathew, M.P. Laurent,* Rush University Medical Center*, A. Fischer,* University of Duisburg-Essen*, J. Jacobs*, Rush University Medical Center **INVITED**

One of the bearing combinations for total hip replacement is a self-mating metal-on-metal (MoM) articulation based on cobalt-chromium-molybdenum alloy. Wear of these implants is of concern, because they are intended to stay a life-time in the patient's body Wear particles can cause detrimental biological effects if released in too high quantities into the tissues. Studies have suggested that among the major wear mechanisms of MoM joints tribochemical reactions (TCR) are predominant. These TCRs result in the reaction of the metal surface with the interfacial medium (i.e., synovial fluid), and form a tribomaterial at the surface. The tribomaterial consists of a mixture of nanocrystalline ceramic and metallic constituents together with organic matter and forms a patchy coating on the surface. While this mechanism has shown advantageous effects on MoM wear, its corrosive (and tribocorrosive) behavior is unknown. In one of the studies, three different surface conditions were electrochemically investigated in a protein containing solution mimicking synovial fluid: (i) new, out of box, (ii) retrieved MoM head with tribomaterial, (iii) retrieved MoM head after enzymatic digestion of the tribomaterial. Because the number of retrievals was limited, we substantiated the study using samples with artificially prepared tribomaterial. Its nanocrystalline structure was verified using TEM before the experimental investigation. Results depicted a shift in the corrosion potential to higher anodic potential of the MoM samples with tribomaterial, suggesting a more noble behavior with better corrosion resistance than samples without tribomaterial coverage. However, the capacitive behavior of the tribomaterial under impedance measurements was inferior to samples without coverage. It was concluded that, in addition to being protective, the tribomaterial delays the corrosion kinetics and protective oxide films are generated slower than on samples without tribomaterial. This is an important finding because the tribomaterial is at risk of being abraded during articulation. Therefore, the talk will highlight the need of further investigations to better understand the formation and retention of this natural, dynamic coating layer. Further, we will look into necessary studies to better understand the role of the tribolayer on corrosive and tribocorrosive challenges in vivo.

3:30pm **D3-10 Fabrication of Superhydrophobic Surfaces on Stainless Steel Substrates for Potential Biomedical Applications**, *S. Beckford, **M. Zou** (mzou@uark.edu)*, University of Arkansas

The benefits of superhydrophobic surfaces are commonly seen in the biomedical field. For example, bacterial adhesion to biomedical implant surfaces can be greatly reduced if the surface is superhydrophobic. Since the superhydrophobicity of water repellant leaves in nature is often attributed to their microstructures combined with the presence of water repellant waxy nanocrystals on these microstructures, mimicking nature to create micro-/nano-scale topography and chemistry on material surfaces to render superhydrophobic surfaces has attracted much attention. This poster reports the fabrication of micro and nano-textured surfaces on stainless steel surfaces to produce superhydrophobic surfaces for possible use in biomedical applications. Various fabrication techniques, including sandblasting, thermal evaporation, aluminum induced crystallization (AIC) of amorphous silicon (a-Si), and deep reactive ion etching C_4F_8 passivation, were investigated to change the topography as well as chemistry of the stainless steel surfaces. The topographies resulting from these surface modifications were analyzed through scanning electron microscopy and surface profilometry. The wetting properties of these surfaces were characterized by water contact angle measurement. This study determined that the most effective process for creating superhydrophobic surfaces is to perform AIC of a-Si on plain stainless steel, leading to a water contact angle of more than 160°. The results of this study also showed that sharp nano textures fabricated by AIC of a-Si produced higher water contact angles than smooth nano textures produced by thermal evaporation.

3:50pm **D3-11 What is the Role of Lipopolysaccharide (LPS) on the Tribocorrosive Behavior of Titanium in Dentistry?**, ***V.A.R. Barao** (ricardo.barao@hotmail.com),* Univ Estadual Paulista, Brazil*, M.T. Mathew,* Rush University Medical Center*, J.C. Yuan,* University of Illinois at Chicago*, W.G. Assuncao,* Univ Estadual Paulista, Brazil*, M.A. Wimmer,* Rush University Medical Center*, C. Sukotjo*, University of Illinois at Chicago

Titanium has been widely used to fabricate dental implants due to its resistance to corrosion and biocompatibility. However, during mastication, implants are exposed to mechanical, chemical and microbiological actions, which can be considered a continuous complex degradation process. Studies have looked at chemical corrosion of titanium; however, very few have reported on the effect of combined chemical, mechanical and microbiological actions, which resemble the oral environment. A new multi-disciplinary research area, tribocorrosion, can address such issues.

This study aimed to investigate the tribocorrosive nature of titanium in artificial saliva (pH 6.5) with the presence of *Escherichia coli* lipopolysaccharide (LPS). A total of 24 titanium discs, 12-mm diameter and 7-mm thickness, were used. Samples were divided into 8 groups (n=3) as a function of different titanium type (commercially-pure titanium and Ti-6Al-4V alloy) and LPS concentration (0, 0.15, 15 and 150µg/ml).The sliding duration (2000 cycles), frequency (1.2Hz) and load (20N) parameters were selected to simulate the oral environment and mastication process. Electrochemical impedance spectroscopy was conducted before and after tribocorrosion to comprehend the changes in the corrosion kinetics. Worn surfaces were examined using white-light-interferometry microscopy and scanning electron microscopy. Total weight loss (K_{wc}) and roughness values were calculated. Data were analyzed using one-way ANOVA, and Tukey's HSD and paired-T tests were used where appropriate (α=.05).

LPS influences the tribocorrosive behavior of both titanium types. LPS statistically accelerated the ions exchange between titanium and saliva, and reduced the resistance of titanium surface against corrosion ($p<.05$). Sliding tends to decrease the protectiveness of titanium surface against corrosion. In general, Ti-6Al-4V alloy exhibited better corrosion behavior. Both titanium types showed similar K_{wc} values ($p>.05$). LPS increased the weight loss of commercially-pure titanium ($p=.041$), and the roughness values ($p<0.001$). The study clearly indicates that LPS negatively affect the corrosion/wear behavior of titanium, which might increase the failure rate of dental implants.

4:10pm **D3-9 Bio-Tribological Properties of UHMWPE Against Surface Modified Titanium Alloy**, ***D. Xiong** (xiongds@163.com), L. Xiong*, Nanjing University of Science and Technology, China

Wear is primarily cause of failure of artificial joints. In this study, two–step plasma immersion ion implantation technique, thermal oxidation (TO) treatment, laser surface texturing (LST) treatment and TO+LST treatment were developed and applied for modification of Ti6Al4V alloy. The surface layer structures and the wettability of the modified alloys were investigated. A pin-on-disc tribometer has been used to evaluate the tribological response of UHMWPE to untreated, two–step ion implanted, TO treated, LST treated and TO+LST treated Ti_6Al_4V counterfaces under distilled water and serum lubricated. The result showed that the after the ion implanted or TO-Treated, the TiO,Ti_2O film was formed in the subsurface of Ti_6Al_4V alloys. The wettability of the modified alloy surfaces were increased significantly. The friction coefficients and the wear rates of UHMWPE against the modified Ti_6Al_4V alloy decreased significantly.

Tribology and Mechanical Behavior of Coatings and Thin Films
Room: California - Session E1-2

Friction and Wear of Coatings: Lubrication, Surface Effects, and Modeling

Moderator: J.C. Sanchez-Lopez, Instituto de Ciencia de Materiales de Sevilla (CSIC-US), H. Evans, University of Birmingham, S.M. Aouadi, Southern Illinois University, Carbondale

1:30pm **E1-2-1 Developing Coatings for Increased Operational Life in Gears**, ***S.J. Bull** (s.j.bull@ncl.ac.uk), A. Oila*, Newcastle University, UK

Improvement of the life of components which undergo a combination of rolling and sliding in service, such as gears, remains an engineering challenge in particular as components get smaller and loads and slide-roll ratios increase. The major failure mode in such cases is micropitting originating from cracking generated by surface contact fatigue. Reducing the frictional tractions at asperity contacts should reduce the stresses driving such behaviour and reduce micropitting and there has been considerable work aimed at developing lubricant additive packages to achieve this. The most successful of these packages contain chemical constituents with high environmental impact and indeed several are potent carcinogens so there is a need to identify more benign solutions to the problem. Recently it has been shown that inorganic fullerene materials (IFLM) based on WS_2 have the potential to produce low friction transfer layers when added to lubricants and coatings. However, the majority of work to date has been carried out under pure sliding conditions. Thus, the objective of the work presented here was to assess the influence of IFLM in hard coatings on the fatigue and wear performance of tribological contacts subjected to rolling/sliding motion such as gears.

Preliminary wear tests were carried out using a double disc rig with specimens manufactured from carburized S156 steel in the uncoated form and coated with CrN containing WS_2 fullerenes. The results show that significant increase in the operational life of rolling/sliding components can be achieved by using coatings incorporating a sufficient volume fracion of inorganic fullerene-like materials. The IFLMs produced a low friction transfer layer on the surface which was responsible for the good performance. Coatings were then developed to produce a similar low friction transfer layer based on the combination of a hard coating and a metal sulphide. Full scale back-to-back gear tests were then performed to see if the improvements could be transferred to the component scale. Good results were achieved when the transfer layer was also formed in this case. The factors affecting transfer layer formation in service will be discussed in this presentation.

1:50pm **E1-2-2 Understanding Lubrication Mechanism of Novel Boron-Based Lubricant Tested on ta-C Coating for Automotive Applications**, ***K. Mistry*** *(kmistry@anl.gov), J.-H. Kim, E. Briggs, O.L. Eryilmaz, A. Erdemir*, Argonne National Laboratory

Improvement of fuel economy and component durability along with reduced emissions are important concerns for future engine systems. On other hand, the operating conditions are becoming more severe due to continual need of high power as well as light weight engines. Conventional lubrication (ZDDP and MoDTC) were optimized for conventional material surface (steel) thus, gave good tribological performance but had concerns associated with emissions. On other side, advanced surfaces like Diamond-like-Carbon offered improved tribological performance for conventional lubricants than the steel surfaces. Solid lubricants like Graphite, MoS_2, WS_2, PTFE, BN, Boric acid offered high bearing-load and low friction due to their lamellar structure orient parallel to the sliding surface along with low toxicity. Colloidal lubricant of nano-particles of solid lubricants like MoS_2, WS_2, onion-like-carbon (OLC), BN, Boric acid offered good tribological performance on steel.

The current work presents tribological performance of novel Boron based Lubricant on the ta-C coated steel surface. High frequency reciprocating rig (HFRR) tribometer was used to evaluate the friction and wear behavior of these lubricants. The performance of the lubricants was investigated under boundary lubrication regimes. High temperature and high contact pressure conditions on the HFRR tribometer. Optical profilometry was used to analyze the wear on the contact surfaces.

It was observed that novel Boron additive tested on ta-C surface gave low friction and extremely low wear. In order to understand the lubrication mechanism for the observed novel boron based additive on ta-C surface, the chemistry of the tribofilm formed on the contact surfaces were characterized by ToF-SIMS (Time of Flight - Secondary Ion Mass Spectroscopy), XPS (X-ray Photoelectron Spectroscopy) and FIB-TEM (Focused Ion Beam – Transmission Electron Microscopy). The post-test surface analysis validates the influence of the novel Boron additive that form reaction film on ta-C surface with super lubricious characteristics and hence gave good performance.

2:10pm **E1-2-3 Influence of the Lubricant on the Frictional Behaviour of Amorphous Carbon Coatings Sliding Against Steel**, ***C. Heau*** *(cheau.hefrd@hef.fr), P. Maurin-Perrier, L. Mourier*, HEF R&D, France

Reducing friction in the engine is a key factor towards lowering the automotive CO_2 emissions. A 25 to 30% friction reduction is commonly observed in a a-C:H coated tappets valvetrain system at low rotational speed when the system operates in boundary lubrication regime. Such tests are both time consuming and expensive. The purpose of the study is to define a simple test where the friction reducing is correlated to the one observed in car engine. Particularly, the purpose is to define the effect of oil, additives and coating nature on friction reduction. To ensure representativeness in terms of interaction between coating and oil, it must be operated in boundary lubrication condition all along the test.

Friction tests were carried out using a ball on disk configuration. The hard coating was deposited on the flat sample. The ball wear is correlated to small variations in coating roughness as determined by AFM. The stabilised friction coefficient is correlated to the wear of the ball and the resulting decrease of pressure at the end of the test. The lubrication regime could change along the friction test from boundary to elastohydrodynamic regime.

To overcome this problem, the tribology configuration was changed. The coating was deposited on the ball. The wear on the ball is negligible and the contact pressure remains constant even after 25000 cycles. The friction reducing was similar to the one observed in an engine test. That configuration enabled to test oils such as SAE 5W30, 0W20, Polyalphaolefine (PAO) and PAO with 1% Glycerol Monooleate (GMO). Using PAO oil, the stabilized friction coefficient of a-C:H coating was drastically reduced (0.060) compared to the friction coefficient using fully formulated engine oils (0.085). The experiments have shown that the degradation of friction is correlated to the formation of the anti-wear film on the steel. When using fully formulated oils, ZnDTP decomposes and forms a coloured film on steel, mainly composed of O, P and Zn. To demonstrate the detrimental effect of the anti-wear film building up on steel, a test was carried out using 5W30 oil. When the anti-wear film was built, the 5W30 oil was rinsed with solvents and replaced by PAO oil. Instead of decreasing to 0.06, the friction coefficient was drastically increased to 0.13. Changing the friction track to a radius where the DLC coated ball was slide against steel without anti-wear film, the friction coefficient immediately started at 0.060, thus evidencing that anti-wear additives did not lead to film build up on the coating. The use of GMO addition to PAO produces a further reduction of friction to 0.05.

2:30pm **E1-2-4 Nanocomposite Ti-Ni-C Coatings for Electrical Contact Brush Applications**, ***M. Malmros*** *(martina.malmros@angstrom.uu.se), U. Wiklund*, Uppsala University, Sweden

Nanocomposite Ti-Ni-C coatings are investigated for their electrical and tribological properties. It has been shown that nanocrystalline TiC in an amorphous carbon matrix has a contact resistance comparable to metallic coatings but preferable tribological properties. The addition of a non-carbide forming metal helps to ensure the presence of a lubricating layer in the contact for compositions with little carbon matrix.

The intended application is a type of contact brush for signal and power transmission where the coating deposited on a spring steel wire slides against a rotating metal-graphite composite. In such metal-graphite composites, graphite provides a good conductivity and it is a well known solid lubricant and the metal is added to further enhance the conductivity. The accuracy of the power- and signal transmission is of highest priority in the application but if the wear rate could be lowered, possibly by the use of a Ti-Ni-C coating, the life time of the carbon contact brush may be improved.

Different compositions of the Ti-Ni-C coatings are investigated in order to find the optimal composition with balanced low wear of both the coating and the metal-graphite. The amount of amorphous carbon matrix in the coating affects the hardness which is of importance for the wear of the system, where the coating is by far the hardest component. The amount of matrix also affects the friction as it acts as a solid lubricant.

The wear rate of the metal-graphite, without current passing through it, is measured for different spring loads and rotational speeds. The coated spring is examined after 20 million revolutions using SEM and EDS to study the wear and the formation of tribofilms. For one certain spring load and rotational speed it is investigated how the current affects the wear rate of the metal-graphite and the formation of tribofilms in the contact. The transmitted current is monitored to investigate the stability over time.

A second experimental setup with cylinders in reciprocal motion allows for investigation of the contact resistance at a higher contact pressure. The coating is examined both self-mated and against the metal-graphite.

The usefulness of the nanocomposite Ti-Ni-C coating for this particular electrical contact application as well as for electrical contacts in general is evaluated and discussed.

2:50pm **E1-2-5 Space Tribometers: Experiments on Orbit**, *B.A. Krick*, ***G.W. Sawyer*** *(wgsawyer@ufl.edu)*, University of Florida **INVITED**

Eight pin-on-disk tribometers have been made for testing materials in space on board the International Space Station. They will be exposed directly to the low earth orbit environment on board the "Materials on the International Space Station Experiments" (MISSE) platform where they will be exposed to extreme conditions including atomic oxygen, ultrahigh vacuum, radiation (including UV radiation), and thermal ranges from -40°C to 60°C. In order to survive launch and the low earth orbit, these tribometers were designed to be extremely compact, rugged, and reliable. Pin-on-disk tribology experiments are now being performed with a 13.2 mm/s sliding velocity (14 RPM at 9mm wear track radius) and a 1N normal load with hemispherical pin of 1.5875mm radius. Materials tested include $MoS_2/Sb_2O_3/Au$, $MoS_2/Sb_2O_3/C$, $YSZ/Au/MoS_2/DLC$, and SiO doped DLC coatings, and bulk samples of PTFE alumina nanocomposites and gold.

3:30pm **E1-2-7 Ultra-Low Carbon (ULC) Steel Modified by Triode Plasma Nitriding and PVD Coating: Effects on the Micro-Abrasive Wear Behavior**, ***C.A. Llanes Leyva*** *(carloslleyva@ucl.br), C. Godoy,* Universidade Federal de Minas Gerais, Brazil, *A.C. Bozzi,* Universidade Federal do Espírito Santo, Brazil, *J.C. Avelar-Batista Wilson*, Tecvac Ltd, UK

Ultra-low carbon (ULC) steels show low yield strength and excellent formability. Plasma Assisted Physical Vapor Deposition (PAPVD) could be a potential coating method for enhancing mechanical resistance (MATTHEWS, 1995). However, in low mechanical resistance alloys PAPVD coatings may undergo premature failure if the substrate plastically deforms under heavy loading. An extra loading support is necessary for hard coatings to perform satisfactorily. Combined treatments involving plasma nitriding and PAPVD coating have been used to improve the load-bearing capacity of hard films (Avelar-Batista, 2006). This work describes the characterization and micro-abrasive wear behavior of Ti-stabilized ULC steel after surface modification by D.C Triode Plasma Nitriding (DC-TPN) and sequential coating with Cr-Al-N by Electron Beam Plasma Assisted Physical Vapor Deposition (EB-PAPVD). The Ti-ULC substrate, the nitrided steel and the Ti-ULC duplex systems were investigated for chemical composition and via characterization techniques as SEM, EDS, XRD, micro hardness, instrumented indentation hardness and stylus profilometry. Micro-abrasive wear tests were performed in fixed-ball configuration up to 1350 revolutions (in 150 revolutions intervals) using

SiC abrasive slurry and 25mm - 52100 steel ball. Micro-abrasion mechanisms are discussed. When compared to untreated Ti-ULC, nitrided steel is 2.7 times harder while the duplex system is 3.6 times harder (HV0.1). The wear coefficient for the nitrided steel is 22% lower than the one for the steel substrate, both them calculated for the steady state. Regression technique was used for calculating both substrate (kc) and coating (ks) wear coefficients of the duplex system, the latter being 6.6 times lower than the one for the nitrided steel. Coating thickness (3µm max.) was determined from inner and outer diameters of the wear craters. The results indicate that it is feasible to manufacture duplex Ti-ULC steel via PAPVD, with wear resistance improvement from the Ti-ULC to the nitrided steel and especially for the duplex system.

3:50pm **E1-2-9 Application of the Friction Energy Density Approach to Quantify the Fretting Wear Endurance of MoS_2 Solid Lubricant Films: Influence of Temperature and Frequency**, ***S. Fouvry*** *(siegfried.fouvry@ec-lyon.fr), H. Gallien*, Ecole Centrale de Lyon - LTDS, France

The selection of low friction coatings is of great interest to industrial applications. Nevertheless, regarding the lubricant lifetime of the coatings, the selection criteria often depend on the experimental apparatus and contact configuration and then cannot be directly applied to real cases. In this study, we use a model based on the local dissipated energy due to friction under gross slip conditions in fretting wear. Indeed, the maximum value of the local dissipated energy is a unique parameter that takes into account the two major variables in fretting wear experiments: the normal force and the sliding amplitude. Hence by plotting the “lifetime” versus the “local energy density” a single master curve defining the intrinsic endurance of the coating can be defined. To identify the intrinsic “energy density capacity” variable, characterising the coating fretting wear endurance (i.e. used to model the endurance master curve), a flat on flat contact configuration, allowing constant pressure conditions, is applied. This approach is considered to investigate various commercially available polymer bonded MoS2 solid lubricant film used in aeronautical applications to protect titanium surfaces in contact. The effects of contact pressure, displacement amplitude, frequency and temperature are investigated. The results show that, the local energy wear approach is suitable to characterize the lubricant performance for variable mechanical loading conditions (i.e. sliding amplitude and pressure). By contrast, elevate sliding frequencies and temperatures, by activating severe tribo oxidation processes, sharply modify the wear processes so that the endurance values, which are significantly reduced, can not be transposed on the fretting wear master curve. Using this friction energy concept, a first quantitative description is nevertheless provided to formalise the solid lubricant endurance reduction induced by severe thermal exposures.

4:10pm **E1-2-12 The Onset of Plastic Yielding in Coated Spherical Contact**, *R. Goltsberg, G. Davidi,* ***I. Etsion*** *(etsion@technion.ac.il)*, Technion, Israel

Thin film coatings are widely used in many tribological applications. So far the selection of coating properties is done mainly by trial and error approach. For example, optimization of the thickness of coating for minimum friction and wear or for maximum electrical conductivity, based on scientific theory, does not yet exist. Failure mechanisms of coatings such as delamination, for example, are not well understood. The main goal of the present theoretical study is to analyze the effect of material properties of substrate and coating, as well as asperity tip curvature and coating thickness on the onset of plastic yielding in a typical asperity contact of a coated rough surface subjected to normal loading. This may enable optimization of the coating thickness for best performance in various applications.

4:30pm **E1-2-10 Tribological Properties of Laser Surface Texturing and Molybdenizing Duplex-Treated Steel**, ***J.L. Li*** *(jiangliangli@163.com), D. Xiong*, Nanjing University of Science and Technology, China

For reducing the friction and wear of steel at elevated temperatures, laser surface texturing and double glow plasma surface molybdenizing were performed on the steel by duplex-treating process. The surface texture were ablated by Nd:YAG pulse laser with wavelength of 1064nm and pulse width of 450ns. Surface molybdenizing were performed on the textured surface. The friction and wear properties of duplex-treated steel were tested on a pin-on-disk tribometer rubbing against alumina from room temperature to 600^{o}C. The topography of laser surface textured steel was observed by three dimensional profiler and optical microscopy. The element distribution of alloyed layer was investigated by SEM attached with EDS. The micro-dimples ablated by laser were 200µm in diameter and 45～50µm in depth. The molybdenized layer was approximately 30 µm in thickness. The hardness of molybdenuming layer decreased gradually from HV480 (coating) to HV235 (matrix). Friction coefficient of alloys decreases from 0.40 to 0.26 at room temperature and from 0.40 to 0.34 at elevated temperature by duplex-treatment. The wear rate of duplex-treated alloy was one order of magnitude lower than that of pristine alloy at elevated temperature due to the lubrication of trioxides of molybdenum. Furthermore, the micro-dimples can relieve abrasive wear by storaging hard wear particles, which is responsible for the reduction of wear rates.

Coatings and Materials for Fuel Cells and Batteries
Room: Sunrise - Session TS2

Coatings and Materials for Fuel Cells and Batteries
Moderator: E. Yu, Newcastle University, G.V. Dadheech, General Motors

1:30pm **TS2-3 Development of Li-Mn-O Thin Film Cathodes for Lithium-Ion Batteries by Magnetron Sputtering and Laser-Assisted Structuring and Annealing**, *C. Ziebert (Carlos.Ziebert@kit.edu), J. Fischer, N. Thiel, J. Proell, R. Kohler, M. Rinke, W. Pfleging,* ***S. Ulrich***, Karlsruhe Institute of Technology, Germany

Li-Mn-O thin film cathodes for Li-ion batteries have been deposited onto Si and gold coated stainless steel substrates by non-reactive r.f. magnetron sputtering at a constant power of 200 W and various working gas pressures ranging from 0.25 to 25 Pa. The composition, crystal structure and thin film morphology were examined using inductive coupled plasma optical emission spectroscopy (ICP-OES), inert gas fusion analysis (IGFA), X-ray diffraction (XRD), Raman spectroscopy, atomic force microscopy (AFM) and scanning electron microscopy (SEM). Intrinsic stress and film density were determined and battery tests have been performed in Swagelok cells with Li-Mn-O film as cathode, Li metal as anode and standard EC:DMC (1:1) electrolyte containing 1 mol $LiPF_6$.

Using ICP-OES and IGFA a pressure-dependent variation of the stoichiometry from $LiMn_{0.9}O_{1.9}$ at 0.25 Pa to $LiMn_{2.3}O_{3.3}$ at 25 Pa was found. As slight Li loss and an increase in the O content upon furnace annealing were expected based on our previous study on $LiCoO_2$, we focused on a gas pressure of 10 Pa, because the related composition $LiMn_{1.9}O_{3.13}$ offered the best conditions for the formation of the desired $LiMn_2O_4$ spinel phase. B y XRD and Raman spectroscopy it was revealed that during furnace annealing at 600 °C for 3 hours in argon/oxygen atmosphere ($Ar:O_2$=4.5:5) of 10 Pa the layered orthorhombic $LiMnO_2$ phase developed. Thus laser annealing using a high power diode laser with a maximum laser output power of 50 W and a wavelength of 940 nm was performed. It was shown that at 600 °C the spinel phase could be adjusted by an appropriate choice of laser annealing time. After 10 s the inactive monoclinic Li_2MnO_3 rock salt phase formed, which could be transformed into the spinel phase using annealing times up to 100 s.

To investigate the effect of different surface morphologies on the battery performance, selected Li-Mn-O films were patterned by laser ablation with a UV laser of wavelength λ = 248 nm. For the systematic investigation of topography, erosion rate and roughness parameters an ablation array was generated by systematically varying the number of lasers pulses and the laser fluence and were studied by SEM. The formation of flat and smooth ablation profiles was observed at laser fluences above 0.5 J/cm^2 independent of the process gas (He, O_2). The battery performance of the as grown, the structured and the annealed thin film cathodes was studied and it was revealed that the discharge capacity strongly depends on the crystal structure, the morphology and the surface structure of the thin films, which offers further opportunities for the optimisation of the performance of future 3D thin film batteries.

1:50pm **TS2-4 Lithium Insertion into Vertically-Aligned Carbon Nanotubes During Growth**, *K. Rana (kranaiitr@gmail.com), G. Kucukayan,* ***E. Bnegu***, Bilkent University, Turkey

The possibility of growing vertically-aligned carbon nanotubes using Li-containing catalysts was investigated, and insertation of lithium into carbon nanotubes (CNTs) during the growth process was examined in this work. CNTs were synthesized by chemical vapor deposition technique. The catalyst layers were prepared by the calcination of Li, Co and Al nitrate containing ethanol-based solutions. Two different solutions were studied in the present work containing (i) Co and Al nitrate and (ii) Li, Co and Al nitrates. These solutions were applied on oxidized Si (100) wafers using a dropper and left to dry at room temperature. Then, subsequent calcination, reduction and reaction for CNT growth were run in a vacuum-capable atmosphere-controlled tube furnace. Final products at the end of CNT growth were analyzed to understand the effect of lithium on CNT chemistry and structure. Scanning electron microscopy analysis confirmed the growth of CNTs with the use of both Li-containing and non Li-containing catalyst. Raman spectral analysis of these CNT arrays indicated a shift in the G-band for those grown with lithium-based catalyst. This observation is related to charge transfer between CNTs and lithium, which is a result of insertion of lithium into CNT structure. Furthermore, we have analyzed these materials using x-ray photoelectron spectroscopy (XPS). We have observed shifts in binding energy of Li1s and C1s peaks confirming the presence of lithium in CNTs grown with lithium-based catalyst. In this study, we have shown that it is possible to grow vertically aligned CNTs using Li-containing metallic catalysts. Under proper synthesis conditions, we demonstrated that Li can be inserted into CNT structures during growth without the need for further post-processing. We believe that this material can be potentially used as an anode material for lithium ion batteries to improve the performance.

2:10pm **TS2-5 Influence of a Coating on the Oxidation Resistance and Resistivity of Several Chromia Former Alloys for High Temperature Vapor Electrolysis Application**, ***S. Guillou*** *(sebastien.guillou@cea.fr), C. Desgranges,* CEA, France*, S. Chevalier*, University of Bourgogne, France

High Temperature Vapor Electrolysis (HTVE) has been studied since several years as a promising solution for future hydrogen massive production plant. HTVE device is similar to SOFC system and consists in several stacks. Each stack is composed of a pile of ceramics cells working at a temperature range about 700°C to 900°C . Cells are connected together via metallic interconnects that separate anodic and cathodic parts, and permit the current supply of the cells for the electrolysis reaction. To guarantee the HTVE lifetime with a good efficiency, interconnects have to resist to high temperature environment. Chromia former alloys are good candidates for interconnects because it forms at high temperature a compact and dense Cr_2O_3 scale that protects the alloy from the oxidant atmosphere as a barrier. However, the volatility of chromium oxides and hydroxydes may cause degradation of cells efficiency, particularly in presence of water vapor.

Increase in the performance of the alloys can be achieved using MOCVD (Metal-Organic Chemical Vapor Deposition) coatings. In a previous study performed for SOFC application, La_2O_3 coating applied by MOCVD improved kinetics oxidation rate in SOFC type atmospheres[1,2] and also modified the electronical properties of the oxide layer by increasing its conductivity[2,3,4].

Hence, in the present work, the same La_2O_3 coating has been applied to several alloys, such as Haynes®230, Haynes®242 and K41X (AISI441). The alloys were oxidized at 800°C in the both atmospheres representative of the HTVE operating conditions: ie Ar-1%H_2-9%H_2O (on cathodic side) and air (on anodic side). Oxidation kinetics were measured with a thermobalance and the Area Specific Resistance (ASR) was evaluated via contact resistance measurements. XRD, SEM coupled with EDS analyses were used to characterize the thermally grown oxide scale. Results are discussed through the comparison of the behaviors in HTVE type atmospheres of uncoated and La_2O_3 coated samples.

Beyond the possible coating beneficial influence, several additional experiments was carried out to understand the mechanism involved in presence of the coating or/and the oxide scale. ^{18}O tracer experiments and PhotoElectroChemistry characterizations were used in order to identify the diffusion mechanism. The possible role played by the protons on the conductivity and the oxidation kinetics was investigated using atmospheres enriched in deuterium.

[1]S. Fontana and al, J. Power Sources 193 Issue 1 (2009) 136-145.

[2]S. Fontana and al, J. Power Sources 171 (2007) 652-662.

[3]W.Z. Zhu, S.C. Deevi, Mater. Res. Bull. 38 (2003) 957-972.

[4]Chandra-Amborn, PhD report, Grenoble Institute of Technology, (2006)

2:30pm **TS2-6 Deposition and Post-Annealing of Ceria Films Deposited by Pulsed Unbalanced Mangetron Sputtering**, ***I.-W. Park*** *(ipark@mines.edu), J.J. Moore, J. Lin,* Colorado School of Mines*, M. Manuel,* University of Florida*, A. El-Azab,* Florida State University*, T. Allen, P. Xu,* University of Wisconsin*, D. Hurley, M. Khafizov*, Idaho National Laboratory

Ceria films were deposited on silicon wafer substrates in argon-oxygen atmosphere using pulsed unbalanced magnetron sputtering (P-UBMS) from a pure Ce target (99.99%) with a substrate heating capability system. Ceria films were also annealed using a rapid thermal annealing (RTA) with much higher temperatures in a range from room temperature to 1100°C. The crystallinity of the annealed samples was characterized by x-ray diffraction (XRD, PHILIPS, X'pert-MPD) using CuKα radiation. X-ray photoelectron spectroscopy (XPS, PHI XPS System, 5600LS) using a monochromatic Al source was also performed to determine the contents of Ce and O and to observe the bonding status of the annealed ceria samples. A MTS nano-indenter equipped with Berkovich diamond indenter was used to perform depth sensing nanoindentation testing on the annealed CeO_2 films and to obtain mechanical values of nanohardness and Young's modulus with a Poisson's ratio of 0.25. In the present work, microstructural changes and properties of the films were investigated and correlated with deposition parameters.

2:50pm **TS2-7 Sputtered Lanthanum Silicate Electrolytes for SOFCs**, ***J.C. Oliveira*** *(joao.oliveira@dem.uc.pt),* University of Coimbra, Portugal*, M.M. Vieira,* Polytechnic Institute of Leiria, Portugal*, A.L. Shaula, A. Cavaleiro*, University of Coimbra, Portugal

The development of IT-SOFCs will also require electrolyte materials with ionic conductivity higher than the conventional yttria-stabilised zirconia (YSZ) at moderate temperatures. Recently, lanthanum silicates materials ($La_{9.33}Si_6O_{26}$) with an apatite-like structure have attracted considerable interest as potential low cost electrolyte materials. Some of these materials show conductivities comparable to, or better than, YSZ at 875 K, and are thus potential electrolytes for economic feasible fuel cells. Their high level of oxide ion mobility is related to the presence of oxygen channels along the c axis which facilitate the diffusion of anionic species (O^{2-} for SOFC applications).

Magnetron sputtering has already been used to synthesize thin film electrolytes for SOFCs owing to its versatility as well as the ability to control composition and morphology. Most of the reported work focuses on the deposition of thin dense yttria-stabilised zirconia (YSZ) gadolinium doped ceria (GDC) and lanthanum gallate electrolyte layers. The main objective of this work is the production of apatite-like lanthanum silicates thin films by magnetron sputtering. La-Si-O films with the appropriate La/Si atomic ratios were deposited by reactive magnetron sputtering from La-Si and Si targets and subsequently annealed in controlled atmosphere to obtain the targeted lanthanum silicate oxide.

The chemical composition of the coatings was determined by electron probe microanalysis (EPMA). The structure of the coatings was studied by X-ray diffraction (XRD) using a Phillips diffractometer operated in Bragg-Brentano configuration with Co(Kα) radiation. The cross section and surface topography of the La-Si films were examined on a JEOL scanning electron microscope (SEM) equipped with an EDAX energy dispersive spectrometer (EDS). The electrical properties of the films were measured by AC impedance spectroscopy (HP4284A precision LCR meter, 20 Hz – 1 MHz).

3:10pm **TS2-9 Electrolytic Co-Deposition for Synthesis of $(Mn,Co)_3O_4$ Spinel Coatings to Protect SOFC Interconnect Alloys**, ***J.H. Zhu*** *(jzhu@tntech.edu), M.J. Lewis*, Tennessee Technological University

A novel process to synthesize the $(Mn,Co)_3O_4$ spinel coating for protecting ferritic interconnect alloys has been developed, which is based on thermal conversion of an electrolytically co-deposited composite layer. Simultaneous electrolytic deposition of Co and Mn_3O_4 onto a Crofer 22 APU substrate resulted in a composite coating layer consisting of a Co matrix embedded with the Mn_3O_4 particles. Thermal conversion of the as-deposited layer in air at 850ºC led to the formation of a dense and adherent $(Mn,Co)_3O_4$ spinel coating on the substrate. The spinel coating was effective in blocking Cr migration and improving the electrical performance of the interconnect alloy.

3:30pm **TS2-10 Development of Low Cost Protection Coatings for SOFC Interconnect Applications**, ***G. Xia*** *(guan-guang.xia@pnl.gov), X.H. Li, J.D. Templeton, R.C. Scott, J.W. Stevenson*, Pacific Northwest National Laboratory

Due to their low cost, high temperature oxidation resistance, and comparable thermal expansion coefficient to adjacent components of anode-supported planer SOFC stacks, chromia-forming ferritic stainless steels, such as AISI 441, are among the most promising candidate materials for interconnect applications. However, bare alloys cannot be directly used for interconnects because the rapid growth of chromia scale will lead to high internal electrical resistance and the migration of chromium species via this scale can cause cathode poisoning and cell performance degradation. To mitigate these issues for long term SOFC operation, protection coatings on ferritic stainless steel interconnects have been developed at PNNL. Manganese-cobalt spinels, particularly, $Mn_{1.5}Co_{1.5}O_4$, are proven to be highly effective protection coating materials. Currently, considerable efforts have been devoted to the cost reduction for materials and processing via investigating alternative precursors and compositions for interconnect coatings while maintain their protection effectiveness. Recent progress in this area will be summarized in this paper.

3:50pm **TS2-8 Nanostructured Titania Materials for PEM Fuel Cell Water Management**, *M.A. Elhamid,* ***G.V. Dadheech*** *(gayatri.dadheech@gm.com)*, General Motors

Transition-metal oxide surfaces play an important role in a wide range of applications such as heterogeneous catalysis, photo catalysis, photo-electrolysis of water, biocompatibility, functional materials and green energy applications. More recently, transition metal oxide films are being considered as important materials for the removal of water in fuel cell applications. Defects such as oxygen vacancies present in such oxide film structure often dominate the electronic and chemical properties of transition-metal oxide surfaces. In this study, we explore the use of nanocrystalline titanium oxide material structures to improve water management on bipolar plates inside PEM fuel cells. Titanium oxide nanotubes structures and nanoparticles structures are more stable than other forms of hydrophilic surface treatments. Furthermore, these materials are also found to be contamination robust.

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

Coatings to Resist High Temperature Oxidation, Corrosion and Fouling
Moderator: Y. Zhang, Tennessee Technological University, J.R. Nicholls, Cranfield University, L.G. Johansson, Chalmers University of Technology, D. Naumenko, Forschungszentrum Julich

8:00am **A1-1-1 Oxidation Failure of TBC Systems: An Assessment of Mechanisms**, ***H. Evans*** *(h.e.evans@bham.ac.uk)*, University of Birmingham, UK **INVITED**

Thermal barrier coating systems are used in both aero-engines and land-based gas turbines and offer oxidation protection to alloy substrates under heat flux conditions. They consist of an yttria-stabilised zirconia (YSZ) top coat, of low thermal conductivity, bonded to the alloy substrate by an Al-rich metallic layer. This bond coat may be a MCrAlY overlay-type coating or may be produced by diffusion processes. In each case, an important function is to develop a protective alumina layer during high-temperature exposure. This is the thermally-grown oxide (TGO) layer. Spallation of the outer ceramic layer, with or without the TGO, does occur, however, and this is a life-limiting event, the prediction of which has proved a difficult problem. The driving force for spallation is the release of strain energy generated within the top coat and the TGO layer both at the exposure temperature and during cooling. Most of this strain energy develops during cooling as a result of thermal strains and the values generated can be orders of magnitude larger than the intrinsic work of adhesion of interfaces within the coating (e.g. >100 $J.m^{-2}$ compared with <1 $J.m^{-2}$). This available strain energy should be sufficient to produce spallation during the first thermal cycle but patently it does not. Protracted lifetimes arise because energy dissipation processes exist within the TBC system and no mechanism exists in the early stages of exposure to produce delamination. Fracture damage develops over time and processes that can lead to the formation of sub-critical cracks are outlined in this paper. The intention is to provide a critical assessment of proposed mechanisms that implicate bond coat oxidation in the failure process. Particular attention will be given to: the influence of the mechanical constraint imposed by the top coat on the mechanical stability of the bond coat interface; the role of phase changes in the bond coat; the effect of the growth of the TGO on a non-planar interface on stress development; the importance of localised Al depletion in nucleating a fast-growing non-protective TGO.

8:40am **A1-1-4 The Effects of Ni:Co Ratio on the Phase Stability and High-Temperature Corrosion Resistance of (Ni, Co)CrAlY Alloys and Coatings**, ***Z. Tang*** *(zhtang08@gmail.com),* Iowa State University*, F. Zhang,* CompuTherm, LLC*, B. Gleeson*, University of Pittsburgh

The effects of Ni:Co ratio on the phase stability, high-temperature oxidation and hot corrosion resistances of several cast (Ni, Co)CrAlY alloys were systematically investigated. The microstructure and phase constitution of each cast alloy were experimentally determined after equilibrium treatment using SEM, EPMA and dilatometry. Thermodynamic calculations using the CALPHAD method were employed to predict the phase equlibria, and the results showed good agreement with experiment. The isothermal and cyclic oxidation behavior of the alloys in air at 700, 900 and 1150ºC were then examined, with assessment of the results being aided by CALPHAD predictions and dilatometric measurements. The alloys were also subjected to low- and high-temperature hot-corrosion testing. It was found that the "quality" of the thermal-grown oxide formed on a given alloy is a critical factor in determining hot-corrosion resistance. Finally, oxidation and hot-corrosion behavior of commercial NiCoCrAlY and CoCrAlY coatings were examined and compared to the results obtained from the cast model alloys.

9:00am **A1-1-5 The Development of New Bond Coat Compositions for Thermal Barrier Coating Systems Operating in Industrial Gas Turbine Conditions**, ***M. Seraffon*** *(maud.seraffon@cranfield.ac.uk), N.J. Simms, J. Sumner, J.R. Nicholls*, Cranfield University, UK

Environmental and economic issues raised over the last two decades mean that gas power plant efficiency must improve in the near future. An important step to achieve this is components which can operate with longer lifetimes and at higher temperatures. Currently, inlet temperatures of gas turbine engines, such as those employed in aerospace and defense, are reaching limits posed by the melting temperatures (i.e. 1300 - 1350°C) of nickel-based superalloys. Due to this, thermal barrier coatings (TBCs) are used on hot-section parts for oxidation and corrosion protection. The bond coating, an important part of TBCs, oxidizes to form a protective oxide layer and also provides adhesion between the ceramic topcoat and the substrate. NiCoCrAlY is one of the most commonly used bond coatings and extensive research has been done to find the best bond coating composition for turbine structures operating at temperatures in excess of 1000°C.

This paper reports upon the deposition of bond coatings with different compositions as well as their oxidation and degradation mechanisms at temperatures used for industrial turbine blades (900 - 950 C). Physical vapour deposition technique, magnetron sputtering, was used to deposit a range of Ni-Cr-Al-Co coatings on 10 mm diameter sapphire substrates. This was achieved through co-sputtering two targets: a Ni10Cr, Ni20Cr, Ni50Cr, Ni20Co40Cr or Ni40Co20Cr (target changed after deposition) and another pure Al target. About a hundred samples with varying compositions were produced by this method. The coatings were then isothermally oxidised in air for 500 hours in furnaces set at 900 and 950°C.

All samples were then assessed with pre- and post-exposure metrology (coating thickness, specimens weights) which showed that magnetron sputtering successfully deposited 20 to 30 µm thick coatings and allowed the calculation of oxide growths rates. Energy dispersive x-ray (EDX) analysis was used to characterise the exact composition of each sample. Additionally, x-ray diffraction (XRD) identified the oxides formed during exposure. The selective growth of protective chromia or alumina oxide (depending on the initial composition) was observed. This influenced the oxide scale's growth rate indicating which coatings were more protective and allowing future optimisation of the bond coating to be planned.

9:20am **A1-1-6 The Effect of Composition on the Durability of β-phase Bond Coats**, ***R.W. Jackson*** *(rwesleyjackson@engineering.ucsb.edu),* University of California, Santa Barbara*, R. Adharapurapu,* GE Global Research*, B.T. Hazel,* GE Aviation*, D.M. Lipkin,* GE Global Research*, C.G. Levi, T.M. Pollock*, University of California, Santa Barbara

The effect of platinum group metal, reactive element and chromium additions on the durability of NiAl, β-phase, bond coats, deposited by ion plasma deposition, has been investigated, and compared with state-of-the-art platinum aluminide coatings. Interdiffusion with superalloy substrate, oxide spallation, and the rumpling behavior under thermal cycling conditions has been investigated, focusing on the relationship between these properties and the evolution of bond coat structure and composition. The durability of EB-PVD thermal barrier coatings deposited on the modified bond coats has been analyzed and the dependence of TBC failure on bond coat structure and properties will be discussed.

9:40am **A1-1-7 Structure and Cyclic Oxidation Resistance of Pt, Pd and Pt/Pd Modified Aluminide Coatings on CMSX-4 Superalloy**, ***R. Swadźba*** *(rswadzba@gmail.com), B. Witala*, Silesian University of Technology, Poland

Palladium-platinum modified aluminide coatings can be considered as an economically beneficial alternative for platinum modified aluminide coatings. The article presents results of Pt, Pd and Pt/Pd modified aluminide coatings structure investigation on a single crystal CMSX-4 superalloy. In the experimental part of the research Pt and Pd layers were produced by electroplating 5 micrometers of respective element on the samples. Pd/Pt layer was produced by electroplating 3mm and 2mm of Pd and Pt respectively. Electroplating process was followed by heat treatment and out of pack aluminizing at 1050ºC for 5 hours. Cyclic oxidation tests were conducted using laboratory apparatus at 1100ºC in 23h cycles. The Pd/Pt modified aluminide coatings demonstrate cyclic oxidation resistance comparable to this of Pt modified aluminide coatings. The structures of the coatings were studied using scanning electron microscopy. EDS method was used to determine chemical composition in micro areas as well as distribution of elements in the cross section of the coatings. Depth profile analysis of elements was investigated using GDOS method

10:00am **A1-1-8 Compositional Effects on the Hot Corrosion of β -NiAl Alloys**, ***M.N. Task*** *(mnt2@pitt.edu), F.S. Pettit, B. Gleeson, G.H. Meier*, University of Pittsburgh

Hot corrosion is a highly accelerated form of high-temperature oxidation caused by the presence of a salt deposit, commonly Na_2SO_4 or a molten reaction product from this deposit. Despite its longstanding prevalence in commercial applications, a thorough understanding of the manner by which compositional, microstructural, and environmental factors influence the hot corrosion behavior of alloys and coatings has proven elusive. For instance, the mechanism by which Pt enhances the hot corrosion resistance of β-NiAl coatings is not clear. Moreover, elements such as Cr and Co are nearly always found in β-NiAl coatings as a result of interdiffusion with the superalloy substrate, and the effects of such elemental additions on the hot corrosion behavior of these coatings have not been systematically investigated. In this study, cast NiAl alloys with small additions of Pt, Cr, and Co were exposed to Type I (900° C) hot corrosion conditions, and the amount of degradation was compared using SEM/EDS characterization coupled with measurements of the weight-change kinetics. Differences in hot corrosion resistance are explained by thoroughly investigating the nature of the corrosion products formed on these alloys during the early stages of 900°C oxidation and hot corrosion.

10:20am **A1-1-9 Thermal Cycling Behavior of TBC Systems with Doped Pt-rich γ-γ' Bond Coatings Made by Spark Plasma Sintering (SPS)**, ***S.D. Selezneff*** *(serge.selezneff@ensiacet.fr), M. Boidot, D. Oquab,* Institut Carnot CIRIMAT ENSIACET, France*, C. Estournès,* CIRIMAT & PNF2/CNRS, France*, D. Monceau*, Institut Carnot CIRIMAT ENSIACET, France

In the last 7 years, Pt rich γ- γ' alloys and coatings have been studied by several research groups and have shown good oxidation and corrosion resistance. They can be considered as an alternative to β-(Ni,Pt)Al for bond coatings in thermal barrier coating system (TBC). Several studies have shown that Pt rich γ-γ' alloys can be excellent alumina formers at high temperatures (1100°C-1200°C), depending on their composition. Moreover, an optimized doping of these alloys can lower significantly the growth rate of the alumina. In our previous work, Spark Plasma Sintering (SPS) has been proved to be a fast and efficient tool to fabricate coatings on superalloys including entire TBC systems. In the present study, this technique was used to fabricate doped bond coatings on AM1® superalloy substrate. The doping elements were reactive elements such as Hf, Y or Zr and metallic additions such as Cu, Au or Ag. Thin films of these elements were deposited on the superalloy substrate by radio frequency PVD before SPS. The SPS step was followed by an annealing treatment to obtain the Pt-rich γ-γ' phases in the coatings. These samples were then coated by EB-PVD with an yttria partially stabilized zirconia (YPSZ) thermal barrier coating. Such TBC systems with Pt rich γ-γ' bond coatings were compared to standard TBC system composed of a β-(NiPt)Al bond coating. Thermal cycling tests were performed during 1000-1h cycles at 1100°C under laboratory air. Spalling areas were monitored during the oxidation test. Most of the Pt rich γ-γ' samples exhibited a better adherence of the ceramic layer than the β-samples. After the oxidation test, cross sections have been prepared to characterize by scanning electron microscopy the thickness and the composition of the oxide scales, mostly alumina. In particular, the influence of the doping elements on the oxide scales formation was controlled. Moreover, compositions of the bond coats, still γ-γ' after 1000-1h cycles, were analysed.

10:40am **A1-1-10 Coating Performance on Low Re Superalloy**, *B.A. Pint (pintba@ornl.gov), J.A. Haynes,* Oak Ridge National Laboratory*, Y. Zhang,* Tennessee Technological University*, **A. VandePut***, CIRIMAT - ENSIACET Toulouse

With the high price of Re, there has been significant interest in reducing the quantities present in single crystal superalloys. General Electric has developed a version of their second generation superalloy with the Re level reduced from 3% to 1.5%. Coupons of this material have been coated with simple aluminide, Pt-modified aluminide and Pt diffusion bond coatings. Cyclic oxidation testing was conducted to evaluate the reaction kinetics, surface roughening, scale adhesion and lifetime of a ceramic topcoat on this substrate compared to conventional second generation superalloys with similar coatings.

Research sponsored by the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Industrial Technologies Program.

11:00am **A1-1-12 Type I Hot Corrosion of PGM-Modified NiAl Bond Coat**, ***V.S. Dheeradhada*** *(dheeradh@research.ge.com), D.M. Lipkin,* General Electric*, T.M. Pollock,* University of California, Santa Barbara*, B.T. Hazel,* GE Aviation*, A. Van der Ven, R. Adharapurapy*, University of Michigan

Pt-modified NiAl is widely used in aerospace industries where high temperature and high pressure are required. The additions of Pt have been shown to improve oxidation and hot corrosion resistance in NiAl coatings. However, the exact mechanisms have not been established. This study focuses on the beneficial role of Pt and Pd in improving Type I hot corrosion resistance of beta-NiAl coatings. Several Pt- and Pd-containing coatings are studied and compared with commercial PtAl and PGM-free NiAl baseline. The results indicate that Pt and Pd promote the formation of alumina, decrease beta-to-gamma prime transition rate, and reduce spallation. The differences between Pt and Pd will also be highlighted.

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

PVD Coatings and Technologies
Moderator: P. Eklund, Linköping University, J. Vetter, Sulzer Metaplas GmbH, J.-H. Huang, National Tsing Hua University

8:00am **B1-3-1 Cylindrical Magnetrons Sputter Deposition of Ti-Si-C-N Nanocomposite Coatings on Inner Surface of Cylinders***, **R. Wei** (rwei@swri.org)*, Southwest Research Institute

In this paper, we present a preliminary study of Ti-Si-C-N nanocomposite coatings deposited on the inner surface of cylinders using a plasma enhanced magnetron sputtering (PEMS) technology. Wear, erosion, abrasion and corrosion may occur to the inner surface of cylinders of various industrial components including gun barrels, internal combustion engine cylinders for passenger cars and electromotives, and liners and valve seats of various pumps for petroleum/natural gas exploration and transmission or hydraulic engineering. In many cases, the damage is quite severe due to the heavy work load and, very often, the presence of sand and corrosive media. Although cost of the components is generally high, the cost to shut down the equipment for the replacement of the component is often much higher. To address these issues, we developed a cylindrical magnetron sputter deposition technology. Using this technology, steel cylinders of 100 mm in diameter by 300 mm tall were deposited with Ti-Si-C-N coatings to a thickness up to 60 µm were deposited aiming at heavy duty applications. These coatings were studied using SEM, EDS, and XRD, and the nanocomposite structure was found to contain crystalline TiN and TiCN in the amorphous SiCN matrix. The hardness of the coatings reached HV3300. Erosion testting was conducted at two incident angles of 30° and 90° using 50 µm alumina. The Ti-Si-C-N coatings significantly reduced erosion of the steel substrate. In this paper, we will discuss the magnetron design and the characteristics. We further present the detailed microstructural, mechanical and tribological properties of the coatings.

8:20am **B1-3-2 Arc Deposited Ti-Si-C-N Hard Coatings from Ternary Ti_3SiC_2 Cathodes***, **A. Eriksson** (ander@ifm.liu.se), J.Q. Zhu, N. Ghafoor,* Linköping University, Sweden*, M. Johansson,* Seco Tools AB Fagersta, Sweden*, J. Sjölén,* Seco Tools AB, Sweden*, J. Jensen, G. Greczynski, M. Odén, L. Hultman, J. Rosén*, Linköping University, Sweden

We have explored Ti-Si-C-N coatings onto WC-Co substrates, synthesized using an industrial scale cathodic arc system with ternary Ti_3SiC_2 cathodes and various N_2 pressures. Substrate fixturing on a non-permeable cylinder with one-fold rotation leads to a trapezoid compositional modulation in the coating on a 10 nm scale. This effect is particularly pronounced in depositions without reactive gas, where two sub-layers are formed for each substrate revolution, as visible in transmission electron microscopy. One sub-layer is Si-depleted and has larger crystallites compared to the Si-rich sub-layer. We attribute the layering to preferential resputtering of Si by the energetic deposition flux arriving with high incidence angles in segments of rotation when the substrates are facing away from the cathode. Over the entire range of N_2 pressures the coatings are rich in Si and C, up to 12 and 27 at%, respectively, which results in fine grains. At moderate N-content (~30 at%) the microstructure is characteristically feathered with nanograins fanning out from the growth direction, connected by low-angle grain boundaries. These coatings have nanoindentation hardness of up to 50 GPa. At higher N_2 deposition pressure hardness is drastically reduced, as C and Si segregate to form a low-density grain boundary phase, coupled with the formation of C-N bonds, as determined by XPS. The results show that arcing ternary cathodes is a method to expand the range of attainable composition and microstructure of coatings in the Ti-Si-C-N system.

8:40am **B1-3-3 Atomic Scale Studies of Nanocomposite Coatings with Atom Probe Tomography***, **J.M. Cairney** (julie.cairney@sydney.edu.au),* University of Sydney, Australia*, F. Tang,* The University of New South Wales, Australia*, P.J. Felfer,* The University of Sydney, Australia*, A. Bendavid, P. Martin*, CSIRO, Australia **INVITED**

Arc deposited nanocomposite coatings such as Ti-Si-N are of great technological interest due to their very high hardness, high temperature stability and corrosion resistance. Such coatings (Ti-Si-N, Zr–Si–N, Ti–Al–Si–N and Ti–Al–V–Si–N) have recently been fabricated, by a vacuum arc deposition process, with a great deal of control over the resulting microstructure and properties [1]. In addition, similar nanocomposite structures can be achieved by combining Ti/Hf/Zr oxides with DLC to create hard, inert coatings that may be highly suitable for biomedical applications [2].

The examination of the structure of these nanocomposite materials is extremely challenging. Cross-sectional transmission electron microscopy (TEM) has been made considerably simpler through the use of focused ion beam (FIB) – based specimen preparation methods. However, due to the fine size scale of the crystalline phases (5-50nm), the overlap of grains in transmission electron microscope (TEM) specimens makes it impossible to study the interfaces between the crystals in order to determine whether secondary amorphous phases are present. Atom probe tomography is a technique that provides atomic-scale 3D maps showing the distribution of elements within a selected area of material. New FIB-based specimen preparation methods and the development of new laser-pulsing technology makes this method available to the examination of arc-deposited hard coatings.

This paper will include the results of a study of Ti-Si-N, in which no evidence was found for the presence of a Si-rich phase at the boundaries between the crystallites. We will discuss the challenges and limitations around the application of atom probe tomography in studying arc-deposited hard coatings.

[1] P. J. Martin , A. Bendavid , J. M. Cairney and M. Hoffman, *Surf. Coat. Technol.*, [200], 2228 2005.

[2] L.K. Randeniya, A. Bendavid, P. Martin, J.M. Cairney, A. Sullivan, S. Webster, G. Proust, R. Rohanizadeh, *Acta Biomaterialia* , 6 (2010) 4154-4160 .

9:20am **B1-3-5 Structural and Mechanical Property of (TiCrAlSi)N Coating with Different Si Contents**, ***H. Ito*** *(ito.hirotaka@kobelco.com), K. Yamamoto, T. Okude*, Kobe Steel Ltd., Japan

Various TiAlN based coatings are most commonly used composition for cutting tool application. Recently, more thermal stability and the higher film hardness are demanded because of the needs for dry cutting of harder work-pieces at higher cutting speed. Considering this circumstance, we have examined the effect of the Si addition on (Ti,Cr,Al)N films, and have developed an excellent film with high hardness and improved thermal stability. We have examined effect of Si content in (Ti,Cr,Al)N up to 5 at% [1]. In this report, further improvement of film characteristic was achieved by increasing the Si content more than 5 at%. Cutting performance of (Ti,Cr,Al,Si)N film with different Si compositions and the correlation with the film structure was investigated.

(Ti,Cr,Al,Si)N films with different Si content were deposited by a cathodic arc ion plating (AIP) equipment. Ti–Cr–Al–Si targets were prepared by powder metallurgy process and used for the deposition. Their compositions were Ti0.2-Cr0.2-Al0.55-Si0.05, Ti0.2-Cr0.2-Al0.52-Si0.08 and Ti0.3-Cr0.18-Al0.42-Si0.12. Deposition was conducted in the AIP coater in pure N2 atmosphere at a pressure of 4.0 Pa. WC-Co cutting inserts, platinum foils (0.1mmt) and WC-Co ball end-mills were used as substrates. The substrate bias during deposition was varied from 30 to 200 V to investigate the effect of substrate bias on film's properties.

XRD analysis result shows that crystal structure of the (Ti,Cr,Al,Si)N films deposited with bias 30V has mixed structure with hexagonal phase (Wurzite structure) and cubic rock-salt structure (B1 phase), the films deposited with bias more than 65V has B1 cubic single phase regardless of the Si content. Indentation hardness is about 30 GPa for (Ti,Cr,Al,Si)N films with 8 % of Si although the indentation hardness of the 5% Si film is approximately 26 GPa. Additionally, by increasing the Si content, oxidation resistance was greatly improved. The formed oxide layer is about 1100 nm for 5% Si film after annealing in dry air at 1000˚C for 30 minute, while the oxide layer of oxides is approximately 400 nm for 8% Si film. The detailed relationship between the cutting characteristic and the film structure will be included in the presentation.

[1] K. Yamamoto, S. Kujime, K. Takahara; Surf. Coat. Technol. 200 (2005) 1383

9:40am **B1-3-6 Seed Layer Influence on the Texture, Orientation and Piezoelectric Properties of Pulsed-DC Sputtered AlN Thin Films**, ***M. Hasheminiasari*** *(mhashemi@mines.edu), J. Scales, J. Lin, J.J. Moore*, Colorado School of Mines

Piezoelectric aluminum nitride (AlN) thin films were deposited by reactive sputtering of Al metal target in nitrogen atmosphere using a pulsed closed field unbalanced magnetron sputtering system on various substrates using different seed layers such as Cr, Ti/TiN, Pt, Mo and Al. The texture, orientation and piezoelectric properties of AlN films were characterized by means of x-ray diffraction, field emission scanning electron microscopy and laser interferometry. A Michelson laser interferometer was designed to obtain the converse piezoelectric response of the deposited AlN thin films. It was found that the incorporation of different seed layers in the sandwiched structure, significantly affected the (002) orientation and the piezoelectric response of AlN thin films.

10:00am **B1-3-7 Industrial-Scale Sputter Deposition of Photocatalytic Active Titania (TiO_2) and Thin Film (YSZ/CGO) for Solid Oxide Fuel Cells**, ***L.P. Nielsen*** *(lpn@dti.dk), K.P. Almtoft, I.H. Andersen, B.H. Christensen,* Danish Technological Institute, Tribology Centre, Denmark*, M.B. Sørensen,* Danish Technological Institute, Plastic Technology, Denmark*, A.J. Nielsen, C. Vahlstrup, J. Bøttiger,* Aarhus University, Denmark*, S. Sønderby*, Linköping University, Sweden **INVITED**

Industrial-scale synthesis of oxide coatings with tailored properties is of vital importance for bringing fundamental R&D small-scale research results into commercial applications and consumer products.

The Tribology Centre at Danish Technological Institute has performed large-scale reactive pulsed DC sputter deposition of TiO_2 and Cu-doped TiO_2 for photocatalytic and anti-microbial applications. In addition, cerium gadolinium oxides (CGO) and yttria stabilized zirconia (YSZ), and alternating layers hereof, have been synthesized for intermediate temperature solid oxide fuel cell applications. The various coatings were deposited on a commercial CemeCon CC800/Sinox unit.

For the TiO_2 system it will be shown that reproducible growth of dense as well as highly porous (featherlike) TiO_2 coatings can be synthesized in the rutile and the anatase crystal phase (or mixtures hereof) as evident from SEM and XRD results. It will be demonstrated that by carefully controlling the deposition temperature and the substrate bias voltage, nucleation and growth of the photocatalytic active anatase can be tailored. The photocatalytic activity has been quantified by oxidation of acetone into CO_2 and correlated to the obtained structure and film morphology, thicknesses and choice of substrate material (silicon, stainless steel, glass, aluminium and polycarbonate). The effect on the film structure and the photocatalytic activity upon doping with e.g. Cu and the impact on antimicrobial properties will be addressed.

For solid oxide fuel cell (SOFC) applications YSZ is frequently encountered as the electrolyte material. In order to reduce operating temperature of the SOFC, thin YSZ electrolyte coatings are of great interest. In this respect, it is of utmost importance to control the crystal structure and morphology of the deposited YSZ thin films – not only on ideal model substrates. To prevent strontium diffusion to the electrolyte from strontium-containing cathode materials, gadolinia-doped ceria (CGO) barrier layers can be applied.

YSZ and CGO single and multilayer thin films were synthesized by reactive pulsed DC magnetron sputtering from $Zr_{0.84}Y_{0.16}$ and $Ce_{0.9}Gd_{0.1}$ targets, respectively. Crystal structure and morphology were investigated by XRD, TEM and SEM analysis showing that dense films could be grown with a cubic fluorite crystal structure. The grain size and texture of both YSZ and CGO films could be controlled through substrate bias and temperature variations. When depositing multilayers of CGO and YSZ, significant template effects could be identified, i.e. local epitaxial growth was observed.

10:40am **B1-3-9 Antibacterial Activity of TiO_2 Coatings Deposited by CAE-PVD**, ***J. Esparza*** *(jegorraiz@ain.es)*, A. I. N., Spain

Antibacterial activity of TiO_2 thin films prepared by *Cathodic Arc Evaporation-Physical Vapour Deposition* (CAE-PVD) was studied with respect to *E. Coli* and *S. Aureus* in UV radiation conditions. TiO_2 thin films were deposited on stainless steel (AISI 304) and commercial ceramic samples. The effect of doping TiO_2 has been analyzed; silver and nitrogen ions have been tested as dopants. Silver was added by a coevaporation process during the TiO_2 deposition process, while nitrogen ions were implanted using a WHICKHAM IBS 200 ion implantation equipment. A specific UV lamp emitting at 360-390 nm wavelength (OSRAM L36W/76) has been utilized to activate the photocatalytic response of the titanium oxide surface in contact with the bacteria.

The characterization of the coatings includes FE-SEM, AFM and Contact Angle analyses, moreover, a complete study of the mechanical properties of the TiO_2 thin films have been performed, including adhesion analyses (scratch test) and nanoindentation measurements.

11:00am **B1-3-10 Preparation of $BiFeO_3$/$LaNiO_3$ Multiferroic Oxide Superlattice Structure Prepared by RF Sputtering**, ***Y.-T. Liu***, National Chiao Tung University, Taiwan*, S.-J. Chiu,* National Tsing Hua University, Taiwan*, H.-Y. Lee (hylee@nsrrc.org.tw),* National Synchrotron Radiation Research Center, Taiwan*, S.-Y. Chen*, National Chiao Tung University, Taiwan

Artificial superlattices consisting of multiferroic $BiFeO_3$ (BFO) and conductive $LaNiO_3$ (LNO) were epitaxial grown on Nb-doped $SrTiO_3$ (001) single crystal substrate at temperatures in a range of 560–810°C by a RF magnetron sputtering system. X-ray reflectivity and high-resolution diffraction measurements were employed to characterize the microstructure of these films. The formation of a superlattice structure was confirmed from the appearance of Bragg peaks separated by Kiessig fringes in x-ray reflectivity curve and a diffraction pattern. The clearly discernible main feature and satellite features on both sides of the substrate about the (002) $SrTiO_3$ Bragg peak indicate the high quality of the BFO/LNO artificial superlattice structure formed on a $SrTiO_3$ substrate at all temperatures of deposition.

X-ray measurements show that these superlattice films become subject to greater tensile stress along the c-axis, increased compressive stress parallel to the surface plane and increased crystalline quality with increasing the temperature of deposition except for the film deposited at ≧ 750℃.

11:20am **B1-3-11 Evolution of the Structure and Optoelectrical Performance of ZnO Thin Films Deposited by DC Magnetron Sputtering after Post Deposition Annealing Treatments**, ***M. Yuste*** *(miriam.yuste@icmm.csic.es), R. Escobar Galindo, I. Caretti, O. Sánchez*, Instituto de Ciencia de Materiales de Madrid, Spain

Zinc oxide (ZnO) is a semiconducting, photoconducting, piezoelectric and optical waveguide material that shows a wide range of scientific and technological applications. ZnO thin films can be grown (or synthesized) by a variety of deposition techniques, such as sol-gel process, pulsed laser deposition, molecular beam deposition, chemical vapour deposition, sputtering, etc. The most commonly used technique is sputtering, and more concretely, non-reactive RF magnetron sputtering because of the good quality of the films obtained. In this work, we have used room temperature DC reactive magnetron sputtering at different oxygen partial pressures for the deposition of the films. In this way we have performed a systematic study of the stoichiometry and the related changes in the texture and the optical properties of the coatings. In addition, the effect of post deposition annealing treatments on the structure and electrical performance has been investigated. The chemical composition has been assessed by Rutherford Backscattering Spectroscopy (RBS) and Infrared absorption spectroscopy (IR) . The structural, morphologic and topographic changes have been characterized by X-Ray Diffraction (XRD), Scanning Electron Microscope (SEM) and Atomic Force Microscope (AFM). In selected samples we have completed the analysis of the bonding structure and phase composition by x-ray absorption near edge structure (XANES) using synchrotron radiation. Finally, the optical (transmittance in the visible region, band-gap, refractive index and UV emission) and electrical properties (resistivity) have been assessed by UV-Vis spectroscopy, Spectroscopic ellipsometry (SE) and four-point probe measurements.

11:40am **B1-3-12 Characterization and Piezoelectric Properties of Reactively Sputtered (Sc, Al) N Thin Films on Diamond Structure**, ***M.-Y. Wu****, J.-L. Huang, J.-H. Song,* National Cheng Kung University, Taiwan*, J.-C. Sung,* KINIK Company, Taiwan*, Y.-C. Chen,* National Cheng Kung University, Taiwan*, S. Wu,* Tung Fang Design University, Taiwan*, D.-F. Lii (dflii888@csu.edu.tw)*, Cheng Shiu University, Taiwan

In this research, we demonstrated the viability of oriented AlN layer doped with scandium to enhance its piezoelectricity. Wurtzite (Sc, Al) N thin films were deposited on a diamond/silicon structure by a co-sputtering system. Due to the piezoelectricity is very sensitive to the film microstructures, the relationship between the microstructures and process conditions were examined with x-ray diffraction, electron spectroscopy chemical analysis, electron probe micro-analyzer, transmission electron microscope and atomic force microscope analysis. The piezoelectric response microscope was used to measure the piezoelectric coefficient, d_{33}. The results showed that the piezoelectricity was strongly depended on the c-axis orientation of samples. Besides, the piezoelectric coefficient would enhance obviously after doping scandium element into thin films. The d_{33} value increased with increasing scandium concentration up to the solution limit of scandium in aluminum. We found the maximum of piezoelectric coefficient of (Sc, Al)N thin film is five times larger than pure AlN layer, which could be expected to boost the properties of surface acoustic wave filter devices.

Hard Coatings and Vapor Deposition Technology
Room: Golden West - Session B6-1

Application-Oriented Coating Design and Architectures
Moderator: C. Mitterer, Montanuniversität Leoben, M. Stueber, Karlsruhe Institute of Technology

8:00am **B6-1-1 Phase Diagram Based Design of a Spinel-Corundum Coating**, ***J. Ramm*** *(juergen.ramm@oerlikon.com),* OC Oerlikon Balzers AG, Liechtenstein*, M. Döbeli,* ETH Zürich, Switzerland*, D. Kurapov, H. Rudigier, M. Sobiech,* OC Oerlikon Balzers AG, Germany*, J. Thomas,* IFW Dresden, Germany*, B. Widrig*, OC Oerlikon Balzers AG, Germany

Reactive cathodic arc evaporation is a deposition method with high versatility for the design of oxide coatings. The utilization of binary composite targets in this method facilitates the synthesis of binary and ternary oxides. While the metallic ratio in the oxide coating can be adjusted by the composition of the target constituents, the chemical reactions occurring during the oxide synthesis can be controlled additionally by the oxygen flow.

It has been shown that for targets consisting of elemental powders, the target surface undergoes reactions during arc evaporation in oxygen. As a result of these reactions, solid solutions and intermetallic compounds are formed [1]. A simple empirical model based on the binary phase diagram can be utilized to predict the compounds produced at the target surface. The Al-Ni material system is utilized to demonstrate the design procedure of an oxide coating based on this model. Three different target compositions ($Al_{85}Ni_{15}$, $Al_{70}Ni_{30}$, $Al_{45}Ni_{55}$) were selected. The prediction of the phase formation at the target surfaces are compared with the analytical results obtained by X-ray diffraction measurements.

The influence of the material changes at the target surface on the evaporation process is discussed. The microstructure and composition of the synthesized Al-Ni-O layers are investigated by XRD, RBS and TEM. It is shown that the synthesized coatings consist either of mixtures of $NiAl_2O_4$ (spinel) in a nanocrystalline Al_2O_3 (corundum) matrix or of spinel and Ni-O phases. Also in this case, the phase diagram of the Al-Ni-O system can be utilized to explain the phase compositions in the synthesized oxide layer. As expected from the phase analysis, the synthesized coatings show high hardness and excellent interface matching with coatings of cubic structure.

[1] J. Ramm, A. Neels, B. Widrig, M. Döbeli, L. de Abreu Vieira, A. Dommann, H. Rudigier, accepted for publication in Surf. Coat. Technol., 10.1016/j.surfcoat.2010.08.152

8:20am **B6-1-3 Controlled Phase Transformation for Local Property Design in MAX Phase Coatings**, ***O. Schroeter*** *(olaf.schroeter@tu-dresden.de), C. Leyens, R. Basu*, Technische Universität Dresden, Germany

Based on their specific microstructure and properties MAX phases have recently be shown to offer a substantial potential for erosion protection of gas turbine hardware. In this paper, single phase Cr_2AlC MAX phase coatings were deposited onto a nickel-base superalloy using a sintered powder target in conventional DC magnetron sputtering and high power impulse magnetron sputtering (HIPIMS) mode. Controlled phase transformation during heat treatment resulted in marked improvement of erosion resistance. The Rietveld method was used to quantify the phase transformations. Notably, the lattice parameter of DCMS and HIPIMS coatings responded differently to heat treatment. Coatings deposited at low temperatures were amorphous and could be transformed into crystalline MAX phase by heat treatment. Unlike highly textured columnar Cr_2AlC coatings sputtered at high temperatures, nearly no texture was observed in crystalline coatings transformed from the amorphous state. Local heat-treatment in vacuum triggered selective phase transformation. When aluminium was reduced in the coating during heat treatment, a continuous transition from Cr_2AlC MAX phase to chrome carbide occurred. This effect can be used to control the local properties in the coatings.

8:40am **B6-1-4 Quantum Design of Hard Boron-Rich coatings**, ***D. Music*** *(music@mch.rwth-aachen.de), J.M. Schneider*, RWTH Aachen University, Germany **INVITED**

It is generally accepted that hard coatings are made of light elements, namely B, C, O, and N, or a combination thereof with transition metals. Here, we focus on B-rich compounds, constituted of icosahedral (B_{12}) units, ranging from amorphous (B_6O based) to crystalline ($MgAlB_{14}$ based, space group *Imma*) hard coatings. We have studied the correlation between chemical composition, structure, chemical bonding, and elastic properties of amorphous B_6O based hard coatings using *ab initio* molecular dynamics. These films are of different chemical compositions, but the elasticity data appear to be a function of density. This is in agreement with our experimental observations. This may be understood by analyzing the chemical bonding of these compounds. C and N promote crosslinking of B_{12} and thus increase the density, while H hinders the crosslinking by forming OH groups. The presence of B_{12} bonding is independent of density. Further increase in density, and hence stiffness, can be achieved if crystalline compounds are formed. The effect of valence electron concentration (VEC) and size of the *X* element in $XMgB_{14}$ (X = Al, C, Si, Ge, Mg, Sc, Ti, V, Zr, Hf, Nb, Ta) on stability and elastic properties has been studied using *ab initio* calculations. Based on the chemical bonding analysis, *X* elements and Mg transfer electrons to B_{12}. Hence, the stability of the compounds studied increases as more electrons are transferred. As the VEC of the *X* element increases, fewer electrons are transferred to B_{12}, and therefore the phase stability decreases. We have also designed a new compound by replacing Mg with Y in the structural prototype and probed this by magnetron sputtering. It has been shown that the most stable configuration is $Al_{0.5}YB_{14}$, corresponding to a charge transfer of 2 electrons from metals to B_{12}. The bulk moduli for all $MgAlB_{14}$ based investigated phases are in the range 196 – 220 GPa, rather close to known hard phases such as α-Al_2O_3.

9:20am **B6-1-6 DFT Combinatorics by Extending the Rule of Mixture to Sub Unit-Cell Level**,
M. to Baben *(to_baben@mch.rwth-aachen.de), D. Music, J. Emmerlich, J.M. Schneider*, RWTH Aachen University, Germany

Probably, there are only few principles in materials science that are used as often as the "rule of mixture". Based on the properties of the constituting phases this rule allows for estimating a variety of composite properties ranging from the heat capacity of ivory to effective Young's modulus of concrete. For the calculation of the bulk modulus, for example, the only input data needed are the bulk moduli of the constituting phases and their volume fractions. This is commonly used for macroscopic composites as well as multilayers with layer thicknesses of a few nanometers. The applicability of the rule of mixture on smaller length scales, i.e. on the atomic level has not been considered. Here, the rule of mixture is extended to the sub unit-cell level. It is shown that the theoretical bulk modulus of a single phase with layered crystal structure is reliably estimated from calculated bulk moduli data of the constituents adopting the symmetry within the individual layers of the layered structure. The strength of the here-proposed model is demonstrated for $M_{n+1}AX_n$ phases (M: early transition metal, A: A-group element, X: C or N, n = 1-3), $M_nAl_4C_{n+3}$ phases (M: Hf or Si, n = 1-3) as well the ionic quaternary compound $KAg(CN)_2$.

This strategy enables a combination of combinatorics and DFT: a database can be built up by calculating a variety of hypothetical phases constituting the building blocks of the layered structure. Suitable combinations thereof may be identified, thus reducing calculation time by some orders of magnitude. This work is a significant step towards knowledge-based materials design since "sub unit-cell composite" materials with tailor-made elastic properties can be predicted based on hypothetical phases assembling the composite.

9:40am **B6-1-7 Growth and Characterization of Single-Crystal $V_xW_{1-x}N(001)$ Thin Films**,
H. Kindlund *(hanki@ifm.liu.se), J. Birch, L. Hultman*, Linköping University, Sweden

Coatings of ternary B1-type transition metal nitrides, such as Ti-Al-N, often exhibit superior hardness and protective properties in harsh environments compared to the constituent binaries. However, the performance of such coatings is eventually limited by brittleness. The Ti-W-N materials system presents an electronic structure with alternating high and low electron density regions that lead to an enhancement of the hardness/ductility relation [1]. Analogous to Ti-W-N, the V-W-N system has been predicted to have similar qualities [2], making it a promising hard coating material candidate with increased toughness.

In this work we have experimentally studied growth and properties of single-crystal $V_xW_{1-x}N(001)$ thin films, with concentrations in the range $0.04 \leq x \leq 0.96$, grown on MgO(001) substrates by reactive magnetron sputter epitaxy (MSE). Metallic V and W targets in a pure N_2 atmosphere was used and the deposition temperature was varied from 500 to 1000°C.

For temperatures higher than 800°C, a mixture of B1 VWN and W_2N was observed by XRD. At 700°C and $x \geq 0.4$ (as determined by RBS), XRD indicates a single phase B1 $V_xW_{1-x}N$ (001)-oriented growth with a lattice parameter slightly smaller than that of the MgO substrate. For $x < 0.4$, a phase mixture of W and VWN is observed. Cross-sectional HR-TEM and selected area electron diffraction of a $V_{0.4}W_{0.6}N$ film confirmed the single crystal cubic B1 structure. High resolution XRD reciprocal space mapping showed that x=0.4 yields a tetragonally-strained film, with a lateral (in-plane) lattice parameter a=4.212 Å, equal to that of MgO, and a transverse lattice parameter c=4.201 Å. For x=0.62, on the other hand, the film is relaxed with c=4.202 Å and a=4.192 Å. Hardness and elastic moduli data obtained through nanoindentation will be reported.

[1] D. G. Sangiovanni, V. Chirita and L. Hultman, Phys. Rev. B 81, 104107 (2010)

[2] D. G. Sangiovanni et al, 57th AVS Symposium, 17-22 October 2010, Abstract nr. 673.

10:00am **B6-1-8 Ductility Enhancement in Transition Metal Nitrides by Alloying and Valence Electron Concentration Tuning**,
D.G. Sangiovanni*, V. Chirita (vio@ifm.liu.se), L. Hultman*, Linköping University, Sweden

We use Density Functional Theory (DFT) calculations in the generalized gradient approximation (GGA) to predict the properties of a number of novel ternary nitride thin films in the B1 (NaCl) structure. The compounds are obtained by alloying TiN and VN, in concentration of 50%, with M = Nb, Ta, Mo and W. Our results show that as the valence electron concentration per unit cell is increased in these ternaries, one can significantly enhance their ductility while retaining hardness values comparable with the respective binaries. This trend is in line with our recent predictions [1] and can be explained as due to the increased occupancy of d-t_{2g} states induced by higher concentrations of electrons [2]. As it will be shown, this is however solely the effect of alloying, since binaries with identical valence electron concentrations do not exhibit the layered electronic arrangement found in ternaries. To further investigate the electronic structure of these compounds, herein we calculate real-space charge densities and crystal orbital overlap populations to resolve the changes in ionic and covalent bonding during shearing. Our analysis clarifies the electronic mechanism leading to a gradual weakening of bonds with increasing strains, and ultimately favoring dislocations glide in the {110}[1-10] slip system, known to be a primary channel for dislocations motion in NaCl transition metal nitrides. We note that significant progress has been made in the synthesis V-W-N thin films, the ternary with the highest vacancy electron concentration (10.5) per unit cell [3].

[1] D.G. Sangiovanni, V. Chirita and L. Hultman, Phys. Rev. B **81**, 104107 (2010).

[2] D. G. Sangiovanni et al, 57th AVS Symposium, 17-22 October 2010, Abstract # 673.

[3] See abstract submitted by H. Kindlund et. al. in session B6.}

10:20am **B6-1-9 Microstructural Study and Mechanical Properties of TiC/C Composite Coatings Deposited by hybrid PVD/PECVD Process**,
A.-A. El Mel*, E. Gautron, B. Angleraud, A. Granier,* Université de Nantes, France*, V. Buršíková, P. Vašina, P. Souček,* Masaryk University, Czech Republic*, P.-Y. Tessier (Pierre-Yves.Tessier@cnrs-imn.fr)*, Université de Nantes, France

Titanium carbide/carbon hard coatings were deposited by a hybrid plasma process combining physical vapour deposition and plasma enhanced chemical vapour deposition at room temperature. Argon gas was used to sputter a titanium target in an RF magnetron discharge; whereas methane was used as a source of hydrogenated carbon. An additional RF plasma, independent of the magnetron plasma, was generated by a coil located between the target and the substrate. By adjusting the Ar/CH_4 ratio and the species impinging on the substrate during the deposition, films with a variety of chemical composition and microstructure were prepared. The evolution of the microstructure and the chemical composition were studied by X-ray photoelectron spectroscopy, X-ray diffraction, transmission electron microscopy and Raman spectroscopy. Titanium carbide nanoparticles of different sizes embedded in an amorphous carbon matrix can be formed depending on plasma conditions. The grain size of the different coatings were determined by using Scherrer's formula or from a statistical study extracted from the high resolution transmission electron microscopy micrographs. The internal residual stress in the coatings deposited under different deposition conditions was calculated by the curvature method using Stoney's formula. In addition, nanoindentation tests were performed on different samples in order to investigate the mechanical properties of the coatings. It was observed that the measured hardness varies between 15 and 30 GPa according to the carbon concentration present in the coatings. The evolutions of the internal residual stress, of hardness and of Young's modulus are correlated to the evolution of the microstructure of the coatings which depends on the carbon content in the coatings.

10:40am **B6-1-10 In-Situ XRD Investigations of Interface Reactions in Nanoscale Cr/ta-C Multilayers**,
U. Ratayski *(ulrike.ratayski@iww.tu-freiberg.de), D. Rafaja, U. Mühle,* TU Bergakademie Freiberg, Germany*, C. Baehtz,* Forschungszentrum Dresden-Rossendorf*, H.-J. Scheibe, M. Leonhardt*, Fraunhofer-Institut für Werkstoff- und Strahltechnik IWS Dresden

The Cr/ta-C multilayers are regarded as diffusion barriers due to the formation of chromium carbides with a narrow homogeneity range at their interfaces. In order to get insights into reactive diffusion kinetics in the Cr-C system running on the nanoscale, *in-situ* XRD measurements were carried out at the BM 20 beam line at the European Synchrotron Radiation Facility

(ESRF) in Grenoble. The interface reactions were visualized via changes of the layer thickness, interface morphology and crystallinity during a heat treatment in a temperature range between room temperature and 600°C.

The individual layer thickness and the interface roughness were obtained from X-ray reflectivity measurements, additional information about the correlation of the interface corrugations from the resonant small-angle diffuse scattering. The changes in the interface morphology were confirmed by TEM. These nanostructure parameters were complemented by the phase composition concluded from the glancing angle X-ray diffraction (GAXRD) patterns.

The effect of the initial nanostructure of the multilayers on the reactive diffusion kinetics was investigated with the aid of multilayers having different individual layer thicknesses and interface morphologies. These layers were deposited using different energies of the carbon ions during the deposition of the tetrahedrally bonded carbon (ta-C) layers. The thickness of these layers was varied between 6–10nm. The Cr layer thickness was kept almost constant at 10nm. The interface roughness between both layers varied between 5-15Å. Additionally, it was found that the amount of the sp^3 bonds in the carbon layers and the crystallinity of the Cr layers changed depending on the carbon ion energy.

We were able to describe the reactive diffusion process as a function of the layer thickness, interface roughness and interface morphology. Between 300°C and 400°C, a large increase of both, the interface roughness and bilayer thickness, was observed, as driven by a significant acceleration of the reactive diffusion process above this critical temperature in the Cr-C system. The large interface roughness was a result of carbon diffusion; the increase of the bilayer thickness was related to an expansion of the molar volume during the diffusion process. Furthermore, it was observed that the degradation of the multilayer structure depends mainly on the initial phase compositions at the Cr/ta-C interfaces. The degradation of the Cr/ta-C multilayers was less pronounced if the chromium carbides were already present at the Cr/ta-C interfaces and acted as diffusion barriers. The formation of chromium carbides at the interfaces was verified via GAXRD and HRTEM.

11:00am **B6-1-11 Fabry-Perot Based Layer Systems with Embedded Public, Hidden and Forensic Information for Anti-Counterfeiting Applications**, ***U. Beck*** *(uwe.beck@bam.de), R. Stephanowitz, A. Hertwig,* BAM, Germany*, R. Domnick, M. Belzner,* ARA Coatings, Germany*, D. Hönig, S. Schneider*, ACCURION, Germany

The embedding of information on surfaces is state-of-art for various fields of application such as product identification (e.g. manufacturer, price, use-by date), material identification (e.g. type of material, brand name, batch number), identification of persons (e.g. ID-cards, driving licenses, admittance passes) and identification of documents (banknotes, securities, tickets). In many instances, the legal authentication of a product, a material, a person or a document is required.

Public, hidden and forensic features either encoded or directly legible is used for authentication. Fabry-Perot layer stacks as information carriers provide in conjunction with imaging ellipsometry as optical read-out system all-in-one anti-counterfeiting features. Different designs are described with respect to public features such as color either in reflection or transmission, tilt effects perceptible by the human eye, hidden features in the UV or IR spectral range or even forensic features such as the ellipsometric quantities ψ and Δ as a function of wavelength and angle of incidence. In addition to interference effects within the Fabry-Perot cavity, additional scattering effects can be superimposed which affect color and brightness and depend on the source of illumination and the angle of perception.

Besides stratified Fabry-Perot stacks, also patterned layer systems have been investigated. Bar codes and data matrices are used as information carrier. Layer pattern are produced by laser writing systems either in terms of a modification of the metallic film in the Fabry-Perot cavity or by pre-structuring of the substrate-based bottom reflector. In addition to bar-code or data-matrix readers, imaging ellipsometry is used both for forensic encoding of substrate or Fabry-Perot-based information. Object-in-object features and their specific ellipsometric fingerprint are shown and discussed in dependence on the stack design.

It could be shown that physically uncloneable functions (PUF) could be realized as a result of a multi-material and a multi-parameter deposition approach as well as due to specific design features of the Fabry-Perot layer stack. Hence, they are not subject to any reverse engineering strategies. Examples of micro-structured and laser-modified Fabry-Perot layer systems are considered that may be used at all perception levels (e.g. human eye, bar code reader, imaging ellipsometry) for authentication against product counterfeiting and related areas.

11:20am **B6-1-12 Simulation of a Variety of Applications for Complex Coating Structures**, ***N. Bierwisch*** *(n.bierwisch@siomec.de), N. Schwarzer*, Saxonian Institute of Surface Mechanics, Germany

In the fields of material development and material optimization more and more often coatings are used to get the wanted and needed material properties. Unfortunately most of the analysis theories and measurement procedures can't be used for such coated systems.

This talk will present some extended analysis methods for the most of the measurement procedures classically used. With these new methods it is possible to determine the correct generic material parameters like Young's modulus and yield strength for coated, viscous, gradient and microstructured systems.

Beside the analysis of the measurement data to determine generic coating parameters the simulation of the real contact situation also plays a more important role. Based on such an extended test analysis true initial failure mechanism can be derived and used for later optimization and development [1]. With such simulations with completely analytical models (www.siomec.de/filmdoctor) one can save a great amount of development time and money, because inapplicable material structures, materials (or material combinations) can be excluded before the creation of new usually expensive prototypes. Moreover, the actual search vector for the optimization procedure can be defined/narrowed much better exluding irrelevant failure mechanisms with respect to the practical application.

In the second part of the talk some ways for the simulation of real applications and practical tests (e.g. scratch tests) will be presented.

Fundamentals and Technology of Multifunctional Thin Films: Towards Optoelectronic Device Applications
Room: Sunset - Session C3

Optical Characterization of Thin Films, Surfaces, and Devices

Moderator: U. Beck, BAM, E. Schubert, University of Nebraska-Lincoln

8:00am **C3-1 Analysing Solid Surfaces by FT-IR Imaging ANR AFM-Raman-Spectroscopy**, *J. Sawatzki,* ***Boese*** *(Matthias.Boese@brukeroptics.de)*, Bruker Optik GmbH, Germany **INVITED**

To understand chemical structures on surfaces it is essential to analyze two dimensional samples by FT-IR with high spatial resolution. The conventional approach would be to acquire sequentially single point spectra at predefined locations of the sample. However, for the complete study of bigger areas this “mapping technique” is extremely time consuming. To overcome this hindrance, modern FT-IR imaging instrumentation is based on focal plane array (FPA) detection systems. Using this technology large sample areas can be measured simultaneously while reducing the acquisition time considerably.

Atomic force microscopy is a powerful tool for the characterisation of surfaces down to the molecular and even atomic level. It is based on a microscopically small oscillating tip which fixed to a cantilever. The tip is moved across the sample to obtain topographical information.

Recently, AFM and Raman microscopy were combined to allow morphological/topographical as well as chemical imaging of the same sample area. Raman microscopy ideally complements AFM imaging since it is adding molecular spectroscopic information. In this paper typical examples for analyzing surfaces by FTIR imaging and AFM/Raman microscopy are presented. Data from polymer structures on metallic substrates as well as from polymer structures on different semiconductors are shown. To avoid any modification of these samples during the optical inspection, all experiments were performed contact-free in transmission or reflection mode.

8:40am **C3-3 X-Ray Fluorescence as a Powerful Tool for the Study of Chemistry of Thin Films**, *A. Siozios, D.F. Anagnostopoulos, M.A. Karakassides,* ***P. Patsalas*** *(ppats@cc.uoi.gr)*, University of Ioannina, Greece

X-ray fluorescence (XRF) is one of the most well-established optical, non-destructive techniques for elemental analysis of bulk materials. Unlike X-Ray Photoelectron Spectroscopy, which is considered the most sensitive technique for chemical analysis of surfaces and thin films, XRF was considered too vague for thin film studies. However, new advances in XRF instrumentation enable today its implementation in studies of thin films and coatings, as well.

In this work we present a case study of XRF analysis of AlN and AlN-based nanostructured thin films. We have selected AlN as an extreme case of a ceramic material, which consists exclusively of light elements where Auger emission and not fluorescent X-Rays is more probable for the recombination of the 1s vacancy and a high-energy level electron.

We have considered AlN and AlN_x films grown by reactive magnetron sputtering and pulsed laser deposition and we observed the chemical shifts of the Ka and Kb lines and the emergence of the Kb' line of Al due to the chemical environment around it (Al or N first neighbors). We compared the chemical shifts observed in AlN thin films to those observed for Al_2O_3 (useful for studying oxidized Al and AlN) and $AlCl_3$ (the most popular solid precursor for AlN growth by chemical vapor deposition) and we show that there is a rational variation according to the electro-negativity of the ligand. We note that XRF has been able to identify the formation of stoichiometric, yet amorphous, AlN where X-Ray Diffraction was useless due to the absence of crystalline periodicity. Finally, we identified the film thickness limits for which XRF can provide reliable results.

XRF has been also applied in investigating the oxidation of AlN by recording the evolution of oxygen's Ka line. The strength variation of this line for various AlN thicknesses indicates whether an oxide layer is located at the surface or the interface of the film.

In order to investigate the potential of XRF to study more complex materials, we have employed it for the study of AlN-based films with Ag inclusions in various forms. Thus, we have studied films where Ag was: 1) atomically dispersed into the AlN lattice, 2) nanospheres (~3.5 nm) embedded into an AlN matrix, and 3) Ag nano-sheets into AlN (i.e. AlN/Ag nano-multilayers). Comparing the Ka, Kb and Kb' chemical shifts in these films to those observed for Al, AlN and AlAg intermetallics, we were able to evaluate the nature of AlN-Ag bonds for the various considered cases.

9:00am **C3-4 Electrochromic Properties of Nanocrystalline MoO_3/V_2O_5 Composite Thin Films**, ***C.-C. Chang*** *(ccchang1978@phys.sinica.edu.tw), C.-H. Hsu, K.-W. Yeh,* Academia Sinica, Taiwan*, C.-S. Hsu, C.-C. Chan, C-.K. Lin,* Feng Chia University, Taiwan*, M.-K. Wu*, Academia Sinica, Taiwan

In the present study, MoO_3/V_2O_5 composite thin films were prepared by sol-gel spin-coating technique. The spin-coated MoO_3/V_2O_5 thin films were amorphous before calcining, nanocrystalline MoO_3/V_2O_5 thin films were afterward. The surface morphology of crystallized MoO_3/V_2O_5 thin films was examined by scanning electron microscope (SEM). X-ray diffraction for phase identification was performed by an X-ray diffractometry . Electrochromic properties of these thin films were evaluated by cyclic voltammetry, using a standard three-electrode cell system. All CV measurements were performed from -2 to 2 V at a scan rate 30 mV/sec at room temperature. Transmittance spectra of the films were examined by a spectrophotometer.

The effect of annealing temperature ranged from room temperature to 400 ^{o}C on film morphology was investigated. Experimental results showed that after heat-treated MoO_3/V_2O_5 composite thin films exhibited batter electrochromic properties among the films examined in the present study.

9:20am **C3-5 Nitrogen-Doping Induced Changes in the Microstructure and Optical Properties of Nanocrystalline WO_3 Thin Films**, ***R.S. Vemuri***, *S.K. Gullapalli, C.V. Ramana (rvchintalapalle@utep.edu)*, University of Texas at El Paso

Tungsten oxide (WO_3) is a wide band gap (E_g) semiconductor (E_g~3.2 eV), which exhibits excellent properties suitable for the development of integrated chemical sensors, electrochromics, and photoelectrochemical cells. Recently, band gap modification with anoion doping has received a significant attention in view the materials' application as photo-electrode for hydrogen generation by photo catalytic water splitting. The present work was performed to understand the effect of nitrogen-doping induced changes in the microstructure and optical properties of WO_3 films grown by reactive magnetron sputter-deposition. The objective of this work is to optimize the conditions to produce materials suitable for photo-electrodes for hydrogen generation by water splitting. The characterizations performed using grazing incidence X-ray diffraction and optical absorption measurements indicate that the effect of reactive nitrogen pressure is significant on the microstructure evolution and optical properties. The films grown at various reactive gas pressures (0–5.6 mTorr) while keeping the deposition temperature fixed at 400^{o}C shown the degradation of crystal quality for the initial nitrogen-doping while higher end nitrogen-pressure leads to the formation of morphological disorders. Optical spectroscopy analysis of the films indicates that Eg becomes narrowed upon nitrogen indicating the electronic structure changes. Eg decreases from 2.98 eV to 2.12 eV with increasing nitrogen pressure. The results will be presented and discussed.

9:40am **C3-6 Effect of Growth Temperature on the Structure, Electrical and Optical Characteristics of Sputter-Deposited Y_2O_3 Thin Films**, ***V.H. Mudavakkat***, *K. Bharathi,* University of Texas at El Paso*, V.N. Kruchinin, L.D. Pokrovsky, V.V. Atuchin,* Institute of Semiconductor Physics, Russia*, C.V. Ramana (rvchintalapalle@utep.edu)*, University of Texas at El Paso

Significant research efforts have been directed in recent years on the growth of Y_2O_3 thin films because of their interesting physical, electronic, and optical properties. The diverse range of potential applications of Y_2O_3 films includes storage capacitors, random access memory (RAM) and metal−insulator−semiconductor (MIS) devices, protective and antireflective coatings for IR detectors, and optical filters. In the present work, Y_2O_3 films have been produced by the reactive magnetron sputter-deposition. The effect of growth temperature (T_s) on the microstructure, electrical and optical characteristics Y_2O_3 films has been investigated. The results indicate that the films grown at room temperature (RT) are amorphous while the films grown at the substrate of T_s=300-500ºC are nanocrystalline crystallizing in cubic phase. Scanning electron microscopy analysis of Y_2O_3 films indicates the fine microstructure and uniform distribution of dense particles. Grain-size increases from ~5 to 50 nm with increasing T_s. Frequency variation of the electrical conductivity measurements in the range 20 Hz - 1 MHz indicate that the conductivity increases with increasing frequency. The conductivity data fits to a modified Debye's function, which considers multiple ions contributing to the relaxation. Spectroscopic ellipsometry measurements indicate that the refractive index (at 300 nm) of Y_2O_3 films increase from 2.03 to 2.25 with increasing T_s. This is attributed to the increased packing density and crystallinity of the films with increasing T_s. The results will be discussed and presented to derive a correlation between microstructure, electrical and optical properties in Y_2O_3 films.

10:00am **C3-7 Characterization of Nanometer Films by X-Ray and EUV Reflectometry**, ***S. Braun*** *(stefan.braun@iws.fraunhofer.de), M. Menzel, S. Schädlich, A. Leson*, IWS Dresden, Fraunhofer Institute for Material and Beam Technology, Germany **INVITED**

Physical properties of nanometer films are decisive for many optical and electronic devices. Characteristics like thickness, roughness, density and reflectance have a strong impact on the performance of functional coatings. Currently, one of the main driving forces for the development of optical thin films is the extreme ultraviolet (EUV) lithography. EUV lithography will be used for the production of next generation integrated circuits of the 22 nm node. In this technology nanometer multilayers are applied as reflection coatings on every optical element of the beam path (source collector, illumination and projection optics, photomask).

In order to measure the necessary properties of the films X-ray reflectometry is a very powerful tool. Due to the short wavelength the interaction of the radiation with the films results in interference associated with distinctive features in the reflectance spectra.

Initially a short overview about the theoretical background, commonly used experimental equipment and available software algorithms of the reflectometry method will be presented. The influence of specific thin film parameters on the reflectance spectra will be discussed.

Using the example of nanometer single and multilayers for X-ray mirrors the method will be practically applied and current capabilities of X-ray and EUV reflectometry will be shown. It will be demonstrated that thickness differences in the picometer range can clearly be distinguished over macroscopic dimensions of about 500 mm. Furthermore densities of graphite-like and diamond-like carbon layers will be analyzed and roughness results obtained with X-ray reflectometry and atomic force microscopy will be compared.

10:40am **C3-10 Morphological Evolution and Optical Characterization of ZnO Thin Films on PET and Glass Substrates by RF-Sputtering Technique**, ***J.R. Bortoleto*** *(jrborto@sorocaba.unesp.br),* State University of São Paulo - UNESP, Brazil*, E.P. da Silva, E. Amorim, E. Martins,* UNESP - Universidade Estadual Paulista, Brazil*, S.F. Durrant,* State University of São Paulo - UNESP, Brazil*, P.N. Lisboa-Filho*, UNESP - Universidade Estadual Paulista, Brazil

Zinc oxide has been used as transparent and conducting oxide film in solar cells and electrochromic devices. Also, ZnO thin films have great potential for applications in flexible display technology. In this work, surface morphology evolution, and optical and electrical properties of ZnO thin films deposited by RF sputtering technique onto polyethylene terephthalate and glass substrates have been investigated. Surface morphology was measured with atomic force microscopy (XE-100, Park Instruments) operating in air. Both 5 um x 5um and 1um x1um AFM images were acquired and the surface roughness was characterized in terms of root mean square roughness. Optical Transmittance was performed using a Uv-Vis-NIR spectrometer (Lambda 750, Perkin Elmer) ranging from 190 nm to

3300 nm. The crystalline degree of ZnO thin films was measured using a X-ray diffractometer system (D/MAX-2100/PC, Rigaku). X-ray diffraction patterns confirm the proper phase formation of the material. Optical transmittance data show high transparency (more than 85%) of the films in the visible range. Electrical characterizations show the room-temperature conductivity of the films deposited onto polyethylene terephthalate substrates. For films deposited on glass substrates the surface resistivity measures are less than 40 Ω/sq. The authors would like to thank Brazilian agencies CNPq and FAPESP for financial support.

11:00am **C3-11 Enhanced Photoluminescence from $Zn_{0.55}Cd_{0.45}$S:Mn/ZnS Core Shell Nanostructures**, *S. Singhal, **A.K. Chawla**, H.O. Gupta, R. Chandra (ramesfic@iitr.ernet.in)*, Indian Institute of Technology Roorkee, India

We hereby report the synthesis of $Zn_{0.55}Cd_{0.45}$S:Mn/ZnS core shell structured QDs with varying shell thickness by a two step co-precipitation technique at 280K. With increase in shell thickness the intensity of the XRD peaks of core decreases while that of shell increases which is an indication of the formation of core shell nanoparticles. UV-Vis measurements showed a red shift with increase in the shell thickness. The TEM micrograph confirms the formation of core/shell structures. The particle size obtained from TEM and UV-Vis measurements are in well agreement with each other. Photoluminescence spectra reveal that the maximum intensity of the band at ~ 590 nm (which is a characteristic emission of Mn^{2+} ion) is found for a shell thickness of 0.2 nm and is ~ 35 times higher than the Core QD's.

11:20am **C3-12 Environment Sensitivity and Film Stability of InGaZnO TFT with Annealing Temperature Dependence**, ***Z.-X. Fu***, National Chiao Tung University, Taiwan, *Z.-Z. Li,* Minghsin University of Science and Technology, Taiwan, *Y.-T. Chou, P.-T. Liu (ptliu@mail.nctu.edu.tw),* National Chiao Tung University, Taiwan, *B.-M.. Chen*, Minghsin University of Science and Technology, Taiwan

We investigated the effect of post-annealing temperature with non passivation a-InGaZnO TFT. As increasing the annealing temperature from 25°C to 45°C, the electrical parameter such as threshold voltage、subthreshold swing and mobility improve apparently. The bonding energy of oxygen in a-InGaZnO film became stronger with higher annealing temperature shows in XPS data. In addition to that, the storage of 45°C annealed device was excellent with ±0.5V of V_{th} variation under the environment after 9 days and the anti-UV ability was also better with 1.5V threshold voltage shift under UV light illumination. After being gate bias stress, the Vth shift decrease with higher post-annealing temperaure and that mean the improvement of film quality were actually better in 45°C. The passivation-free a-InGaZnO TFT annealed in higher temperature performs a better electrical characteristic and the binding energy of oxygen increases in a-InGaZnO film. According to that, the environment storage is stable after 9 days because the film is stable which avoiding the oxygen desorption in the ambient atmosphere. Besides, the anti-UV ability also improves with higher annealing temperature. The V_{th} shift is also smaller with less interstitial oxygen. The positive gate bias stress (PGBS) also shows a good performance caused by less absorption of oxygen in the ambient atmosphere with high annealing temperature. The thermal annealing could actually improve the a-InGaZnO TFT to be more stable and insensitive to UV light.

11:40am **C3-13 Structural and Optical Properties of Chlorinated Plasma Polymers**, *R. Turri,* State University of São Paulo - UNESP, Brazil, *C.U. Davanzo,* UNICAMP, Brazil, *W.H. Schreiner,* State University of Paraná, Brazil, *J.H. Dias da Silva, M.B. Appolinario, **S.F. Durrant** (steve@sorocaba.unesp.br)*, State University of São Paulo - UNESP, Brazil

Amorphous hydrogenated chlorinated carbon (a-C:H:Cl) films were produced by the plasma polymerization of chloroform/acetylene/argon mixtures in an rf PECVD system. The main parameter of interest was the ratio of chloroform to acetylene in the chamber feed. Films were deposited onto aluminum covered glass slides and aluminum plates, respectively, for subsequent characterization by infrared reflection-absorption spectroscopy (IRRAS) and X-ray photoelectron spectroscopy (XPS). IRRAS spectra revealed the presence of C-Cl groups and XPS confirmed the presence of chlorine. Several optical properties were obtained via film thickness data and ultraviolet-visible-near infrared spectra. The latter were obtained using a Perkin Elmer Lambda 750 spectrophotometer. Thus dependencies of the refractive index, n, absorption coefficient, α(E), and optical gap, E_{04}, on the degree of chlorination were obtained.

Applications, Manufacturing, and Equipment
Room: Royal Palm 4-6 - Session G3

Atmospheric and Hybrid Plasma Technologies
Moderator: H. Barankova, Uppsala University, S. Dixit, Plasma Technologies, Ltd.

8:00am **G3-1 Atmospheric Pressure Plasma Treatment of Polymers for Ink-Jet Deposition of Flexible Solar Cell Platforms**, ***D.D. Pappas** (daphne.pappas@us.army.mil), V. Rodriguez-Santiago, M.S. Fleischman, A.A. Bujanda,* U.S. Army Research Laboratory, *V. Chhasatia, B. Lee, Y. Sun*, Drexel University

The use of low-cost, high-volume inkjet printing technologies for the delivery of solution processed photovoltaic materials onto flexible substrates has shown great potential over bulky, rigid silicon technologies and is likely to be at the forefront of revolutionary solar cell manufacturing processes. The main advantages of inkjet printing over other commonly used deposition techniques lie in its high repeatability, pattern flexibility, and roll-to-roll compatibility. The ease of fabrication via low temperature evaporation and/or solution processing opens up a potentially wide market for these energy harvesting and storage devices to be integrated onto or into other applications such as textiles, composite and packaging materials.

However, the use of polymer-based flexible platforms raises some technical challenges related to poor adhesion between the substrates and the deposited materials, as well as the development of conformal, pinhole-free coatings. To overcome these issues, we employed atmospheric plasma technology to functionalize the surface of polyethylene naphthalate (PEN) and polyethylene terephthalate (PET) substrates prior to the subsequent coating with ZnO nanorods and CdSe nanoparticles, which act as photosensitive materials. The goal of this work is to investigate the contribution of the He-O_2 and He-H_2O plasma pretreatment step to the surface properties of PEN and PET. Towards this direction, we used contact angle goniometry, x-ray photoelectron spectroscopy and scanning electron microscopy to study the physicochemical changes of the plasma treated polymers. Results show improved hydrophilicity due to the grafting of oxygen-containing groups which are expected to participate in the formation of covalent bonds with the photoactive coatings. Also, we studied the effect of ink-jetting parameters, including drop volume, velocity, frequency, temperature, substrate translational speed, orifice/substrate offset distance, and others, on the microstructure of the deposited photoactive materials on the flexible substrates.

8:20am **G3-2 Investigation on the Discharge Formation Mechanisms and Surface Analysis of SiO_2-Like Layers on Polymers Synthesized Using High Current Dielectric Barrier Discharge at Atmospheric Pressure**, ***M.C.M. van de Sanden** (M.C.M.v.d.Sanden@tue.nl), A. Premkumar Peter,* Eindhoven University of Technology, Netherlands, *S.A. Starostin, H.w.d. de Vries,* FUJIFILM, Netherlands, *M. Creatore*, Eindhoven University of Technology, Netherlands

The dielectric barrier discharge is recognized as a promising tool for PECVD of thin films at atmospheric pressure. Emerging applications including encapsulation of flexible solar cells and flexible displays requires low costs production of transparent uniform and dense layers with low level of coating defects. Among the two discharges Townsend like discharge (TD) and glow like discharge (GD) the latter offers more flexibility for the high growth rates in plasma enhanced deposition. In this investigation we demonstrate the utilization of glow like discharge in, He free, industrially relevant gas mixture comprising Ar/N_2/O_2/HMDSO for the deposition of high quality silica like films on large area polymeric substrates (PET or PEN) in a roll-to-roll configuration. While the discharge physics exhibiting the glow like behaviour is investigated via fast ICCD camera, voltage-current waveforms and optical emission spectroscopy, the deposited silica like films is comprehensively analyzed using AFM, SEM, XPS, SE and FTIR. The time evolution of the diffuse atmospheric discharge showed several phases starting from the initial ignition of the low current Townsend-like mode followed by the transition to glow like discharge which then undergoes lateral expansion providing uniform treatment of the whole substrate width. As a generic characteristic of the developed technology, it is observed that, irrespective of precursors (TEOS or HMDSO) and process gases (Ar, N_2 or air) employed, the films are smooth, both locally and globally, and of near stoichiometric silica with very low carbon content (< 2%). Detailed AFM morphology description and surface statistical analysis on SiO_2 dynamics showed that no film roughening in growth front and lateral directions observed and the synthesized layers (~ 350 nm) grow in a self-similar fashion following the topology of the substrate. The films are uniform with no defects or particle being incorporated during the deposition process and exhibit excellent barrier performances towards O_2 and H_2O permeation.

8:40am **G3-3 Surface Modification of Inks, Coatings and Adhesives - The Interfacial Effects**, ***R. Wolf*** *(RWolf@enerconmail.com)*, Enercon Industries Corporation **INVITED**

It is well-documented that polymer film surface modification techniques can greatly improve the acceptance of a wide variety of coatings, adhesives and inks for improved flexible packaging structures. By increasing the hydrophilic characteristics and surface-free energy of polymers, bond strengths can be improved dramatically. It is theorized that interlayer adhesion between ink and coating formulations can also be improved by applying atmospheric plasma surface modification techniques. This study examines experimental data which relate correlations between surface modification and interlayer adhesions of inks, coatings and adhesives.

9:20am **G3-6 Effects of Coating Morphology on *In-Situ* Impedance Spectra of Plasma Electrolytic Oxidation Process**, ***C.-J. Liang****, A. Yerokhin (a.yerokhin@shef.ac.uk),* University of Sheffield, UK*, E.V. Parfenov,* Ufa State Aviation Technical University, Russia*, A. Matthews*, University of Sheffield, UK

Plasma electrolytic oxidation (PEO) is an atmospheric pressure surface treatment that provides excellent wear- and corrosion-resistant coatings on light-weight metals, in particular on aluminum. Formation of PEO coatings is affected by different factors, which requires in-depth understanding. New insights into coating formation mechanisms and means of process control can be attained using *in-situ* impedance spectroscopy which is an emerging characterization and diagnostic tool to study time-variable and non-linear processes, such as PEO. *In-situ* impedance spectra of the PEO process often feature evidence of distributed and far-out linear elements present in the system; however the nature of such behavior is not always clear. In most cases, the distributed properties are modeled by constant phase elements (CPE) that can be associated with different factors, including variable coating thickness, topology or composition. In this work, the effects of coating morphology on *in-situ* impedance spectra of the PEO process on Al are studied using fractal approach. The fractal analysis is a useful method to investigate the properties of heterogeneous (e.g. rough, porous or multiphase) materials, which can provide a direct link to the CPE characteristics. The fractal analysis was applied to surface plane and cross-sectional SEM images of PEO coatings with a range of nominal thicknesses produced during different treatment times. Additionally, coating elemental and phase distributions were studied using EDX and nanoindentation mapping respectively. Fractal dimensions of morphological characteristics of PEO coatings were derived and compared to the values of CPE elements obtained from model fitting of the impedance spectra. Further comparisons were made with the results of conventional electrochemical impedance spectroscopy analysis performed on the PEO coatings in working silicate-alkaline electrolytes.

9:40am **G3-7 The Effect of Current Mode and Discharge Type on the Corrosion Resistance of Plasma Electrolytic Oxidation (PEO) Coated Magnesium Alloy AJ62.**, *R.O. Hussein, P. Zhang, X. Nie,* ***D.O. Northwood*** *(dnorthwo@uwindsor.ca)*, University of Windsor, Canada

Magnesium alloys are increasingly being used as lightweight materials in the automotive, defense, electronics, biomaterial and aerospace industries. However, their inherently poor corrosion and wear resistance have, so far, limited their application. In this work, plasma electrolytic oxidation (PEO) process in an environmentally friendly aluminates electrolyte was used to produce oxide coatings with thicknesses of ~80 µm on an AJ62 magnesium alloy. Optical emission spectroscopy (OES) in the visible and near ultraviolet (NUV) band (285 nm – 800 nm) was employed to characterize the PEO plasma. It was found that the plasma discharge behavior significantly influenced the corrosion resistance, microstructure and the morphology of the oxide coatings. Scanning electron microscopy (SEM) and X-ray diffraction (XRD) were used to characterize the coating morphology and microstructure, and potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) in a 3.5% NaCl solution were used to determine the corrosion behaviour. It was found that the corrosion resistance of the coated alloy could be significantly increased by changing the current mode from unipolar to bipolar, where the strong discharges have been reduced or eliminated.

10:00am **G3-8 An Integrated Microwave Atmospheric Plasma Source**, ***R. Gesche*** *(roland.gesche@fbh-berlin.de)*, Ferdinand-Braun-Institut, Berlin, Germany **INVITED**

The development of a novel integrated atmospheric microplasma source is presented. A mi-crowave resonator for impedance transformation contains the plasma electrodes. An oscillator circuit containing a GaN HEMT power transistor is directly attached to the resonator. This leads to a compact device, powered by a simple 24 V DC power supply. The integrated con-cept allows a compact and cost efficient realization of a low-power plasma source for small area applications in the medical and industrial field.

The source operates at a frequency of around 2.45 GHz with a maximum oscillator power of 30 W. The complete source module including electrode, resonator and microwave oscillator has a length of approx. 150 mm and a diameter of approx. 30 mm. The visible afterglow plasma flame has a diameter of approx. 1 mm and a length up to 5 mm. The plasma source works with ambient Air as well as with Oxygen, Argon, Helium, and Nitrogen.

Several procedures of microwave characterization including specialized calibration and de-embedding procedures are presented. Ignition voltages are measured as well as transient microwave plasma impedances during ignition which are important for the design of a stable and efficient oscillator.

Data are presented for several applications, e. g. for the surface activation of polymers. The possibilities of integration in manufacturing processes are discussed.

10:40am **G3-10 Nanocoating System with Focused ICP Atmospheric Plasma Torch for Anti-Reflective Coating**, ***Y. Glukhoy*** *(glukhoy1@aol.com), A. Usenko*, American Advanced Ion Beam Inc.

A focused ICP atmospheric plasma torch has been used for yttrium oxide (Y_2O_3) nanocoating to prolong lifetime of the immersed in a plasma etching chamber parts with the non-flat surfaces like showerheads holes, steps of focusing rings, etc. Although Y_2O_3 has a high melting point our torch can provide for injected nanoparticles enough residential time in a high temperature area to be completely melted , evaporated in and delivered inside of deep holes , trenches and the porous structures. Another application such a torch is developing the nano-structured arrays used for anti-reflective, anti-glare and light capturing surfaces. It is possible using simultaneously with yttrium oxide as precursor nanopowder of silicon oxide or other material with a low resistance to etching plasma to develop the large scale moth's eye like repetitive arrays nanostructures with cones approximately 200 nm high and 200 nm apart. But it requests a fine focusing of the torch in combination with a precise motion of substrate and one by one injection of two precursors synchronized with motion.

The torch is sustained by two saddle-like ICP antennas with the different frequencies, i.e. 27.12 and 13.56 MHz. Each antenna comprises two or more spiral coils in a mirror position and in series or parallel connection. These coils are distributed with an angular uniformity and envelop a quartz tube of a plasma reactor. Such a design allows generation of a transversal RF field directed normally to axis of this reactor that broaden and lengthen the high temperature area. . A plasma fluid is fixed on the axis due to buoyancy in the centrifugal force field created by a swirling injection of a discharge gas and two sheath gases in clockwise and a counterclockwise directions . .Such a triple vortex stabilization provides intensive flow rotation and the pressure minimum on the axis and prevents approaching of plasma to the quartz tube. Nevertheless, such a torch is highly charged especially in area of a tip causing diffusing of the spot. We have developed a method of compensation of these charges that minimize such a spot. Behavior of an inductively coupled plasma torch with non-axial generation, mechanisms of balancing of saddle-like antenna coupling, dynamic of the vortex stabilization of the plasma fluid and gas focusing will be discussed.

1. Y.Glukhoy, I. Ivanov RF Atmospheric Plasma Systems for Nanopowder Production and Deposition of Nanocrystallines. AVS 53rd International Symposium, San Francisco, California, November , 2006 CA, USA.

2. Y.Glukhoy. Saddle-like ICP Antenna for RF Atmospheric Plasma Processes. AVS 56th International Symposium, San Jose, California, November , 2009 CA, USA.

11:00am **G3-12 Plasma Characteristics of Hollow Cathode Discharge in Plasma Ion Implantation of Slender Bore**, ***C.Z. Gong****, X.B. Tian (xiubotian@163.com), H.F. Jiang, S.Q. Yang,* Harbin Institute of Technology, China*, R.K.Y. Fu, P.K. Chu*, City University of Hong Kong, China

Plasma ion implantation has been receiving much interest in interior surface modification of cylindrical bore. However, the uniformity of incident dose relies on plasma characteristics inside the tube, especially for slender tube. Hence, it is very beneficial to produce steady plasma with high density, and to be slightly subject to the restrictions of diameter of tube. Aiming at this object, a novel hollow cathode plasma source is utilized to treat the interior surface of tube in this paper. Stable plasma can be sustained in the tube with dimension such as 30mm in diameter and 200mm in length. The plasma characteristics of the hollow cathode plasma source has been investigated using Langmuir probe with different instrumental parameters including rf power, gas pressure, and length of tube, etc. As for the confined hollow cathode discharge configuration(e.g. in tube), the plasma density decreases from hollow cathode outlet along the axial direction of tube, and plasma density increases with rf power increasing, but it exhibits nonlinear relationship with increasing gas flow and gas pressure. The inner diameter of hollow cathode has a great effect on plasma density.

Applications, Manufacturing, and Equipment
Room: California - Session G4/E4

Coatings for Machining Advanced Materials and Advanced Manufacturing Methods
Moderator: M. Arndt, OC Oerlikon Balzers AG, X. Nie, University of Windsor

8:00am **G4/E4-1 Nanocomposite (Ti,Cr,Al,Si)N Coatings for Hard Machining of PM High Speed Steel**, *K. Bobzin, F. Klocke,* RWTH Aachen University, Germany, *K. Arntz,* Fraunhofer-Institut für Produktionstechnologie IPT, Germany, *N. Bagcivan,* RWTH Aachen University, Germany, *M. Stolorz,* Fraunhofer-Institut für Produktionstechnologie IPT, Germany, ***M. Ewering*** *(ewering@iot.rwth-aachen.de), L. Stalpers*, RWTH Aachen University, Germany

PM (powder-metallurgical) high speed steels are increasingly employed as tool materials for cold work applications due to their high abrasion resistance and toughness. Nevertheless, the machining of these materials is very challenging due to vanadium and iron carbides which lead to high abrasive wear on the cutting edges as well as the high toughness of these materials which leads to adhesive wear.

To meet these challenges nitride nanocomposite coatings seem to be promising. In the present work (Ti,Cr,Al,Si)N coatings were deposited on cemented carbides via MSIP (Magnetron Sputter Ion Plating) and investigated using XRD, SEM and scratch test. Different working points within the nitrogen hysteresis were chosen to optimize the coating's morphology and mechanical properties.

The developed coating was deposited on ballnose end mills and tested in milling of S790PM, 62HRC (1.3345, M3 class 2) in comparison to two different commercial coatings: (Ti,Al)N deposited via MSIP and (Ti,Cr,Al,Si)N deposited via Arc Ion Plating. As tool life criterion a flank wear width of 100 µm was chosen. It could be shown that, depending on the cutting parameters, the tool life is increased by 20 - 30% by the new developed coating.

8:20am **G4/E4-2 Substrate Surface Etching Effects on Machining Performance of Diamond-Coated Cutting Tools**, *R. Thompson, D. Nolen,* Vista Engineering, ***F. Qin***, *K. Chou (kchou@eng.ua.edu)*, University of Alabama

For carbide tools, the cobalt binder phase is a very good solvent of carbon, and thus, in diamond deposition process, diamond nucleates on these substrates through a non-diamond layer. The weak graphite layer at the interface results in poor adhesion, which is the main technical challenge to enhance machining performance of diamond-coated tools. Substrate surface modifications are the key solutions to grow highly adherent diamond on carbide tools. Chemical etching is a widely applied method. Though low-cost, the control of material removal process is lack of precision and uniformity. Thus, variations in the etching effect and consequent tool performance may be significant.

In this study, both conventional etching (CE) and electrolytic etching (EE) methods were tested to remove substrate surface cobalt. The substrates used were 6 wt.% cobalt fine-grain tungsten carbides of square-shape inserts . After etching, diamond films were produced by a high-power microwave plasma-assisted CVD process, with a thickness of about 20 µ m. A computer numerical control lathe was used to perform machining experiments to evaluate the wear behavior of differently etched tools. Workpieces were round bars made of A359/SiC-20p composite. Machining parameters used consisted of two levels of cutting speeds and feeds. During machining testing, the cutting inserts were periodically inspected by optical microscopy to measure flank wear-land. Worn tools after testing were also examined by scanning electron microscopy.

The preliminary results show that (1) the coated EC tools have better delamination resistance under indentation loads, (2) The coated CE tools have rougher surfaces, (3) the EC tools have less flank wear, though same wear patterns, and a longer tool life compared to CE tools. The results indicate that electrolytic etching can be an effective alternative to enhance interface adhesion, and thus, tool wear resistance. In addition, effects on machining performance are dependent upon machining conditions.

8:40am **G4/F4-4 Influence of Edge Micro-Geometry and Coating Design on the Drilling of Titanium Alloys with Carbide Drills**, ***A. Pilkington*** *(antony.pilkington@rmit.edu.au), S.J. Dowey, J.T. Toton,* RMIT University and Defence Materials Technology Centre, Australia, *D. Griffett,* Cuttertec Pty, Australia, *O. Smith,* Sutton Tools Pty, Australia, *E.D. Doyle*, RMIT University and Defence Materials Technology Centre, Australia

The increasing use of Titanium alloys in advanced civil and military aerospace manufacturing has created a demand for continuous improvement in the performance and reliability of round shank tooling. Evolutionary advances in tool design are achieved by optimising the substrate, macro and micro geometry, surface finish and through PVD coating with the latest generation high performance ceramic materials.

In this work Ti6Al4V titanium alloy plate was drilled with 6.5mm diameter carbide drills with conventional soluble oil coolant. Machining parameters were varied between 25-80m/min and feed rates of 0.1-0.25mm/rev. The drill performance was quantified by metal removal rate and compared to an un-coated tool. A force dynamometer was used to measure torque and thrust forces. Hole quality metrics were investigated using an infinite focus microscope (IFM) to measure hole surface roughness and burr height on entry and exit. Different edge treatments of 3-30 microns were applied to the tooling. The as-ground sharp drill lips were modified by a conventional chamfer, which was ground during tool manufacture and a blended radius was applied by nylon abrasive filament brushing (NAF) with a 500 grit SiC peripheral brush. The effect of PVD coating the drills was also investigated, both in the as deposited condition and after post-polishing by aluminium oxide NAF brushing. The torque and thrust data from the drilling tests was compared to a model derived by treating the drill cutting lip as an assembly of concentric single point tools. This practical model used data generated from orthogonal cutting tests using single edge carbide tooling with systematically varied rake, clearance and edge micro-geometries. IFM measurements of the edge micro-geometry were made to determine the detail of the shape factors created by the edge treatments. The effects of the edge offsets a,b and radii R on the cutting forces were investigated during the turning experiments. The results contribute to improved drill design for the optimisation of high performance hole-making in titanium components.

9:00am **G4/E4-5 Coating and Tool Wear in Composite Machining**, ***J. Bohlmark*** *(johan.bohlmark@sandvik.com),* Sandvik Tooling Stockholm SE, Sweden, *E. Merson, W.T. Goh*, Sandvik Tooling Sheffield, UK **INVITED**

Composite materials are compositions of two or more materials with significantly different physical properties with their respective properties kept intact on a microscopical level in the finished structure. The most commonly used composites are Carbon Fibre Reinforced Plastics (CFRP) and Glass Fibre Reinforced Materials (GFRP). These materials can offer high strength in combination with low weight, and are therefore popular structural materials in, for example, modern aircrafts. Machining operations of these materials can differ significantly from traditional metal machining, and are usually very challenging for cutting tools. Composite materials are abrasive, and obtaining long tool life is always a challenge in composites drilling. The abrasiveness of these materials is thought to be affected by their fibre volume, cure temperature, glass transition temperature, fibres types, cutting conditions used, etc. Research into various coatings and polycrystalline diamond (PCD) has been carried out and tests on different materials to study the wear behavior and the wear resistance of these coatings on tool wear have been performed. Although uncoated drills are commonly used in industries, test results reveal that coated WC/Co and PCD insert drills offer better tool life. Different types of tools are subjected to different wear mechanisms. Tools coated with non-diamond coatings (e.g. nitrides, oxides, borides) typically exhibit flank wear. Tools with diamond coatings show the problem of coating flaking. PCD tools exhibit edge rounding. Results from testing also show that only the diamond based solutions such as the Chemical Vapour Deposition (CVD) diamond coatings and PCD could significantly reduce tool wear rate. The reduced wear rate is believed to be connected to the very high hardness of the diamond.

9:40am **G4/E4-7 Fatigue Behavior of TiN Coating on WC-Co Cemented Carbides**, ***J.-F. Su***, *X. Nie (xnie@uwindsor.ca), H. Hu*, University of Windsor, Canada

Titanium nitride (TiN) is used as a protective coating on cemented carbide cutting tools to improve tool life and superficial quality of the workpiece. However, TiN is relatively brittle and could fail due to fatigue cracking-induced wear under localized contact stresses during the milling operation in which the combined motion of impact and sliding displacement between cutting tools and chips from the workpiece. In the present work, the fatigue behavior of TiN coatings on WC-Co carbides was investigated using a novel impact-sliding wear tester, which simulates a reciprocal movement of combined impact and sliding motions. The TiN coatings on the surface and cross-section were studied using Scanning Electron Microscopy (SEM) with Energy Dispersive X-ray (EDX) analysis. The degree and mechanism of the coating failure was evaluated by taking into consideration the properties of TiN coating and WC substrates. The test results provided constructive knowledge in selection and development of coatings for cutting tools.

10:00am **G4/E4-8 Improved Cutting Processes of Austenitic Steels with γ-Alumina Based PVD Coating Systems**, ***S.E. Cordes*** *(s.cordes@wzl.rwth-aachen.de)*, RWTH Aachen University, Germany

The machining of difficult-to-cut materials as austenitic steels is the focus of investigations for a long time now. One approach to overcome the problems when machining these materials is an appropiate coating system for the cutting tool. Especially the γ-phase of alumina is interesting for cutting operations due to its outstanding characteristics, such as high hot hardness, high thermal stability and low tendency to adhesion.

The deposition of alumina by using the Magnetron Sputter Ion Plating (MSIP)-PVD process faces different challenges: Deposition rates are low and insulating layers on the target surface can cause arcing. The development for deposition of oxides was first done by using radio frequency (r.f.) power supplies. This kind of process results in very low deposition rates, mostly amorphous structures of the coatings and expensive costs for ceramic targets and power supplies. During the last years, the deposition of oxides by the use of pulsed power supplies became more economically.

In the present work a (Ti,Al)N/γ-Al_2O_3-coating is deposited on cemented carbide in an industrial coating unit by means of MSIP. The (Ti,Al)N bond coat was employed to improve the adhesion of γ-Al_2O_3 on the substrate. The objective of this work is to study the wear mechanisms and the cutting performance of aluminium oxide based coated tools in turning, drilling and milling operations of austenitic steels, supplementary in combination with innovative environmental friendly lubricants. Based on the remarkable properties of this coating system the performance of the cutting tools is increasing significantly.

10:20am **G4/E4-9 An Investigation into the Tribological Performance of PVD Coatings on High Thermal Conductivity Cu Alloy Substrates and the Effect of an Intermediate Electroless Ni-P Layer Prior to PVD Treatment**, *J.C. Avelar-Batista Wilson (junia.avelar-batista@tecvac.com),* Tecvac Ltd, UK, *S. Banfield,* Tecvac Ltd and University of Sheffield, UK, *J. Eichler, A. Leyland, A. Matthews,* The University of Sheffield, UK, ***J. Housden***, Tecvac Ltd, UK

The use of high thermal conductivity copper alloys in plastic injection moulds provides the benefit of rapid moulding cycles through effective heat transfer. However copper alloys are relatively soft and wear rapidly so manufacturers are developing new copper alloys with increased hardness and wear resistance. This wear resistance can be further improved by the deposition of hard coatings such as electroplated chromium, electroless Nickel and PVD coatings. In this paper, the tribological performance of three proprietary high-strength Cu alloys (Ampcoloy 940, Ampcoloy 944 and Ampcoloy 83) coated with PVD CrN and CrAlN coatings has been evaluated. A medium phosphorous content electroless Ni-P (ENi-P) plated layer was also deposited as a pre-treatment to PVD CrN and CrAlN coatings to increase the load support. The effect of this intermediate ENi-P layer was also evaluated. Surface roughness and ultra-microindentation hardness measurements were used to characterise all coated systems in both plated (i.e., with the intermediate ENi-P coating) and standard (i.e. unplated) conditions. Scratch tests were also performed to evaluate the effect of the ENi-P on PVD coating adhesion to Cu alloy substrates. The tribological behaviour of PVD-coated Cu alloy systems was evaluated by pin-on-disc wear tests and ball-on-plate impact tests. Results demonstrate that the ENi-P layer improves the load support for PVD coatings on Cu alloys, thereby improving their tribological performance. However, for PVD-coated Cu alloys in the standard condition, the Cu alloy substrate type plays an important role in the tribological performance of PVD coatings. For instance, PVD CrN coatings were more suited to a certain Cu alloy type whilst CrAlN to the other two types.

10:40am **G4/E4-10 Mechanical Properties of Partially Oxidized Silicon Nitride Films Deposited by RF Reactive Magnetron Sputtering**, *J. Filla, C. Aguzzoli, V. Sonda, CLG. Amorim,* Universidade de Caxias do Sul, Brazil, *GV. Soares, I. Baumvol,* Universidade Federal do Rio Grande do Sul, Brazil, ***C.A. Figueroa*** *(cafiguer@ucs.br)*, Universidade de Caxias do Sul, Brazil

Hard coatings are widely used in surface engineering for wear protection and friction reduction of mechanical components. Nowadays, dry machining technologies are emerging techniques due to both reduction costs and environmental aspects. In fact, new coatings are being developed for high temperature applications, such as AlCrN, WC/C, Si_3N_4, as well as several multilayered coatings. However, the excellent performance, in terms of wear and corrosion resistance, of Si_3N_4 thin films in cutting tools at higher temperatures than 1000°C is still not fully understood.

In this work, silicon nitride thin films were deposited on Si(100) substrates by rf reactive magnetron sputtering from a Si target in a Ar/N_2 plasma at variable substrate temperatures. In order to reproduce the oxidation conditions of cutting tools in dry machining, the samples were oxidized in ^{18}O atmosphere at temperatures of 500 and 1000°C. Afterward, the thin films were characterized by glancing angle X-ray diffraction, X-ray reflectometry, Rutherford backscattering spectrometry, narrow nuclear resonant reaction profiling, nano-hardness and nano-scratch and friction measurements. Si_3N_4 stoichiometric films are obtained. Although the oxide layer thickness increases with temperature, silicon nitride thin films show a high corrosion resistance where the oxide layer thickness achieves a maximum value of 6-7 nm at an oxidation condition of 1 h and 1000°C. Nanohardness increases with deposition temperature as well as the compound density. Before oxidation, the friction coefficient follows a random behavior. After oxidation at both 500 and 1000°C temperatures, the friction coefficient follows a clear tendency where lower friction forces are measured when lower normal forces are applied. Such lower friction coefficients are attributed to a higher contribution of the oxide layer in the mechanical system. Finally, the thin oxide film obtained after dry machining at high temperature leads to improve the corrosion resistance and decrease the friction forces and, consequently and due to the maintenance of the hardness even at higher temperatures, the wear resistance is enhanced.

11:00am **G4/E4-11 Carbon Based Coatings for Machining of Aluminum and Magnesium Alloys**, ***A.T. Alpas*** *(aalpas@uwindsor.ca), S. Bhowmick,* University of Windsor, Canada, *M.J. Lukitsch*, General Motors Research and Development Center **INVITED**

Carbon-based coatings, particularly diamond like carbon (DLC) coatings exhibit low coefficients of friction (COF) against aluminum and magnesium and allow minimal amount of material adhesion to their surfaces when tested under the ambient conditions. The favourable tribological properties of DLC coatings have generated interest in using them as tool coatings for machining of lightweight aluminum and magnesium alloys. This talk is organized in two parts; first the adhesion mitigating properties of non-hydrogenated DLC (NH-DLC) coatings tested under various environmental conditions will be presented, the role of atmospheric humidity on reducing the COF and the material transfer will be discussed by examining surface passivation and carbonaceous layer formation mechanisms at the interfaces. Then, the performance of DLC coated tools in drilling of commercial cast aluminum and magnesium alloys under minimum quantity water lubrication (H2O-MQL) condition will be considered. Experiments have shown that he H2O (30 ml/h) -MQL drilling of 319 Al alloys using NH-DLC coated tools has improved the tool life and reduced the drilling torques and thrust forces considerably compared to dry drilling of this alloy. The effect of NH-DLC coatings in drilling of and AZ91 Mg alloy was more dramatic as the drilling forces generated during H2O-MQL drilling were found to be as low as those measured during flooded drilling using conventional coolants. The improvements in machining using DLC coated tools will be discussed in terms of their tribological properties and microstructural changes that occur in the workpiece during machining.

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

Coatings to Resist High Temperature Oxidation, Corrosion and Fouling
Moderator: Y. Zhang, Tennessee Technological University, J.R. Nicholls, Cranfield University, L.G. Johansson, Chalmers University of Technology, D. Naumenko, Forschungszentrum Julich

1:30pm **A1-2-1 Effect of Increased Water Vapor Levels on TBC Lifetime**, *A. VandePut,* CIRIMAT - ENSIACET Toulouse, ***B.A. Pint*** *(pintba@ornl.gov), J.A. Haynes,* Oak Ridge National Laboratory, *Y. Zhang*, Tennessee Technological University

While the exhaust in natural gas-fired land based turbines contains 10-15% water vapor, the exhaust with coal-derived fuels or innovative turbine concepts for more efficient carbon capture may be 30-85%. To investigate the effect of increased water vapor levels on thermal barrier coating (TBC) lifetime, furnace cycling tests were performed at 1150°C in air with 10, 50 and 90 vol.% water vapor. The specimens were all from the same batch of a commercial second generation superalloy and had Pt diffusion or Pt-modified aluminide bond coatings and commercially vapor-deposited yttria-stabilized zirconia top coats. The lifetime results will be compared to a prior study where similar coatings were thermally cycled in dry oxygen.

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

1:50pm **A1-2-2 Oxidation Resistance of Nanocomposite CrAlSiN under Long-Time Heat Treatment**, ***H.-W. Chen***, *Y.-C. Chan,* National Tsing Hua University, Taiwan, *J.-W. Lee,* Mingchi University of Technology, Taiwan, *J.-G. Duh (jgd@mx.nthu.edu.tw)*, National Tsing Hua University, Taiwan

As a protective coating, the nanocomposite CrAlSiN reveals better mechanical properties and higher thermal abilities than conventional CrAlN coatings. To investigate the oxidation behavior and structure stability, Si was doped into CrAlN films deposited on silicon wafers and sapphire substrates by RF magnetron sputtering and annealed at temperatures ranging from 1000 to 1200°C for 100 hours. The X-ray diffraction patterns revealed that the grain size of as-deposited $CrAlSi_xN$ (x = 0-12 at. %) coatings became finer with doping silicon. According to SEM micrographs, the growth of oxide layer was retarded with increasing silicon content after heat treatment in air. Additionally, the surface roughness of CrAlSiN using AFM analysis increased slightly even though annealed for a long time. As observed by TEM, the CrAlSiN coatings could well retain the nanocomposites structure after heat treatment at elevated temperature, indicating that CrAlSiN exhibits high structure stability at high temperature. Moreover, the thermal properties of coatings were also analyzed by TGA and DSC. To conclude, doping certain Si content could reduce the grain size and prolong the diffusion paths in CrAlN coatings, thereby effectively inhibiting nitrogen outside diffusion and oxygen penetrate into the coatings. Further, there was no significant variation in the microstructure of CrAlSiN after heat treatment, suggesting that the nanocomposites could preserve the oxidation resistance at elevated temperature.

2:10pm **A1-2-3 HRTEM Study of Arc-Sputtered Nanocomposite TiSiN Thin Films**, ***J. Mooney***, *E.I. Meletis (meletis@uta.edu),* University of Texas at Arlington, *Y.H. Cheng*, American Eagle Instruments, Inc.

Hardened nanocomposite thin film coatings have been the subject of much interest in the research community because of their high potential hardness (~100 GPa) and oxidation resistance. Much work has shown that the proper incorporation of Si into transition metal nitride coatings traditionally used in tribological coatings and diffusion barriers such as TiN can yield a nanocomposite material consisting of both nanocrystalline and amorphous phases. In order to assess the effects of Si content on material properties, large area filtered arc deposition was used to deposit thin film coatings of TiSiN. (1,2) The Si content of the coatings was varied by using TiSi targets with different Si content. Samples with the lowest and highest concentrations of Si (0.5 at% and 8.0 at%) were the subject of a detailed high resolution transmission electron microscopy study to advance our understanding of the relationship between film microstructure and mechanical properties.

1. Cheng, et al. J Phys D: Appl. Phys. 42 (2009)1.

2. Cheng, et al., Surf. Coat. Technol. 204(2010)2123.

2:30pm **A1-2-4 Moisture-Induced Desktop Spallation of TBCs**, ***J.L. Smialek*** *(james.l.smialek@nasa.gov)*, NASA Glenn Research Center **INVITED**

Delayed failure of TBCs is a widely observed phenomenon, even though many of the occurrences are anecdotal and unreported. The phenomenon is characterized by survival of a TBC after considerable thermal cycling and full cooling to room temperature. Yet, after some extended time under ambient conditions, the TBC may be found to be nearly fully delaminated. This has been termed “the weekend effect” or “desktop spallation.” It is generally assumed to result from exposure to ambient humidity, which may be considerably increased compared to the furnace environment. To further demonstrate the humidity factor, oxidized TBCs were subject to water immersion or a water drop exposure after being retained and fully cooled from a thermal cycling treatment. It is often found to then fail quite dramatically in less than a second, after some 10s of seconds of incubation time. To this end, digital video recordings have become a most useful observation technique. We report on early “no bond coat” plasma sprayed coatings, where 1100-1150°C cyclic life and resistance to water immersion are seen to increase as the sulfur content of the superalloy substrate was reduced. EB-PVD coatings using a Pt-aluminide bond coat are also seen to fail by the water drop test after 1150°C cyclic furnace tests. More recently, water drop failure is observed for a commercial TBC coated turbine blade, after oxidation at 1150-1200°C. In support of this phenomenon, colleagues from DECHMA (Rudolphi, Renusch, Schütze) and CNRS Toulouse/SNECMA (Déneux, Cadoret, Hervier, Monceau) have both produced very compelling and informative studies. They have used video, acoustic emission, and extended dry box storage of oxidized TBCs.

The phenomenon is rooted in moisture-induced delayed spallation of the alumina scale formed on the bond coat. In that regard, many studies show susceptibility of alumina scales to moisture, as long as high strain energy and a partially exposed interface exist. The latter result from severe cyclic oxidation conditions, producing a highly stressed and partially damaged scale. In one model, it has been proposed that moisture reacts with aluminum in the bond coat to release hydrogen atoms that ‘embrittle’ the interface. A negative synergistic effect with interfacial sulfur is also invoked.

3:10pm **A1-2-6 A Single Step Process to Form an In-Situ Oxidized Alumina Foam Coating for Alloys for Extreme Environments at High Temperatures**, ***X. Montero*** *(montero@dechema.de), M. Galetz, M. Schütze*, Dechema e.V., Germany

A new approach to manufacture a complete thermal barrier system in a single step is being studied during the European FP7 project called PARTICOAT. Spherical Al particles are deposited by screen-printing and air brush on IN738, Rene80 and CM247 nickel based alloys. During the sintering process in air the Al particles are partially oxidized and converted into hollow alumina spheres forming a ceramic “foam” (top coat), and simultaneously an Al rich diffusion layer (bond coat) is formed in the subsurface zone of the substrate.

The coatings were isothermally exposed at 800 and 1000°C in air for up to 1000 hours. The oxide formation and the microstructure of the coating were studied by thermo gravimetrical analysis (TGA), X-ray diffraction (XRD), scanning electron microscopy combined with energy dispersive X-ray spectroscopy (SEM-EDX).

The coatings were adherent for all the tested substrates and temperatures. The CM247 alloy shows the lowest mass gain whereas IN738 and Rene80 show higher mass gains at the tested temperatures. The use of reactive element oxides in the coating has also been tested, showing an improved bond-coat microstructure in the case of HfO_2. These results demonstrate the flexibility and viability of this low cost coating concept.

3:30pm **A1-2-7 Oxidation Behavior of Slurry Aluminide Coatings on Stainless Steel Alloy CF8C-Plus**, ***J.A. Haynes*** *(haynesa@ornl.gov), B.L. Armstrong, S. Dryepondt,* Oak Ridge National Laboratory, *Y. Zhang*, Tennessee Technological University

A new, cast austenitic stainless steel, CF8C-Plus, has been developed for a wide range of high temperature applications, including diesel exhaust components and turbine casings. CF8C-Plus offers significant improvements in creep rupture life and creep rupture strength over standard CF8C steel, with creep strength close to that of Ni-base superalloy 617. However, at higher temperatures and in more aggressive environments an oxidation-resistant protective coating will be necessary. This preliminary study compared the oxidation behavior of CF8C-Plus and aluminide-coated CF8C-Plus under various conditions, including 800°C in 10% water vapor plus air. Due to their economic viability, slurry aluminides were the primary coating system of interest, but chemical vapor deposition and pack cementation aluminide coatings were also compared. Substantial short-term improvements in oxidation behavior were achieved with each type of aluminide coating. However, as temperature and environmental aggressiveness increased, each coating displayed design challenges that will have to be overcome in order to develop economical coatings that are stable and protective on austenitic steel for the desired component lifetimes.

3:50pm **A1-2-8 Nitriding and Coating of a Stainless Steel for Corrosion Protection in Carburizing Atmospheres**, *V. Melo,* TRAMES SA de CV, Mexico, ***M. Salas***, *E. Oseguera (joaquin.oseguera1@me.com),* ITESM, Mexico, *R. Torres,* Pontificia Universidade Católica do Parana, Brazil, *R.M. Souza*, University of Sao Paulo, Brazil

304 steel is commonly used in applications at high temperatures in carburizing atmospheres. The natural Cr oxide layer that forms on these steels does not provide sufficient protection when they are exposed to those conditions. In the present work, substrates of 304 steel have been first plasma nitrided and then coated with additional Cr oxide by in order to provide a surface that will stand carburization at high temperature. The structure of the nitrided and nitride+coated substrates was characterized by optical microscopy, scanning electron microscopy + x-ray microanalysis, and x-ray diffraction. The results indicate that, despite the difficulty in nitriding materials such as this, that have a passivated surface layer, the advantages of the plasma process allowed the formation of a nitride layer which included the expanded austenite phase. Coating of the nitrided substrates was carried out by reactive magnetron sputtering varying the applied power, the oxygen flow and the application of a bias voltage. The mechanical properties of the coated substrates were investigated by nanoindentation experiments and the adhesion by scratch testing. The response of the coated nitride 304 samples to carburization was evaluated through thermogravimetry in a CH_4 atmosphere at 800°C.

Hard Coatings and Vapor Deposition Technology
Room: Golden West - Session B6-2

Application-Oriented Coating Design and Architectures
Moderator: C. Mitterer, Montanuniversität Leoben, M. Stueber, Karlsruhe Institute of Technology

1:30pm **B6-2-1 Various Approaches to Reveal the Architecture of Nanocomposite Thin Films**, ***C. Sandu*** *(silviucosmin.sandu@epfl.ch), T. Yamada, S. Harada, R. Sanjinés,* EPFL, Switzerland, *A. Cavaleiro,* Coimbra University, Portugal, *N. Setter*, EPFL, Switzerland **INVITED**

The mechanical, optical and electrical (resistivity, dielectric constant) macroscopic properties of nanocomposite films strongly depend on chemical composition and nanostructure. Different types of self-assembled composite material such as: ZrN-SiN, AlN-YN, MoSe-C and $BaTiO_3$-CeO_2 have been investigated. In such nanocomposite thin films the crystallite size is on the order of a few nanometers and hence the grain surfaces and boundaries have an important effect on the physical properties. The arrangement and the chemical composition of the phases must therefore be known precisely.

The limits of the standard characterization techniques in revealing such composite nanostructures will be discussed in order to emphasize the need for physical models. The limits to experimentally confirm such models motivate us to employ unconventional investigation techniques such as electrical and piezoelectric measurements or specialized HRTEM image processing. The continuity of insulating SiNx-layer on conducting ZrN-crystallites or the continuity of $BaTiO_3$-phase from bottom to top electrode were evidenced by electrical measurements.

2:10pm **B6-2-3 Effect of Cathodic Arc Plasma Treatment on the Properties of WC-Co Based Hard Metals**, ***S.A. Akkaya***, Istanbul Technical University, Turkey, *E.S. Sireli,* Böhler Sert Maden ve Takım Inc, Turkey, *M.K.K. Kazmanli, M. Urgen (urgen@itu.edu.tr)*, Istanbul Technical University, Turkey

In this study, the surfaces of WC-Co hard metals were treated by the application of different bias voltages, using a Cr cathodic arc source. The role of kinetic effects and the resulting temperature increase created through bias applications; on the diffusion processes that may take place on the substrates are investigated. It was observed that the depending on the magnitude and duration of the bias voltage significant changes on the structure of the hard metal could be obtained. WC grains close to the surface were observed to enlarge, also formation of eta carbides in the form of M12C and M6C were detected in the XRD measurements. The effects of these structural changes on the mechanical properties of the hard metals are determined and the possible utilization of these modified structures in industrial applications are discussed.

2:30pm **B6-2-4 Influence of Coating Architecture on Thermal Stability and Mechanical Properties of CrN Based Coatings**, ***M. Schlögl*** *(manfred.schloegl@unileoben.ac.at), F. Rovere, J. Paulitsch, J. Keckes, P.H. Mayrhofer*, Montanuniversität Leoben, Austria

High thermal stability, oxidation and abrasion resistance are only a few arguments for the use of ceramic-like hard coatings in industrial applications with severe conditions. Recently, we showed, that by the addition of a small fraction of ~2 mol% YN to sputtered single-phase c-$Cr_{0.46}Al_{0.54}N$ the hardness increases from ~32 to 34 GPa by the formation of a solid solution c-$Cr_{0.45}Al_{0.53}Y_{0.02}N$. These coatings also exhibit lower inherent compressive stresses and increased resistance against oxidation and N_2-release. Here we discuss a further modification of the coatings properties by changing their architecture from monolithic to multilayer and superlattice. For a comprehensive study we prepared (by magnetron sputtering) AlN/CrN, AlN/CrAlN and AlN/CrAlYN multilayer coatings with varying the layer thickness of AlN ranging from ~3 to 10 nm.

The different superlattice coatings were investigated with respect to structure and mechanical properties by using X-ray diffraction (XRD) and transmission electron microscopy (TEM). Independent of their bilayer period the individual AlN/CrN, AlN/CrAlN and AlN/CrAlYN multilayer coatings exhibit no crystalline wurtzite phase in the as deposited state and almost constant hardness values of 24, 30 and 34 GPa, respectively. Nevertheless, differential scanning calorimetric (DSC) investigations in combination with thermo gravimetric analysis (TGA) in He atmosphere and synthetic air up to temperatures of 1500°C suggest a higher thermal stability with decreasing the AlN layer thicknesses. This is confirmed by XRD studies exhibiting an onset of w-AlN and Cr_2N formation at lower temperatures with increasing AlN layer thicknesses of the individual AlN/CrN, AlN/CrAlN and AlN/CrAlYN multilayer coatings.

2:50pm **B6-2-5 Stress Design of Hard Coatings**, ***R. Daniel*** *(Rostislav.Daniel@unileoben.ac.at), J. Keckes, C. Mitterer*, Montanuniversität Leoben, Austria

A deep understanding of the relationship between deposition conditions, layer structure, residual stress state, mechanical and thermal properties and layer stability is one of the most important prerequisites to design and synthesize new coating systems of significantly improved performance. In this paper, the strong dependence of the layer structure on development of the residual stress state and thermal properties will be discussed in detail in the case of nanocrystalline transition metal nitride thin films. A guideline how to adjust and optimize the stress state in such layers by a controlled growth will be given together with a concept for enhancement of mechanical properties by structural design of single and multilayered coatings. For that purpose, analytical modeling and nanoindentation experiments were effectively combined in order to analyze the stress field developed underneath the indenting tip. The improvement of the wear behavior of thin films by an optimized coating architecture will be shown in a particular case of CrN/Cr layered coating system. The importance of the selection of the layer/substrate combination will be furthermore demonstrated by nanoindentation experiments with spherical indenters at high loads. Comprehensive understanding of the stress development in relation to the structure, mechanical properties and functionality will be a key for successful engineering of hard coatings.

3:10pm **B6-2-6 Nano-Beam X-Ray Diffraction Reveals Strain, Composition, Texture and Crystal Size Gradients Across Nano-Crystalline Thin Films**, ***J. Keckes*** *(jozef.keckes@mu-leoben.at), R. Daniel, M. Bartosik, C. Mitterer,* Montanuniversität Leoben, Austria, *S. Schoeder, M. Burghammer*, ESRF, Grenoble, France

Hard nanocrystalline coatings exhibit depth-gradients of crystallographic texture, strain, lattice defects, composition, grain size and morphology. This is a fundamental aspect determining the mechanical and thermal properties of the coatings. Up to now, mostly volume-averaged structural parameters of coatings were determined using X-ray diffraction studies in reflection geometry. The aim of this contribution is to introduce a new X-ray diffraction approach to characterize depth gradients of nanostructure and strain at the cross-section of hard nanocrystalline coatings. The new technique was developed at ID13 beamline of ESRF (Grenoble, France). The approach is based on position-resolved wide-angle X-ray diffraction performed in transmission geometry with a monochromatic beam of 100 nm. The new technique opens the possibility to map the structural properties of the coatings on the nano-scale. In the combination with finite-element modelling, the approach allows to assess the residual stress gradients across compositionally graded coatings. Finally this new approach opens a unique opportunity to correlate coating performance and actual nano-structural design.

3:30pm **B6-2-7 Numerical Modeling of the Stress Degradation Process in Hard Coatings**, ***W. Ecker*** *(werner.ecker@mcl.at), W. Eßl, G. Maier, R. Ebner,* Materials Center Leoben Forschung GmbH, Austria*, C. Mitterer, J. Keckes*, Montanuniversität Leoben, Austria

In this work a material model is presented that describes the degradation of deposition induced compressive residual stresses in hard coatings. The stress relaxation process is modeled assuming an in-plane shrinking of the coating depending on current in-plane stress and temperature. For calibration of the material model isothermal relaxation tests were used. The material model was implemented in the finite element commercial software ABAQUS, in order to simulate a relaxation test under nonisothermal conditions and cyclic thermal shock experiments imitating loading conditions similar to those occurring at cutting edges of tools. A comparison of calculated and experimentally measured residual stresses shows that there is very good agreement in case of the nonisothermal relaxation test. Even under the complex loading conditions occurring in the cyclic thermal shock experiments the behavior of the coating is well reproduced by the material model.

3:50pm **B6-2-8 Application-Driven Design of Wear-Resistant Coatings by Means of an Integrated Multi-Scale Coating Design Tool***,* ***M. Fuchs*** *(m.fuchs@siomec.de),* Saxonian Institute of Surface Mechanics, Germany*, K. Holmberg,* VTT Technical Research Centre of Finland*, N. Schwarzer,* Saxonian Institute of Surface Mechanics, Germany*, P. Kelly*, Manchester Metropolitan University, UK

The design of coatings is done in two major conventional ways: either by trial-and-error development based on empirical knowledge or model-driven using element-based models (e.g. FEM, BEM, MDS), stochastic models (e.g. Monte Carlo for deposition), or models based on empirical knowledge (e.g. for wear rate evolution). Such models are either not natively invertible or have a very limited scope. Consequently, both ways are very expensive, time-consuming, and also dangerous.

The main objective of the authors is the development of an surface design tool in terms of an expert system, which integrates analytical models of all knowledge steps (from surface processing to material structure in all scales to generic material properties to tribological performance) of the surface design process, in order to enable companies to quickly and reliably design or optimize application-tailored coatings and, therefore, drastically reduce trial-and-error testing and complicated modeling. Meaning, that one specifies the intended application as well as the desired lifetime of a surface and the surface design tool automatically derives, firstly, the necessary tribological performance, the mechanical material properties, the material nano-/micro-/macro-structure, and finally an appropriate processing technology and corresponding processing parameters based on the deposition equipment being at one's disposal. Scale-invariant analytical models for complex contact & load situations with arbitrary structured surfaces as well as wear prediction developed earlier [1,2] will be incorporated in order to predict wear and evaluate contact & load situations of the intended application during lifetime. Thus, it will be able to derive requirements concerning the surface with respect to its tribological performance, generic mechanical properties, and macro structure. However, there are no general analytical models for surface processing which enable one to predict the surface structure in all scales and resulting generic mechanical properties. Hence, the development of such a model is one sub-objective of the authors. In this work, the present development progress of this analytical model for the deposition process will be presented.

References

[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

[2] OptiWear: tribology experiment simulation software, http://www.siomec.de/OptiWear

4:10pm **B6-2-9 Coating Design for Metalcutting Applications**, ***A. Inspektor*** *(aharon.inspektor@kennametal.com), R. Penich,* Kennametal Inc.*, P.A. Salvador, N. Patel*, Carnegie Mellon University

The functional surface is a critical component in cutting tools and the ongoing demand for improved tool performance is driving the development of new coatings. This paper will discuss current trends in the design of new coatings for metalcutting applications. It will analyze macro- and nano-scale coating architectures and present case studies in thick multilayer films alongside those in thin epitaxial superlattices of TiN/TaN and TiN/TiAlN. An emphasis will be placed on engineering the coating and its integration into design of the cutting edge.

4:30pm **B6-2-10 The Effect of an AlCrN Based Coating and Post Treatment on Uncoated Carbide Drills Designed for Ti Alloys, in Drilling of Mill Annealed Ti_6Al_4V.**, ***S.J. Dowey*** *(steve@surftech.com.au),* Surface Technology Coatings, Australia*, A. Pilkington, J.T. Toton, E.D. Doyle,* RMIT University, Australia*, O. Smith*, Sutton tools Pty, Australia

A solid carbide, through coolant drill, specifically designed for drilling Ti and Ti alloys and produced without any PVD coating by the OEM, was used in a series of benchmarking studies by a number of collaborating companies. The drill performed well and as expected when used as per the OEM parameters.

However, by applying a state-of-the-art PVD coating and modifying the resulting surface, a significant improvement in productivity of over 45% was demonstrated, as well as a reduction in the measured wear, compared to the untreated drill ran at the standard conditions. This demonstration study also highlighted the potential to increase the productivity and increase lifetime without modification of the uncoated drill.

The commercial coating was produced in an Oerlikon Balzers INNOVA PVD system. Post treatment was based on NAF brushing. The effect of the coating on the finish of the drill, the subsequent post treatment and the progression of the wear were observed and measured using a novel light microscope and a traditional toolmaker's microscope. Quality was determined by measuring the hole diameter, the hole finish and the burr on break through on test pieces cut from the test material. Torque and thrust measurements were carried out on the coated and uncoated drills.

4:50pm **B6-2-11 Towards an Improved Understanding of the Drill Test. A study of Cutting Parameters, Work Piece Material, Coatings and Finish and their Influence on Cutting Forces Measured during Drilling**, ***J.T. Toton*** *(jimmy_toton@student.rmit.edu.au),* RMIT University, Australia*, S.J. Dowey,* Surface Technology Coatings, Australia*, A. Pilkington,* RMIT University, Australia*, O. Smith,* Sutton Tools Pty, Australia*, E.D. Doyle*, Royal Melbourne Institute of Technology University and Defence Materials Technology Centre, Australia

Drill test data is affected by a large number of variables outside the control of a cutting tool manufacturer including different CNC machines, tool holding chucks, work piece holders and coolants. This can influence the determination of optimal machining parameters and therefore material removal rate in a particular application, consequently recommended speeds and feeds are by necessity conservative. At the same time drill manufacturers and end users employ benchmarking techniques, like a drill test, to compare different cutting tools. However, this can be problematic when potentially non-optimal conditions are used for some of the tools in the study. There is therefore a need for a drill testing methodology which is, on the one hand, able to discriminate the effects of tool substrate, surface finish, macro and micro geometry and tribological interactions and on the other, provide meaningful comparative information, given that different design parameters may influence measured outcomes. The main specifiable parameters that influence the forces involved in machining a particular material are the cutting speed, feed rate and depth of cut. This work explores the variability of the cutting forces during drilling in order to assist the development of a drill test by varying a number of controllable design and process parameters. The tools selected for the experimental work were ¼ inch M2 HSS jobber drills. The work piece material variables were AISI D2 and AISI P20 equivalents. Analysis of torque and thrust data while varying the cutting parameters was completed for a range of different tribological conditions in order to compare drills with modified coatings and finishes. The effects of pre and post treatment on the surface finish of the coated tools were quantified using an infinite focus microscope.

5:10pm **B6-2-12 TiN Multilayer Systems for Compressor Airfoil Liquid Droplet Erosion Protection**, ***A. Feuerstein*** *(albert_feuerstein@praxair.com), M. Brennan, M. Romero*, Praxair Surface Technologies, Inc

In modern power generation gas turbines water fogging, i.e. the injection of water mist into the turbine is used to augment the performance and efficiency by reducing the air temperature and increasing the compression ratio. The water droplets hit the leading edge of the first stage compressor with app. the speed of sound and can cause liquid droplet erosion (LDE) of the base metal. This leading edge erosion can lead to a reduction of the cord width over extended periods of operation. With some blade designs, this can lead to fatigue cracks which shorten the life of the blades. Various abatement solutions are presently under investigation: redesign of the airfoil shape to allow more material removal, laser peening to reduce the impact on fatigue life and protective coatings. We have investigated the effectiveness of substoichiometric TiN multilayer coating systems to protect the leading edge of the compressor blades against liquid droplet erosion. A full set of 1st stage compressor blades has been coated with two different Substoichiometric TiN multilayer architectures. After 10,000 hrs of field service the erosion damage progression in both coatings was evaluated. In a parallel effort an accelerated water jet test procedure has been developed to simulate the LDE process. A semi-quantitative correlation between the damage progression in the 10,000 hr field test and the water jet test confirmed the effectiveness of the water jet test as a meaningful tool to predict the coating performance in an LDE environment. The accelerated water jet testing is capable of simulating the LDE damage progression. The better performing coating of the two types investigated has a predicted life in excess of 50,000 hrs for the current environment.

Tribology and Mechanical Behavior of Coatings and Thin Films
Room: California - Session E5

Nano- and Microtribology
Moderator: N. Randall, CSM Instruments, J.-H. Hahn, Korea Research Institute of Standards and Science

1:30pm **E5-1 Microstructural Tailoring of Metallic Multilayer Thin Films by Laser Interference Metallurgy for Enhanced Tribological Properties**, ***C. Gachot*** *(c.gachot@mx.uni-saarland.de), F.Th. Muecklich*, University of Saarland, Germany

Laser-Interference-Metallurgy is a rather new surface processing technology, allowing a quick as well as direct structuring of geometrically precise periodic and long range ordered microstructures on macroscopic areas. In this technique, a high power nanosecond laser pulse is split into several coherent sub beams which interfere on the surface of the sample. This technique facilitates various metallurgical processes such as melting, recrystallization, recovery and the formation of intermetallic phases for example on the lateral scale of the microstructure but also topography effects in metals, ceramics or polymers. With regard to topography effects, laser surface texturing is for many years an established method to reduce stiction in magnetic storage devices or to enhance the tribological properties by the production of micro dimples serving as lubricant reservoirs.

In this research work, we will focus on the microstructural tailoring of metallic multilayer thin films i.e. TiAl multilayer films. The idea is to create lateral periodic intermetallic phase composites consisting of hard and soft regions and therefore providing an improved wear resistance. Many classical wear theories only emphasize the importance of hardness as the main factor influencing wear resistance. According to Archard´s equation, the volume loss per sliding distance is linearly proportional to the applied normal load F_N and reciprocal to hardness H. Recent studies revealed the relevance of the ratio of hardness to Young´s modulus (H/E), called the elastic strain to failure. Therefore, thin films being composed of hard hard intermetallic phases laterally arranged in a ductile matrix could exhibit superior properties. By controlling the size and distribution of the corresponding phases, it could be possible to make a balance between hardness and elastic modulus which is decisive with respect to tribological applications.

1:50pm **E5-2 Nanotribological Properties of CrN Films Deposited in an Industrial Chamber by HIPIMS and DC Magnetron Sputtering**, ***E. Broitman*** *(estbr@ifm.liu.se), G. Greczynski, L. Hultman*, Linköping University, Sweden

The microstructure, composition, throwing power, mechanical, and nanotribological properties of CrN_x films grown by reactive high power pulsed magnetron sputtering (HIPIMS) and direct current magnetron sputtering (DCMS) have been studied as a function of the substrate inclination angle α, defined as the angle between the substrate and target normal directions. Films were deposited on Si(001) substrates using an industrial chamber CC-800/9 from CemeCon. Similar conditions for nitrogen pressure, DC bias, and discharge power were used for both, HIPIMS and DCMS depositions. For all angular positions $0 \leq \alpha \leq 180^o$, DCMS yield thicker films than HIPIMS. However, the last ones have a lower variation in thickness. XPS characterization shows a very low variation in stoichiometry with α. Mechanical and nanotribological properties measured with a Hysitron TI 950 TriboIndenter^{TM} reveal that HIPIMS films have higher hardness and lower wear rate than DCMS ones. For a load of 680 µN and a diamond Berkovich probe, HIPIMS films have a uniform hardness of 17 ± 1 GPa, while the hardness of DCMS films varies with α from 7 to 13 GPa. ScanningWear^{TM} tests using a 1 µm 90º conical probe with a force of 75 µN shows that HIPIMS films have an average wear depth of 6 ± 1 nm for all α values, while the wear depth for DCMS films varies from 12 to 28 nm. The superior throwing power and uniform mechanical and nanotribological properties for HIPIMS films can be correlated to the higher Cr ionization in the plasma, as determined by optical emission spectroscopy.

2:10pm **E5-3 Nano-/Micro Scale Fretting and Reciprocating Wear of Thin Films and Si(100)**, *B. Beake,* Micro Materials Ltd, UK, ***T.W. Liskiewicz*** *(t.liskiewicz@leeds.ac.uk),* University of Leeds, UK, *J.F. Smith*, Micro Materials Ltd, UK

The accelerated nano/micro-wear capability in a commercial ultra-low drift nanomechanical test system (NanoTest, Micro Materials Ltd) has been used on a range of hard and soft thin films on Si and on uncoated Si(100) to optimise for enhanced durability and gain mechanistic understanding of the processes controlling the onset of nano-wear in these materials. The nano-wear test fills a key measurement gap in terms of pressures, forces, contact areas and sliding speed between AFM based wear testing and classical macrotribometers and hence more directly maps onto contact conditions in a range of coating applications including automotive engines and biomedical devices. In situ monitoring of nano-wear over periods of several hours enables tests to be usefully run for greater duration and at lower contact pressures than is typical in previous nanotribological tests. The influence of applied load and its rate of application on the behaviour of uncoated Si(100) in 10000 cycle nano-fretting wear tests with small spherical indenters has been investigated. Damage morphology is contrasted to that after other mechanical contact situations such as nanoindentation, nano-scratch or impact.

2:30pm **E5-4 The Effect of Environmental and Contact Conditions on Micro-Tribology Experiments on Engineering Coatings**, ***M. Gee*** *(mark.gee@npl.co.uk), J.W. Nunn, L.P. Orkney*, National Physical Laboratory, UK

Micro-tribology experiments were carried out with a novel micro-tribology test system to investigate the friction and wear performance of a selection of engineering coatings in model single asperity micro-tribology experiments. Single and multiple pass experiments were carried out at a range of test loads from 50 mN to 200 mN, and with a range of probes including diamond indenters with tip radii from 1 to 200 micrometres and a 2 mm steel ball.

The tests were made in moist air, dry nitrogen and vacuum. The tests made under vacuum made use of the in-situ SEM capability of the micro-tribometer yielding a near realtime image record of the deformation that had taken place.

The coatings that were examined included TiN, TiAlN, CrN, MOST, and various types of DLC coatings.

The deformation that took place was evaluated with confocal optical microscopy and AFM.

It was found that the friction and wear that was found was dependent on both the contact geometry and the test environment. These results are discussed with respect to observations of the scratches made with a high resolution SEM.

2:50pm **E5-6 Nanomechanics of Thin Films: a Cross Sectional Approach**, *C.A. Botero Vega (carlos.alberto.botero@upc.edu),* ***E. Jimenez-Piqué****,* Universitat Politècnica de Catalunya, Spain*, T. Kulkarni,* Boston university*, L.M. Llanes Pitarch,* Universitat Politècnica de Catalunya, Spain*, V.K. Sarin*, Boston University

Nanoindentation has become one of the most widely used techniques for measuring mechanical properties of thin films. Conventionally, nanoscratch and nanoindentation tests are performed on the surface of the films to evaluate its mechanical integrity, elastic modulus and hardness. However, in complex systems such as compositionally graded thin films, small spatial variations in mechanical properties are difficult to distinguish using this approach. In this work, polished cross sections of functionally graded CVD mullite coatings on silicon carbide substrates have been evaluated. To assess the intrinsic mechanical properties and their spatial variation, nanoindentation tests have been carried on mullite coatings with constant and graded Al:Si ratios. Additionally, transverse nanosctratch tests to evaluate the adhesive and cohesive resistance of the coatings and the structural integrity of the system were preformed. Different damage morphologies were identified at the interface and inside the coating by using complementary characterization techniques. In the case of functionally graded coatings a gradual increase in the hardness and elastic modulus with increasing distance from the substrate/coating interface was observed. Nanoscratch on the cross sections allowed the determination of the critical loads for adhesive and cohesive damage. Graded coatings exhibited the best combination of properties for structural applications.

3:10pm **E5-7 Sub-Micro-Pillar Compression Tests on Nanocrystalline Nickel Tribofilms**, ***C.C. Battaile*** *(ccbatta@sandia.gov), S.V. Prasad, J.R. Michael, B.L. Boyce*, Sandia National Laboratories

Frictional contact on metal surfaces can produce complex micro- and nano-structural changes underneath the wear surface. Our previous work has shown that the formation of thin, nanocrystalline material in the subsurface region can result in substantial reduction of the coefficient of friction between a hard sphere and a single crystal of nickel. A direct measurement of the mechanical properties of this tribofilm would be very useful in explaining the friction transitions associated with this phenomenon, but such an endeavor is complicated by the fact that the wear surfaces are rough, and the tribofilm is usually less than 200 nm thick, making quantitative nanoindentation difficult. In order to circumvent these obstacles, wear tracks were created on a {110}-oriented single crystal of nickel in both <110> and <211> directions, by unidirectional sliding of a Si3N4 sphere in a dry nitrogen environment. A focused ion beam was used to mill sub-micro-pillars into both the worn and unworn nickel surfaces. These pillars were cylindrical in shape, with a slight taper, and approximately 250 nm in diameter and 500 nm high. The mechanical properties of the pillars were directly measured by performing compression tests in a nanoindenter with a flat 12 µm diameter platen. The worn material was found to be approximately two to four times softer than the unworn crystal. In addition, the unworn material exhibited significant work hardening, whereas the worn material showed virtually none. Scanning electron microscopy showed that deformation in the worn material was localized near the tops of the pillars, whereas deformation in the unworn material occurred throughout the lengths of the pillars. In this presentation, we will outline the tribological tests used to create the worn material; describe the technique for creating the sub-micro-pillars; and discuss the implications of the results for both the grain size dependent strength, and the tribological properties, of the nanocrystalline tribofilms.

3:30pm **E5-8 Nanoscale Mechanical Imaging of Multilayered Films for Flexible Display Using Contact Resonance Force Microscopy**, ***J.-H. Hahn*** *(juny@kriss.re.kr),* Korea Research Institute of Standards and Science, Korea*, D.-H. Kim, H.-S. Ahn*, Seoul National University of Science and Technlogy, Korea

Contact resonance force microscopy (CRFM) has been used to evaluate the elastic properties of multilayered films for flexible display: LiF, Alq3 and aluminum. With CRFM, quantitative images of the spatial distribution in nanoscale elastic properties were acquired. The average values of plane strain modulus for each layers were 62.1 ~ 65.4 GPa, 11.5 ~ 13.0 GPa and 74.8 ~ 76.3 GPa for the LiF, Alq3 and aluminum, respectively. Obtained values showed good agreement (~ 15 % difference) with values determined by nanoindentation. These results provide insight into using CRFM methods to attain reliable, accurate measurements of elastic properties on the nanoscale.

3:50pm **E5-9 Effect of Surface Coating Topography on the Tribological Properties of Nanoparticle Films**, ***M. Akbulut*** *(mustafa.akbulut@chemail.tamu.edu)*, Texas A&M University **INVITED**

In the tribology research community, efforts are underway to develop improved lubricants and lubricant additives to improve energy efficiency. With the advent of nanotechnology, research into lubricants and lubricant additives has experienced a paradigm shift. New nanomaterials and nanoparticles are currently under investigation as lubricants or lubricant additives because of their unusual properties as alternatives to traditional materials. Most of these investigations focus on the nanoparticle film friction on one type of surface rather than investigating nanoparticle friction in relation to surface roughness and structure. By contrast, it has been shown that even a 1-2 nm roughness can significantly affect adhesion and friction in the case of dry lubrication. However, to date, there is still no general theory for the interactions of rough and structured surface coatings across either nanoparticle films or any systemic experiments that identify the main trends. Therefore, it is increasingly necessary to correlate adhesion and friction of nanoparticle films to surface roughness morphology and compliance. This presentation will highlight the current state of art on these issues and describe our recent results on effects of surface coating roughness, structure, and mechanical properties on the adhesion and friction interactions across nanoparticle films.

New Horizons in Coatings and Thin Films
Room: Sunset - Session F3

New Boron, Boride and Boron Nitride Based Coatings
Moderator: H. Hoegberg, Linkoping University, M. Keunecke, Fraunhofer Institute for Surface Engineering and Thin Films

1:30pm **F3-1 Hardness, Thermal Stability and Oxidation Resistance of Cr_5B_3 Films**, ***D. Pilloud*** *(david.pilloud@ijl.nancy-universite.fr), J.-F. Pierson*, Ecole des Mines de Nancy, France

The binary Cr-B system contains several defined compounds: Cr_2B, Cr_5B_3, CrB, Cr_3B_4, CrB_2 and CrB_4. Although the literature reports information on the deposition of CrB or CrB_2 films using sputtering processes, there is a dramatic lack of detail about the synthesis of others chromium boride films. Furthermore, the properties of borides such as Cr_5B_3 are seldom described in the literature. Then, the aim of this presentation is to bring relevant information to the synthesis and the properties of Cr_5B_3 films.

Cr-B films were deposited on silicon, stainless steel and glass substrates by pulsed DC sputtering of a Cr/B (60/40 at.%) target synthesized by SHS method. The films were deposited without external heating and the deposition temperature was close to 50 °C . X-ray diffraction analyses clearly evidenced that as-deposited films were X-ray amorphous. In addition, as-deposited films were highly reflecting and a value of 166 µW cm was measured for their electrical resistivity at room temperature. The crystallisation of the films was studied by in situ XRD during annealing in an inert atmosphere. The formation of the crystalline Cr_5B_3 phase started at 700°C . SIMS analyses performed on as-deposited and annealed films showed that the chromium to boron atomic ratio is kept constant in the whole film depth, indicating that chromium and boron atoms did not diffuse into the gas phase or in the substrate. Air annealing treatments were also performed on the coatings to evaluate their oxidation resistance. After a 2 hours annealing at 700°C, the oxide layer thickness was estimated at approximately 50 nm. SIMS analyses showed that the oxide layer contained only chromium oxide, indicating that boron atoms diffused into the gas phase. As-deposited films exhibited a hardness of 20 GPa. In contrast, the annealing of the films and their crystallisation induced a softening of the material, values of 15 and 12 GPa were measured on amorphous film annealed at 500°C and crystalline film annealed at 700°C, respectively.

1:50pm **F3-2 Direct Current Magnetron Sputtering of ZrB_2 Thin Films from a Compound Target in an Industrial Scale Deposition System**, ***H. Högberg*** *(hanho@ifm.liu.se),* Linköping University, Sweden*, M. Ottosson,* Uppsala University, Sweden*, J. Lu, J. Jensen, M. Samuelsson, L. Hultman*, Linköping University, Sweden

Thin films of the refractory, oxidation resistant, and conductive ceramic ZrB_2 have been sputtered from a compound target, using an industrial scale deposition system, CemeCon, CC 800®/9 ML, operated at a fixed target to substrate distance of 7 cm. Elastic recoil detection analysis show that close to stoichiometric films with a B to Zr ratio of 2 to 2.1 and total level of contaminants, including H, of less than 5% can be deposited on Si(100) at a growth rate of ~ 100 nm per minute and for Ar pressures ranging from 0.4 to 1.3 Pa. X-ray diffraction patterns show that 0001- oriented films are grown on Si(100) and Al_2O_3(0001) substrates without external heating or pulsed plasma cleaning and using a substrate bias of -80 V. Transmission electron microscopy show that the films deposited on Al_2O_3(0001) consist of an ~100 nm thick amorphous layer closest to the substrate followed by the nucleation of an ~300 nm thick 0001- oriented layer. Scanning electron microscopy (SEM) confirm such a layered growth mode also on Si(100), and for substrate temperatures ranging up to ~150°C. A more intense external heating up to ~500°C, gradually alters the 0001 orientation on Si(100) to a random orientation. For these films, the SEM cross section images reveal a microstructure consisting of broken columns, thus indicating re-nucleation. Four point probe measurements on films deposited on 1000 Å SiO_2/ Si(100) substrates with or without external heating yield resistivity values in the region of 200 to 300 µΩ cm; with no clear trend for the resistivity with respect to the amount of applied external heating. The measured values are considerably higher than the resistivity reported for bulk ZrB_2 with 4.6-9 µΩ cm, but reflects the properties of as deposited films. Growth at ~100°C and using either higher substrate bias, up to -200 V, or at lower, down to floating potential, yield little impact on the preferred 0001 orientation, but result in delamination of the films deposited with bias voltages above -120 V

2:10pm **F3-3 A Combinatorial Effect of Substrate and Surface Terminating Species on Phase Pure Growth of c-BN**, ***K. Larsson*** *(karin.larsson@mkem.uu.se)*, Uppsala University, Sweden **INVITED**

Cubic boron nitride (c-BN) has been in focus for several years due to its interesting and extreme properties, of which some are even superior to diamond. These important properties include extreme hardness, chemical stability, large band gap, wear resistance and chemical inertness. The possibility for large area deposition of c-BN is a requirement for realization of these different properties in various applications. Unfortunately, there are at present severe problems in the vapour phase synthesis of c-BN, which makes the possibility to grow large-area c-BN considerably smaller. It is, hence, urgent to investigate the possibility for new chemical growth pathways. This can be accomplished in a multidisciplinary way by combining experimental efforts with theoretical modeling (e.g., density functional theory under periodic boundary conditions).

Adsorption of growth and surface termination species onto the c-BN surface has been found to be two of the key elementary reactions during growth of c-BN. In addition, the choice of substrate is decisive for an ideal cubic phase to be formed directly onto the substrate surface. The purpose with the here presented study is to theoretically investigate the possibility for a layer-by-layer growth of c-BN, using a careful combinatorial choice of substrate material, surface terminating agent and growth species.

2:50pm **F3-5 Chemical Vapor Deposition of MB_2 and M-B-N Alloys Below 300°C: Highly Conformal, Hard and Wear-Resistant Films**, ***A.N. Cloud*** *(cloud1@illinois.edu), J.R. Abelson*, University of Illinois at Urbana-Champaign

Transition metal diborides are metallic ceramics with high electrical and thermal conductivities, melting temperatures around 3000°C, high hardnesses, and strong resistances to chemical attack. Chemical vapor deposition (CVD) of high quality thin films proceeds readily at low substrate temperatures from single source borohydride precursors that contain no O, C, N, or halogens. The coatings are smooth and extremely conformal; the step coverage is up to 90% in trenches or vias with aspect ratios up to 30:1. Reentrant and interior surfaces of components can thus be protected from mechanical wear or chemical attack using CVD diboride coatings. As-deposited films are X-ray amorphous with a nanoindentation hardness of more than 20 GPa; upon annealing at 700°C they obtain a fine-grained nanocrystalline state exhibiting 'superhardness' of 40 GPa.

Incorporation of nitrogen affords films that are a mixture of HfB_2, HfN, and BN. Growth in the presence of ammonia produces films that contain BN and HfN_x ($x > 1$), but no Hf-B bonds; at 1 mTorr of NH_3 pressure all the boron is displaced, resulting in HfN_x films with a bandgap of ~2.6 eV. N-containing alloys are softer than pure HfB_2 films and do not crystallize upon annealing. The growth of HfB_2 / Hf-B-N multilayers affords a means to adjust the effective elastic modulus of a coating while retaining high hardness.

Tribological measurements are performed using pin-on-disc, nanoscratch, and nanowear methods. HfB_2 films show favorable friction behavior with respect to TiN. The wear rate is significantly reduced for annealed HfB_2 and the critical energy for onset of steady-state wear is enhanced. Coatings on steel substrates have performed very well in dry cutting and aluminum die-casting applications under real-world industrial conditions.

3:10pm **F3-6 The Effect of Deposition Parameters on the Structure, Chemistry and Physical Properties of Deposited B-C-N Films**, ***M.F. Genisel*** *(genisel@fen.bilkent.edu.tr), E. Bengu*, Bilkent University, Turkey

In this study, we investigated the effect of process parameters during synthesis on the properties of the films in the B-C-N phase diagram. These films were synthesized using a reactive magnetron sputtering (RMS). The bonding characteristics of the deposited B-C-N films were investigated using Fourier transform infrared (FTIR) spectroscopy and X-ray photoelectron spectroscopy (XPS). Our findings implied that the chemical environment of the bonds in the B-C-N films is very sensitive to synthesis parameters. We were not able to deduce the crystal structure of the films using X-Ray diffraction (XRD) technique due to the low range order in the films as the transmission electron microscope (TEM) images suggested. Hence, we have used evidence provided from FTIR, TEM, and XPS and using these in complement to clues obtained from some of the measurable bulk physical properties (hardness, optical band gap, electrical conductivity) to understand the chemical environment of the atoms and atomic structure of the films. The, nano-indentation measurements indicated that fully hybridized films produced by grounded substrates during synthesis to have a superior hardness to those deposited using higher substrate bias values. And also optical band gap analysis in which the UV-Vis spectroscopy data was used, shows that the band gap of the films were decrease to certain value when the applied radio frequency generated substrate bias was increase at same atomic composition. In addition to these electrical conductivity analysis shows the applied substrate bias effect the conductivity which is an important clue of the change atomic structure in the film. These suggests a change in the atomic structure of the films as well, which has been confirmed by TEM analysis. As a conclusion, in this study we investigated structural and chemical variations in the B-C-N films and their effect on the material properties.

3:30pm **F3-7 Bonding Structure of B-C-N Ternary Compounds and Their Tribomechanical Properties**, ***I. Caretti*** *(caretti@icmm.csic.es), I. Jiménez*, Instituto de Ciencia de Materiales de Madrid, Spain

In the last three decades, research on B-C-N solid solutions has received considerable attention, inspired by the promising combination of the excellent chemical, thermal and mechanical properties of the hexagonal and cubic allotropic forms of BN (*h*-BN, *c*-BN) and C (graphite, diamond). From the very beginning, special interest has been paid to the BC_xN stoichiometry, understood as a substitution of BN atomic pairs by isoelectronic CC pairs that satisfies the charge neutrality condition expected for a stable ternary compound. However, the synthesis of B-C-N compounds in thin film form often produces a broad range of compositions far from BC_xN. Actually, several theoretical and experimental studies have pointed to the metastable character of B-C-N materials, a fact that is frequently translated into elemental and/or binary phase segregation.

In this work, we present a detailed and systematic study of the X-ray absorption near edge structure (XANES) of B-C-N ternary compounds with $B_2C_xN_3$, BC_xN and B_2C_xN ($0<x<6$) compositions. A large set of thin films representing these compositional lines has been synthesized at room temperature by ion beam assisted deposition (IBAD) using different ratios of the incoming B, C and N independent atomic fluxes. In this way, the influence of the deposition parameters on the composition and the resulting bonding structure of the BCN coatings can be thoroughly addressed.

On the one hand, the B-rich BCN compounds (B_2C_xN) showed clear signs of icosahedral BC_x-like and a-C phase segregation in a hexagonal B-C-N matrix, whilst N-rich samples ($B_2C_xN_3$) exhibited CN_x segregated phases. On the other hand, the spectral features of BC_xN layers could be correlated to a graphitic-like B-C-N single ternary phase, with increasing number of structural defects for increasing nominal B/N ratios of the relative impinging atomic fluxes used for the synthesis.

In addition, the friction and wear resistance of all samples were determined by pin-on-disk experiments, which were performed at 25% humidity, using a WC/Co(6%) tip under 3N normal load and 375 rpm rotation speed. Moreover, nanoindentation measurements were done on the BC_xN ternary thin films. It was found that BC_xN layers with low concentration of defects exhibited the best tribomechanical performance. In this sense, the presence of defects was clearly counterproductive, as it was also the presence of segregated phases for C concentrations below ~50%. As a whole, a comprehensive discussion of the tribomechanical properties of B-C-N coatings with respect to their composition and bonding structure is provided.

3:50pm **F3-8 Influence of Nitrogen and Oxygen Addition on the Energy Flux in a rf-Magnetron Discharge for the Deposition of Superhard c-BN Coatings**, ***S. Bornholdt*** *(bornholdt@physik.uni-kiel.de)*, Christian-Albrechts-Universität zu Kiel, Germany, *J. Ye, S. Ulrich*, Karlsruhe Institute of Technology (KIT), Germany, *H. Kersten*, Christian-Albrechts-Universität zu Kiel, Germany

R.f. magnetron sputtering of a hexagonal boron nitride target in an $Ar-N_2-O_2$ gas atmosphere can be used for the deposition of thick, superhard, oxygen-containing cubic boron nitride coatings. Under these deposition conditions the magnetron plasma is investigated by energy flux measurements with a calorimetric probe and by Langmuir double probe measurements. The results of the energy flux measurements are compared with estimations which are calculated on the basis of related plasma parameters (electron density, electron temperatures and ion fluxes) taken from Langmuir double probe measurements. In addition, SRIM simulations were performed to determine the contribution to the energy influx by sputtered boron and nitrogen atoms. The contributions of energetic plasma species, surface reactions and film growth to the resulting substrate temperature are discussed and the influence of nitrogen and oxygen addition to the process gas as well as the effect of substrate bias on the total energy flux have been determined. The largest contribution to the total energy influx in an argon-nitrogen sputtering atmosphere is caused by sputtered atoms. The variation by the nitrogen admixture, which causes a decrease of electron and ion densities, electron temperature and plasma potential are rather small. The typical hysteresis effect which can be observed during magnetron sputtering in oxygen containing gas mixtures can also be detected in the energy influx measurements.

4:10pm **F3-9 Electrochemical Boriding and Characterization of AISI D2 Tool Steel**, ***V. Sista*** *(vsista@anl.gov)*, Argonne National Laboratory, *O. Kahvecioglu*, Istanbul Technical University, Turkey, *O.L. Eryilmaz, A. Erdemir*, Argonne National Laboratory, *S. Timur*, Istanbul Technical University, Turkey

D2 is an air-hardening tool steel and provides excellent resistance to wear and corrosion, especially at elevated temperatures. Boriding of this steel can further enhance its surface mechanical and tribological properties but with the use of traditional pack boriding it was very difficult to achieve very dense and uniformly thick boride layer. In this study, we explored electrochemical boriding of AISI D2 tool steel in a molten borax electrolyte at 950°C for durations ranging from 15 minutes to 1 hour. We found that depending on the boriding time, a single phase Fe_2B layer or a composite layer of $FeB+Fe_2B$ is produced on the surface. The microstructural characterization and phase analysis was performed using microscopy and x-ray diffraction methods, respectively. The boride layers formed after shorter durations (i.e., 15 min) mainly consisted of Fe_2B phase and was about 30µm thick. The microhardness values of the boride layers varied between 25 and 30 GPa, depending on the phase composition.

4:30pm **F3-10 Ultra Fast Boriding of Nickel Aluminide**, ***O. Kahvecioglu*** *(kahveciog3@itu.edu.tr)*, Istanbul Technical University, Turkey, *V. Sista, O.L. Eryilmaz, A. Erdemir*, Argonne National Laboratory, *S. Timur*, Istanbul Technical University, Turkey

As an intermetallic material, nickel aluminide combines properties similar to both ceramics and metals. In particular, it can offer great mechanical strength and high resistance to high temperature corrosion and oxidizing environments. In this study, in order to further enhance its surface properties, we performed ultrafast boriding in a molten borax electrolyte for 15 minutes at 950°C at a current density of 0.1-0.5 A/cm^2. The resultant boride layer formed on the test samples was about 50µm thick despite the very short boriding duration, i.e., 15 minutes . The mechanical, structural, and chemical characterization of the boride layer was carried out using a Vickers microhardness test machine, optical and scanning electron microscopes and x-ray diffraction. The hardness of boride layer was in the range of 1570 to 1700 ± 20 HV, while x-ray diffraction confirmed that the layer was primarily composed of Ni_3B and Ni_4B_3 phases. Structurally, the boride layer was very homogenous and uniformly thick across the borided surface area.

Applications, Manufacturing, and Equipment
Room: Royal Palm 4-6 - Session G2

Coatings for Automotive and Aerospace Applications
Moderator: H. Rudigier, OC Oerlikon Balzers AG, S. Roy, University of Newcastle

1:30pm **G2-1 Highly Concentrated and Low Friction Slip-Rolling Contacts Through Thin Film Coatings and/or Alternative Steels?**, ***C. Scholz*** *(christian.scholz@bam.de)*, *D. Spaltmann, M. Woydt*, Federal Institute for Materials Research and Testing, Germany

Diamond-like carbon (DLC) coatings are perceived as part of a strategy for low frictional tribosystems. Especially the automotive industry anticipates a benefit in applying such coatings in association with the lightweight construction of mechanical parts, for instance in gear and engine components. Therefore, a-C and ta-C coatings were investigated and it was shown that these coatings are slip-rolling resistant at least of up to ten million cycles using oil temperatures of +120°C and under Hertzian contact pressures up to P_{0max} = 2.9 GPa. The steel substrates investigated here were made of the hardened and tempered steels 100Cr6H and Cronidur 30. The aim of the current work is manifold. The Hertzian contact pressures should be increased up to P_{0max} of 3.8 GPa by using new steel metallurgies with high load capabilities as substrates for DLC and newly designed ZrCN thin film coatings. Furthermore, it will be assessed, if they can compete with thin film coatings as uncoated couples. Two high toughness spring steels and an ultra-high toughness aerospace steel were tested in a twin disc tribometer under mixed/boundary conditions in a factory fill SAE 0W-30 (VP1) engine oil. Different parameters such as influences of the lubrication, surface chemistry and wear behavior were investigated.

1:50pm **G2-2 Study on Fatigue and Wear Behaviors of a TiN Coating Using an Inclined Impact-Sliding Test**, *Y. Chen*, ***X. Nie*** *(xnie@uwindsor.ca)*, University of Windsor, Canada

A new ball-on-plate inclined impact-sliding test method was developed to simulate wear phenomena of coated dies under automotive stamping conditions where the stamping die material undergoes a combination of impact and sliding forces. The test coupon in this study was a TiN-coated M2 steel disc. A bearing steel (AISI 52100) ball with a diameter of 10 mm was used as the counterface material. While each cycle consisted of an impact force (FI) and a pressing force (FP), the tests of different impacting and sliding cycles were conducted to observe progressive failure processes. The severity of the coating failures was investigated through electron microscopic observation on the coating surface and cross-section where the impact-induced crater and sliding-induced wear track existed. It was found that the coating failure behaviour included chipping, peeling, fatigue cracking and materials transfer. The test results also suggested that the fatigue cracks initiated the chipping and peeling when the cracks formed network.

2:10pm **G2-3 Friction and Wear Behaviour of MoN-Cu Nanocomposite Coatings Under Lubricated Conditions**, ***O.L. Eryilmaz*** *(Eryilmaz@anl.gov)*, *J.-H. Kim, A. Erdemir*, Argonne National Laboratory, *M. Urgen*, Istanbul Technical University, Turkey

There is an increasing interest in developing low friction, high wear resistant coatings to improve the fuel efficiency and durability of automotive engines in which DLC and a few other coatings are already used In this study, we investigated the tribological behavior of MoN-Cu based nanocomposite coatings under oil lubricated sliding conditions at 80-100 ºC temperature range. The coatings were produced by sputtering molybdenum and molybdenum-copper targets at different power levels. In order to characterize coatings, calotest, scanning electron microscopy time of flight secondary Ion Mass Spectroscopy (ToF-SIMS), and EDS techniques were used.

The tribological behavior of coatings was investigated using ball on disc and reciprocated test machines against steel ball or cylinders at 80-100 ºC temperature range. The Hertzian contact pressures were kept at around 1GPa. Pure Poly alpha olefin 4 (POA4) , MoDTC and/or ZDDP blended (up to 1% wt.) PAO 4 oils were used as lubricants. Non-hydrogenated and hydrogenated DLC films were also tested under the same conditions for comparison. Wear of tested surfaces was analyzed by using a 3D optical profilometer. MoN-Cu nanocomposite films showed superior friction and excellent wear resistance even under very harsh test conditions. In order to understand superior tribological behaviors of MoN-Cu nanocomposite films, post-test analyses were done on sliding surfaces using ToF-SIMS. Surface analytical findings were correlated with the superior friction and wear behavior of coatings with respect to different lubricant mixtures.

2:30pm **G2-4 Effect of Si Addition on the Friction Coefficients of CrZr-Based Nitride Thin Films at Elevated Temperatures**, ***S.-Y. Lee*** *(sylee@kau.ac.kr)*, *Y.-S. Kim, J.-H. Oh*, Korea Aerospace University, Korea, *J.-J. Lee*, Seoul National University, Korea, *W. Y. Jeung*, Korea Institute of Science and Technology, Korea

Cr-Zr-N coatings have much improved mechanical properties and a very lower surface roughness than CrN coatings. However, above 50^{o}C, their mechanical properties were inferior because of the presence of the zirconium oxide on the surface of Cr-Zr-N coatings. In this study, for the high temperature applications, CrZr-Si-N coatings with various Si contents were synthesized by closed field unbalanced magnetron sputtering (CFUBMS) with CrZr segment and Si targets and their chemical composition, crystalline structure, morphology and mechanical properties were characterized by glow discharge optical emission spectroscopy (GDOES), X-ray diffraction (XRD), scanning electron microscopy (SEM), atomic force microscopy (AFM), and nanoindentation. Also, their tribological properties have been measured by ball-on-disk type wear tester at various temperatures and compared with those of Cr-Zr-N coatings. The experimental results revealed that the CrZr-Si-N coatings exhibit better tribological properties at high temperature, compared to that of Cr-Zr-N coatings. Detailed experimental results will be presented.

2:50pm **G2-5 Optimized DLC Coatings for Fuel Injection Components to Minimize Wear and Friction in Various Fuels**, ***A. Hieke*** *(andre.hieke@ionbond.com)*, *G. van der Kolk*, Ionbond Netherlands BV, Venlo, Netherlands, *G. Hakansson*, Ionbond Sweden AB, Sweden, *F. Gustavsson, P. Forsberg, S. Jacobson*, Uppsala University, Sweden

The continuous pressure on the automotive industry to further reduce the fuel consumption and emissions forces the use of innovative processes and materials in order to increase the efficiencies of their engines. The modern vacuum coating technology is one of the key contributors to match the goals of the automotive industry.

State of the art DLC multilayer coatings designed for fuel injection components were prepared by PVD and PACVD deposition technologies to minimize the wear and friction. Besides the well known tribological properties of DLC coatings also the wetting behavior in motor oil or fuels plays an important role for the performance of the coatings.

The tribological results of different DLC multilayer coatings demonstrated significant differences in various fuels like Gasoline, Diesel, White Spirit, Rasp Methyl Ester (RME) and E85 (Gasoline/Ethanol mixture). The tribological properties of the DLC coatings and the counter body vary over a wide range depending of the used deposition process, coating architecture and the hydrogen content.

3:10pm **G2-6 Deposition and Characteristics of Chromium Nitride Thin Film Coatings on Precision Balls for Tribological Applications**, *M.D. Drory, **R.D. Evans** (ryan.evans@timken.com)*, The Timken Company

Thin film hard coatings on rolling element surfaces can enhance the overall wear resistance of rolling element bearings, as demonstrated previously for coated tapered, cylindrical, and spherical roller bearings. Hard coatings in ball bearings are less common because of the difficulty in achieving uniform film thickness on a ball surface. This limitation is overcome by a new process for depositing chromium nitride coatings with uniform thickness on precision balls using ion beam assisted deposition (IBAD) e-beam evaporation. The structure and composition of samples ranging from Cr2N to CrN were characterized with X-ray fluorescence spectroscopy, Auger electron spectroscopy, and transmission electron microscopy. Nanohardness testing was performed to evaluate film mechanical properties as a function of coating thickness. Lastly, the tribological performance of the chromium nitride coatings was evaluated in angular contact ball bearings using a bearing test rig under an axial loading condition.

3:30pm **G2-7 Recent Advancements in Coatings for Piston Rings**, ***K. Honda*** *(keiji.honda@riken.co.jp)*, Riken Corporation, Japan **INVITED**

Due to the global-level air pollution and global warming, it becomes a pressing need to reduce CO_2 release and to lower emission for automotive internal combustion engines. Improvements on thermal efficiency and mechanical efficiency of the engines are done for fuel economy which is directly connected to these problems. Among them, especially in terms of mechanical efficiency, it is one of the effective methods to the fuel cost reduction by lowering the friction of the piston system that accounts for about 50% of the mechanical loss.

The piston ring is one of the engine components, which is subjected to high gas pressure and reciprocates at high speed in the engine. It mainly has three functions; (1) Gas Sealing Function, (2) Oil Control Function, and (3) Heat Transfer Function from Piston to Cylinder Wall. In order to maintain these functions, base materials for piston rings need to have higher elasticity, better anti-wear property and higher thermal conductivity, and the sliding surface of the piston ring especially requires having better tribological performance. Therefore, based on required performances on applications, various surface modifications have been chosen and applied for piston rings' surface. On this occasion, we will outline features of the surface modifications.

Conventional surface modifications include Cr plating, thermal spray coating, gas-nitriding to stainless steel and Cr-N PVD coating. In recent years, we are focusing attention on low friction and low aggressiveness of DLC and apply it to the piston rings. In Riken, it successfully applies low hardness DLC (PCVD) on piston rings for the aluminum cylinder and high hardness DLC (PVD) with the effect of the friction reduction on piston rings for the cast iron cylinder, and it is expected to expand the scope of application in the future. Above mentioned features of DLC coating applied on piston rings are presented in detail.

4:10pm **G2-9 Surface Energy and Tribochemistry of Ti-DLC Coatings**, ***L.V. Santos*** *(santoslv@ita.br), M.S. Oliveira, S.F. Fissmer,* Technological Institute of Aeronautics, Brazil, *L.C.D. Santos, C.A. Alves,* Universidade Federal do Rio Grande do Norte, Brazil, *P.A. Radi,* Instituto Nacional de Pesquisas Espaciais - INPE, Brazil, *M. Massi, H.S. Maciel*, Technological Institute of Aeronautics, Brazil

Diamond-like carbon (DLC) films received considerable interest due to the outstanding mechanical and tribological properties as well as chemical inertness and hydrophobicity, nowadays metallic nanoparticles were used to improve chemical and tribologycal properties.

This paper presents the correlation between surface energy of titanium nanoparticles (Ti-DLC) before and after oxygen/argon plasma treatment. The Ti-DLC coatings with low and high energy before and after plasma treatment were immerged in ethanol, gasoline and diesel oil to study friction coefficient, and wear. The friction and wear tests were run out with AISI 304 sphere as counter face. The goal was to analyze Ti-DLC surface energy after oxygen and argon plasma treatment and correlated trybological behavior of these coatings in regular fuels. Titanium nanoparticles were introduced in DLC films by sputtering and surface coatings were treated by oxygen and argon plasma. DLC films were obtained by PECVD. Thus, surface energy, electrochemical measurements, friction coefficient, wear, optical profiler images, Raman spectra's and infra-red were use to correlate the most protective coatings to work in contact with AISI 304 and corrosive fuels.

4:30pm **G2-10 Chromium Carbide: A New Coating Approach for Highly Loaded, Low Friction Applications**, ***M. Keunecke*** *(martin.keunecke@ist.fraunhofer.de), K. Bewilogua,* Fraunhofer Institute for Surface Engineering and Thin Films, Germany, *J. Becker, A. Gies, M. Grischke*, OC Oerlikon Balzers AG, Liechtenstein **INVITED**

The application of DLC coatings is well established in the automotive industry as a standard solution to eliminate wear problems in critical designs with a demand for very high load-bearing capacities or potential seizure problems. The friction reduction properties of DLC, both under dry and lubricated conditions, are acknowledged, but were up to now of lower priority. With the actual strong focus on reducing fuel consumption and minimizing the CO_2 emission the reduction of friction losses becomes a major focus.

The friction reduction properties of DLC coatings are in competition with other solutions, like new functional designs and technologies, but especially with developments in the field of improved oil additives. For example MoDTC, a friction modifier, is used in many engine oils. Initial tests indicated, that MoDTC in high concentrations is strongly interfering with DLC coatings used for wear protection. Both friction reduction and wear resistance are affected negatively, asking for adjusted solutions.

In this paper the interference of MoDTC with DLC (here a-C:H) is presented and compared with standard oils. As mentioned above, the use of a MoDTC-containing lubricant decreases the wear resistance of a-C:H and therefore limits the friction reduction induced by the coating. Based on this observation it is demonstrated how the analysis of the MoDTC initiated wear mechanism of a-C:H leads to the development of a potential new solution, a modified CrC-coating type. Indeed, a detailed investigation of CrC-type coatings with different compositions has been carried out with respect to their morphology, functionality and tribological properties. Based on these investigations it is demonstrated that by adjusting the composition and morphology of CrC-type coatings the tribochemical interaction with MoDTC additives in engine oils can be strongly influenced. Laboratory tests and first application tests show that the use of CrC-type coatings affect the interference with MoDTC-containing lubricants positively, leading to increased wear resistance and reduced friction compared to a-C:H coatings running with MoDTC oils .

Surface Engineering for Thermal Transport, Storage, and Harvesting
Room: Royal Palm 1-3 - Session TS3

Surface Engineering for Thermal Transport, Storage, and Harvesting
Moderator: A.A. Voevodin, Air Force Research Laboratory, T.S. Fisher, Purdue University & Air Force Research Laboratory

1:30pm **TS3-1 New Approaches with Organic and Inorganic Films for Thermal Energy Conversion**, ***M. Shtein*** *(mshtein@umich.edu), K.P. Pipe,* University of Michigan, *Y. Jin, H. Sun,* Michigan State University, *A. Yadav*, University of Michigan **INVITED**

Efficient solid-state thermal energy conversion via the thermoelectric effect requires a combination of large Seebeck coefficient, low thermal conductivity, and high electrical conductivity. An additional avenue for performance improvement involves device engineering to enable, for example, substantial increase in the number of thermocouple junction density, flexibility, and cost-effectiveness. In this talk I will discuss strategies for controlling thermal and electrical conductivity in hybrid organic-inorganic materials via interface engineering, and scalable fabrication methods. Time-permitting, I will describe some novel architectures for cost-effective and versatile, textile-integrated thermoelectric generators.

2:10pm **TS3-3 Effects of Ni Diffusion Barrier on CNT Growth on Metal Foils for Thermal Interface Applications**, *S.O. Adewuyi, **A. Bulusu**, S. Graham, B.A. Cola (cola@gatech.edu)*, Georgia Institute of Technology

Thermal interface materials (TIMs) based on carbon nanotube (CNT) arrays are attractive for thermal management of high-power microelectronic devices. However, growth of CNTs using chemical vapor deposition (CVD) requires temperatures that are usually too high for direct growth on devices. A promising approach to circumvent this integration challenge is to grow

CNTs directly on thin, flexible metal foils to produce CNT-based TIMs that can be inserted between the device and heat sink. We simultaneously grew CNT arrays on both sides of thin Al and Cu foils using a trilayer catalyst (30 nm Ti/10 nm Al/3 nm Fe), and thermal CVD with H_2 and C_2H_2 as process gases. The G/D ratios of CNT arrays produced with this catalyst stack were measured with Raman spectroscopy to be 0.9925 on average. Poor adhesion and inconsistent sample-to-sample CNT coverage were qualitatively observed. X-tray photoelectron spectroscopy (XPS) analyses of the catalyzed metallic foils annealed at the CNT growth temperature showed significant amounts of Cu and Al at the surface. This suggests that atoms of the metal foils diffuse through the catalyst stack during CNT growth, thereby changing the structure and chemistry of the catalyst. The catalyst stack was modified by adding 20 to 100 nm of Ni film directly on the thin metal foil substrates to serve as a diffusion barrier before depositing the trilayer catalyst. CNT coverage and sample-to-sample consistency improved significantly with the inclusion of Ni barrier. When the barrier was at least 50 nm thick XPS analysis revealed no trace of Cu or Al atoms near the surface of the trilayer catalyst stack. Use of the Ni barrier increased G/D ratios by 8 percent and lead to significant qualitative improvements to the CNT-substrate adhesion (i.e., the CNTs were more difficult to scratch from the foil substrate)as well as reduced thermal interface resistance in comparison to CNT-foil TIMs fabricated without the Ni barrier.

2:30pm **TS3-4 Carbon Nanotube-Coated Foils as Low-Resistance Thermal Interface Materials***,* ***S.L. Hodson***

(stephen.l.hodson@gmail.com), Purdue University & Birck Nanotechnology Center*, A. Bulusu,* Georgia Institute of Technology*, J.R. Wasniewski, D.H. Altman,* Raytheon Integrated Defense Systems*, B.A. Cola, S. Graham,* Georgia Institute of Technology*, X. Xu,* Purdue University & Birck Nanotechnology Center*, A. Gupta,* Raytheon Integrated Defense Systems*, T.S. Fisher*, Purdue University & Air Force Research Laboratory

Because of their extraordinarily high thermal conductivities and mechanical conformability, carbon nanotubes (CNTs) offer a compelling alternative to traditional thermal interface materials in electronics packages. We note that the conformability feature is particularly advantageous in addressing CTE mismatch under extreme thermal conditions encountered in advanced electronics applications. Prior results for dry CNT array thermal interface materials compare very favorably with state-of-the-art thermal greases and other non-bonded materials. In this work, we report the thermal interface behavior of CNT-coated Cu foils and the commensurate effects of a wide range of synthesis parameters. The results indicate that reasonably low resistance is possible for unbonded form, but when bonded with metals by either diffusion bonding or solder reflow, the performance improves markedly to levels below 10 mm^2K/W as measured by both photoacoustic and steady reference bar techniques. General observations from parametric variations include the effect of CNT array length, in which short CNTs produce superior performance.

2:50pm **TS3-5 Crystalline Thin Film Materials with Anisotropic Thermal Conductivity***,* ***C. Muratore***

(Chris.Muratore@wpafb.af.mil), Air Force Research Laboratory*, V. Varshney,* Air Force Research Laboratory/UTC*, J.J. Gengler,* Air Force Research Laboratory/Spectral Energies*, J. Hu, J.E. Bultman,* Air Force Research Laboratory/UDRI*, T. Smith, A.A. Voevodin*, Air Force Research Laboratory

Transition metal dichalcogenide (TMD) crystals are characterized by their distinct layered atomic structures, with strong covalent bonds comprising each layer, but weak van der Waals forces holding the layers together. The relationship between chemical bonding in a material and its thermal conductivity (*k*) is well-known, however the thermal properties of TMD thin films with such highly anisotropic chemical bonds have only recently been investigated with remarkable results, such as ultra-low k_z. Materials with very low thermal conductivity in the z-axis, but higher k_x and k_y have potential as next-generation thermal barrier or heat spreading materials. Molecular dynamics (MD) simulations predicted $k_x=k_y=4k_z$ for perfect TMD crystals (MoS_2 in this case). Experiments to determine $k_{x,y}$ and k_z were conducted by developing a process to grow crystalline TMD thin film materials with strong (002) (basal planes parallel to surface) or (100) (perpendicular basal planes) crystal orientations. Initially, no correlation between structure and thermal conductivity was apparent, as water intercalation and reactivity to ambient air resulted in a thermal "short-circuit" across basal planes, such that the time between deposition and *k* measurement had a stronger impact on thermal conductivity than film orientation. Experiments to measure intrinsic thermal conductivity of MoS_2 revealed values approximately one order of magnitude lower than those predicted using MD simulations, however, measurement of $k_x=k_y=4k_z$ was consistent with simulation results. Simulations to evaluate the dependence of thermal conductivity on grain size was evaluated, which correlated well to measured values. Comparison of measured *k* values for MoS_2, WS_2 and WSe_2 are discussed in the context of the Slack Law, which accounts for intrinsic physical properties of the crystal, but not film microstructure. Alternatives to TMDs, with less environmental sensitivity, will also be illustrated.

3:10pm **TS3-6 Thermal Conductivity of Si-B-C-N Thin Films***,* ***J.J. Gengler***

(jjgengler@gmail.com), Air Force Research Laboratory/Spectral Energies*, J. Hu,* Air Force Research Laboratory/UDRI*, J.G. Jones, A.A. Voevodin,* Air Force Research Laboratory*, P. Steidl, J. Vlcek*, University of West Bohemia, Czech Republic

Thin films of amorphous silicon, boron, carbon, and nitrogen (Si-B-C-N) were recently shown to have an exceptionally high thermal oxidation resistance and are potential candidates for high temperature protective coatings [1]. Such applications would also require a low thermal conductivity through the coating thickness. Thermal transport was investigated in this study for ceramic films with different Si-B-C-N composition, where the microstructure varied from amorphous to nanocrystalline in order to investigate the effect of morphology on thermal barrier properties. Thermal conductivity trends of several ceramic thin films were characterized with a time-domain thermoreflectance (TDTR) technique. Samples containing two different Si-B-C-N chemical compositions were created by reactive magnetron sputtering and then subjected to annealing at temperatures up to 1400ºC. The thermal conductivity of the samples prepared via a 50% Ar / 50% N_2 gas mixture remained constant near 1.3 $W\ m^{-1}\ K^{-1}$, while samples prepared via a 75% Ar / 25% N_2 gas mixture exhibited an increase in thermal conductivity of 2.2 $W\ m^{-1}\ K^{-1}$ (or higher). X-ray diffraction data demonstrated that the former samples were unstructured, while the latter samples formed silicon nitride (Si_3N_4) crystals. The experiments reveal which chemical composition remains stable in the amorphous state at high temperatures, thereby retaining lower thermal transport properties. These material aspects are ideal for thermal barrier applications such as non-oxide ceramic coatings for cutting tools.

[1] J. Vlček, S. Hřeben, J. Kalaš, J. Čapek, P. Zeman, R. Čerstvý, V. Peřina, and Y. Setsuhara. Magnetron sputtered Si-B-C-N films with high oxidation resistance and thermal stability in air at temperatures above 1500°C, *J. Vac. Sci. Technol. A*, **26**, 1101 (2008).

3:30pm **TS3-8 Thermal Properties of Diamond/Ag Composites Fabricated by Salt Bath Coating***,* ***M.T. Lee****, J.-S. Liu, C.-Y. Chung, S.-J. Lin*

(sjlin@mxnthu.edu.tw), National Tsing Hua University, Taiwan

Thermal management in microelectronic technology has become an important issue due to the increase of device power and integration levels. Diamond and silver were selected for the fabrication of composites with high thermal conductivity and low coefficient of thermal expansion (CTE). However, the low thermal conductivity may be caused from the weak bonding between diamonds and silver in the consolidated composite. Improvements in bonding strength and thermal properties of the composites were achieved. A Cr film with a thickness of 150nm was formed on the surface of diamond particles using salt bath coating with additions of chromium to increase the interfacial bonding in diamond/Ag composites. These Diamond/Ag composites have potential applications for the high integration electronic devices.

3:50pm **TS3-9 Homogeneous Solution of $Ca(BH_4)_2$ as a Thermal Energy Storage Material***,* ***P.B. Amama***

(Placidus.Amama@wpafb.mil), J.E. Spowart, A.A. Voevodin, Air Force Research Laboratory*, T.S. Fisher,* Purdue University & Air Force Research Laboratory*, P. Shamberger*, Air Force Research Laboratory

The development of new and efficient thermal energy storage (TES) materials remains a major challenge in addressing needs in a variety of areas from intermittent solar energy harvesting to thermal management of transient, high-flux heat loads. Calcium borohydride ($Ca(BH_4)_2$) is a potential TES material because of its high thermal storage capacity (2.0 MJ/kg) [1]. However, the high decompostion temperatures at atmospheric pressure (> 300°C) in the solid state and slow kinetics represent significant challenges in its use for TES. To date, research efforts aimed at addressing these challenges have focused on engineering the solid-state reaction of hydrides, and the results, though somewhat promising for fuel cell applications, still do not meet the temperature and rate requirements for TES. To circumvent the complex processes associated with solid-state reactions and further to reduce the desorption temperature for fast, on-demand H_2 release, homogeneous dehydrogenation of $Ca(BH_4)_2$ in various aprotic polar solvents is explored in this work. The modification of $Ca(BH_4)_2$ in solution with traditional catalysts is also studied. Preliminary analysis suggests that decomposition near room temperature is possible with enhanced kinetic rates.

[1] Siegel et al., Phys. Rev. B 76 (2007) 134102.

4:10pm **TS3-10 Infrared Study of Ta_2O_5 and HfO_2 Thin Films on Si Substrates**, *T.J. Bright,* ***Z.M. Zhang*** *(zhuomin.zhang@me.gatech.edu),* Georgia Institute of Technology*, C. Muratore, A.A. Voevodin*, Air Force Research Laboratory

Traditional dielectric materials used in the electronics and photonics industries are intended for use at moderate to low temperatures and do not have suitable properties for high-temperature applications (up to 1000 K). This requires us to experiment with new materials that can be used as high/low refractive index materials at elevated temperatures to engineer surface micro/nanostructures such as photonic crystals. The thermal radiative properties of these materials, such as Ta_2O_5 and HfO_2, have not been well documented and the available data are very limited. We have deposited thin films of tungsten, hafnium oxide, and other films over a range of thicknesses using DC and pulsed DC magnetron sputtering processes on lightly doped, infrared transparent silicon substrates. For oxide films, deposition was conducted in a reactive sputtering process with pure targets of hafnium and tantalum. Post annealing allows the oxide film to crystallize as observed by x-ray diffraction. A Fourier-transform infrared spectrometer (FTIR) was used to measure the transmittance and reflectance (for incidence from either the film side or the substrate side) at room temperature, in the wavelength region from 1 to 20 *m*m. The FTIR system was purged with dry nitrogen to minimize measurement errors due to water absorption. FTIR measurements were tested against samples with known optical properties to minimize experimental uncertainty. The transmittance and reflectance spectra of the film-substrate composite were analyzed to determine the infrared optical constants of Ta_2O_5 and HfO_2 films. The results will be presented and compared with data available in the literature.

4:30pm **TS3-11 Photonically Enhanced Flow Boiling from Nanostructured Surfaces**, *C. Hunter (Chad.Hunter@wpafb.af.mil),* Air Force Research Laboratory*,* ***S.K. Arun****,* Purdue Univeristy*, S.A. Putnam,* Universal Technology Corporation*, N. Glavin,* Air Force Research Laboratory*, T.S. Fisher*, Purdue University & Air Force Research Laboratory

Devices that generate high heat fluxes, such as advanced electronic components, usually require multi-phase cooling because of the extremely high heat transfer coefficients that can be achieved. By operating devices in the so called 'nucleate boiling' regime, large rates of heat transfer can be achieved while maintaining acceptably low device temperatures. The addition of forced convection through flow boiling further enhances heat transfer beyond that of pool boiling. Surface characteristics play a critical role in the transition from nucleate boiling to critical heat flux (CHF), in which a stable vapor film forms at the device interface and results in an uncontrolled increase in substrate temperature. Modifying the boiling surface characteristics through surface roughness, micro/nano patterning and other means has been shown to enhance wetted surface area and nucleation site density, thereby allowing control over the CHF and increase of the boiling heat transfer coefficient. The aim of the present work is to assess new means of heat transfer enhancement by altering surface characteristics such as surface energy and wettability through light-surface interactions during flow boiling. Such photolytic and photocatalytic processes can be potentially controlled by wavelength and intensity of the irradiation emitted from a lamp source or laser diode, and the surface wetting enhancing coating on nanostructures. In this study, conformal TiO_2 surfaces on CNT-coated copper substrates are exposed to parametric variations in UV (395 nm) intensity and mesoscopic spatial pattern during flow boiling in ultra-pure water. Measurements of system parameters such as CHF, and heat transfer coefficient are performed, and the effects of different surface and light characteristics are quantified.

4:50pm **TS3-12 Enhanced Surfaces in Conjunction with Single and Two-Phase Flows for Power Electronics Cooling Applications**, ***S. Narumanchi*** *(sreekant.narumanchi@nrel.gov), P. McCluskey, G. Moreno, C. King*, National Renewable Energy Laboratory

Within the Department of Energy (DOE) Advanced Power Electronics and Electrical Machines (APEEM) program, cooling methodologies are being developed to enable high heat flux dissipation while maintaining low die operating temperatures, and to enable the program goals of weight, volume and cost. Existing hybrid vehicle power electronics cooling systems rely on single-phase, channel flow cooling configurations which provide relatively low heat transfer capability. Consequently, these cooling systems tend to be bulky and add significant mass and volume to the system.

In this study, we investigate efficient cooling schemes such as single-phase jet impingement and two-phase boiling heat transfer in combination with enhanced surfaces, with the overall goal of helping decrease the size and weight of automotive power electronics (PE) cooling systems. With a single-phase liquid (water) free jet impingement configuration, a copper microporous coating (3M) yielded a heat transfer enhancement of about 130% as compared to free jet impingement on a plain surface, while with a submerged jet configuration, the MicroCool finned surface (Wolverine Tube, Inc.) yielded a heat transfer enhancement of about 100% as compared to impingement on a plain surface. In two-phase flow configurations, the copper microporous coating (3M) increased nucleate boiling heat transfer rates by 100 to 500% and increased the critical heat flux (CHF) by 7 to 20% in the pool boiling and spray impingement boiling configurations using HFE7100 dielectric coolant.

The implications of these heat transfer performance enhancements in the context of power electronics package cooling will also be discussed.

Coatings for Use at High Temperature
Room: Sunrise - Session A1-3

Coatings to Resist High Temperature Oxidation, Corrosion and Fouling
Moderator: Y. Zhang, Tennessee Technological University, J.R. Nicholls, Cranfield University, L.G. Johansson, Chalmers University of Technology, D. Naumenko, Forschungszentrum Julich

8:00am **A1-3-1 Effect of Steam Exposure on the Creep Properties of Bare and Aluminized Fe- and Ni-Based Alloys**, ***S. Dryepondt*** *(dryepondtsn@ornl.gov), B.A. Pint,* Oak Ridge National Laboratory*, Y. Zhang*, Tennessee Technological University

One straightforward solution to improve the efficiency of coal-fired power plants, and thereby reduce CO_2 emissions, is to increase the operating temperature and pressure. To ensure the durability of components at the ambitious goal of the ultrasupercritical steam program, 760°C and 350 bar, new material solutions must be developed. Oxidation resistant coatings have been shown to effectively reduce reaction rates in steam at this temperature. However, the impact of the coating on the alloy mechanical properties needs to be evaluated. Creep testing is being conducted on as-fabricated, pre-oxidized and aluminized Fe- and Ni-based specimens to gain a better understanding of how mechanical properties are affected. For comparison, in-situ steam testing of coated and uncoated specimens is being conducted in a new environmental creep rig.

8:20am **A1-3-2 High Temperature Protection of Ferritic Steels by Nano-Structured Coatings: Supercritical Steam Turbines Applications**, ***F.J. Perez*** *(fjperez@quim.ucm.es), M.P. Hierro, M.S. Mato, I. Lasanta, M. Tejero,* Universidad Complutense de Madrid, Spain*, J.C. Sanchez-Lopez,* Instituto de Ciencia de Materiales de Sevilla (CSIC-US), Spain*, M. Brizuela*, TECNALIA-Inasmet, Spain

In many applications at high temperature, micro-structured coatings have been applied in order to protect structural materials against a wide range of different environments: oxidation, metal dusting, sulphidation, molten salts, steam, etc… The resistance achieved by the use of different kind of coatings have been optimum, and with late design such as TBC´s and FGM´s coatings. Although, the lifetime of them are related with inter-diffusion, and different CET as main degradation mechanisms.

In the case of supercritical steam turbines, may attemps have been made in terms of micro-structural coatings design, mainly based in aluminides.

In order to consider another alternatives to minimize those problems, nano-structured coatings, applied by HIPIMS-PVD based in Cr and Al design, have been applied onto high temperature structural materials in order to analyze their high temperature oxidation resistance in steam environments.

The gravimetric results obtained have been analysed upto 2.000 hours, jointly with the evaporation behavior analysed by TG-Mass spectromnetry. Excellent results have been achieved for the nano-structured coatings tested. Those results are comparables with the results obtained for micro-sctructured coatings, and in some case better for nano-structured coatings.

According to the results obtained, the nano-structured coatings have a potential application as protective systems in high temperature, for some applications.

8:40am **A1-3-3 Isothermal and Thermal Cycling Oxidation Behavior of Hot-Dip Alumina Coating on Flake/Spheroidal Graphite Cast Iron**, ***M.-B. Lin*** *(d9603506@mail.ntust.edu.tw), C.-J. Wang*, National Taiwan University of Science and Technology, Taiwan

Two types of cast iron, flake graphite and spheroidal graphite cast iron, with ferrite matrix and similar composition, were aluminized by hot-dip. The aluminized cast iron specimens were subjected to the high-temperature oxidation test to investigate the effects of graphite morphology on the oxidation behavior of alumina coating. For comparison, the high-temperature oxidation test was also carried out on the aluminized mild steel specimens. The isothermal oxidation test revealed that the hot-dip aluminized cast iron had the superior high-temperature oxidation resistance. The thermal cycling oxidation test revealed that the graphite morphology obviously affected the thermal fatigue resistance of alumina coating on cast iron. The alumina coating on the spheroidal cast iron had good thermal fatigue resistance.

9:00am **A1-3-5 Coatings for Severe High Temperature Corrosion Conditions**, ***M. Schuetze*** *(schuetze@dechema.de)*, Dechema e.V., Germany **INVITED**

Due to the demand for higher efficiencies and the use of lower quality fuels (process residues, bio-fuels, waste, etc) in thermal energy conversion plants, a need arises for material surfaces resistant to highly aggressive high temperature environments. The most critical types of such environments exhibit low oxygen partial pressures with high activities of sulphur, carbon, vanadium or halogens. Frequently, conventional metallic alloys are pushed to their limits concerning high temperature corrosion resistance under such conditions so that the need for highly resistant coatings arises.

In this paper recent developments are presented which show coating solutions for high carbon or high chlorine environments. In the first case coking and metal dusting can lead to dramatic and unexpected failure cases, in particular in the petrochemical industries. In other industrial applications even in the case of the use of expensive highly resistant nickel-base alloys coking and metal dusting can also present serious problems. An innovative coating concept based on poisoning of the catalytic effect of metallic surfaces completely suppresses the mechanisms of coking and metal dusting. Several poisoning elements can be used but a particularly effective element turned out to be Sn in combination with a Ni-precursor. For high chlorine containing environments a thermodynamics-based concept led to the development of a Ni-Mo-Al coating with superior corrosion resistance compared to high alloy nickel-base-materials that are usually used as expensive high-end materials in Cl-environments.

The thermodynamic background for the development of the two types of coatings is discussed and the manufacturing procedures are described. Furthermore, examples for the resistance in different highly aggressive environments are presented and analysed. The paper closes with an outlook on other types of coatings for severe environments and the necessary R+D work.

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

Hard and Multifunctional Nano-Structured Coatings
Moderator: C.P. Mulligan, Benet Laboratories, US Army ARDEC, R. Sanjines, EPFL, P. Zeman, University of West Bohemia

8:00am **B5-1-1 Structure and Properties of Ti-Al-Y-N Coatings Deposited from Filtered Vacuum-Arc Plasma**, *V.A. Belous, V.V. Vasyliev,* Kharkov Institute of Physics and Technology, Ukraine*, **V.S. Goltvyanytsya** (vladtnt@gmail.com), S.K. Goltvyanytsya,* Real Ltd., Ukraine*, E.N. Reshetnyak, V.E. Strelnitskij, G.N. Tolmacheva, A.A. Luchaninov,* Kharkov Institute of Physics and Technology, Ukraine*, O.S. Danylina*, Krivoy Rog Technical University, Ukraine

It is known that nanostructured multi-component nitrides like Ti-Al-Y-N may have a unique combination of properties: high hardness, wear resistance, thermal stability and oxidation resistance, which may allow using them as protection coatings on tools and machine parts, working under extreme conditions. Deposition of coatings from filtered vacuum arc plasma leads to additional quality improvement due to formation of more uniform structure and reduction in the surface roughness. In this paper the effect of the amplitude of the pulse substrate bias and percentage of yttrium on structure and properties of Ti-Al-Y-N vacuum-arc coatings, deposited from filtered vacuum arc plasma, were studied.

The coatings were produced in vacuum-arc system with a straight magnetic-electric filter by sputtering of as-cast TiAlY cathodes with the following deposition on the steel substrates at a nitrogen pressure of 0.1 Pa and pulse substrate bias amplitude of 0.5-2.5 kV. The deposition rate reached 14-16 μm/h, the coating thickness was of 6-8 μm. Scanning electron microscopy and atomic force microscopy (AFM) were used for investigation of the structure and surface morphology of the coatings. The elemental composition of the coatings was controlled using X-ray fluorescence analysis. Hardness was measured by nanoindentation. Oxidation resistance tests were performed using the thermal analyzer.

Elemental percentage of Ti, Al, Y in the coatings and cathodes were in a good mutual accordance. At the same time, the coatings were of uniform thickness and homogeneous composition. SEM of the surface samples showed the high quality filtering of the plasma flow, because only few defects on the films surface were observed. Samples cross section showed that the coating Ti-Al-N had a columnar structure like traditional vacuum-arc nitride coatings deposited at a constant substrate bias. Yttrium additions to the cathodes caused the changes in the coatings structure: with increasing of Y content in cathodes from 0 to 2.5 wt.%, columnar film structure became considerably less expressed. In this case, significant surface morphology changes were observed. In the AFM 3D images the surface of the films deposited at pulse bias of 1.5 kV amplitude was characterized by cellular-like microrelief with the cell size of about several hundred nanometers with hardness H=35-40 GPa.

According to the results of the thermogravimetric analysis, all produced Ti-Al-Y-N coatings possess sufficiently high oxidation resistance. The most oxidation-resistant coatings were deposited at pulse bias amplitude of 1.0-1.5 kV and contained of 1.0-2.5 wt. % of Y.

8:20am **B5-1-2 Growth of Hard Amorphous Ti-Al-Si-N Thin Films**, ***H. Fager*** *(hanfa@ifm.liu.se), A. Fallqvist, N. Ghafoor,* Linköping University, Sweden*, M. Johansson,* Seco Tools AB Fagersta, Sweden*, P.O.Å. Persson, M. Odén, L. Hultman*, Linköping University, Sweden

We propose amorphous transition metal nitrides with a preferred covalent bonding for a next class of tough materials with tuneable hardness. $(Ti,Al)_{1-x}Si_xN$ ($0.10 \leq x \leq 0.27$) thin films were grown onto Si (001) and cemented carbide substrates by cathodic arc evaporation of Al-rich Ti-Al-Si cathodes in an Ar-N_2 gas mixture. The as-deposited films were analyzed by elastic recoil detection analysis (ERDA), x-ray diffraction (XRD), nanoindentation, and transmission electron microscopy (TEM). With an incorporation of 19 at.% Si, the film structure changes from microcrystalline to nanocrystalline. With further incorporation of Si (27 at.%), the films assume an x-ray and electron amorphous state. The hardness of amorphous films is as high as 14 GPa. A comparison with magnetron sputtered amorphous Ti-Al-Si-N films will also be reported.

8:40am **B5-1-3 Solid Solutions and nanostructures in Al(Si)N Hard Coatings**, ***J. Patscheider*** *(Joerg.Patscheider@empa.ch)*, Empa, Switzerland **INVITED**

Nitride-based coatings with specific nanostructures such as multilayers with nanoscale dimensions and fully phase-separated nanocomposites are in the focus of scientific interest since two decades. The deposition of transition metal nitrides and silicon leads to the formation of bi- and multiphase coatings containing silicon nitride. Depending on the materials system and preparation conditions, such coatings may show enhanced hardness and other favorable properties. These make such coatings not only a subject of intense research, but are the reason for their application potential as protective coatings on a wide variety of tools and components. Using aluminum instead of transition metals causes the formation of optically transparent Al(Si)N coatings that show, despite enhanced hardness of more than 30 GPa, some interesting differences with respect to transition metal nitride/silicon nitride coatings. A solubility limit exists for silicon contents around 6 atomic %, that seemingly is thermodynamically stable. Correspondingly, the Al-Si-N system forms, as a function of the silicon content, either solid solutions or a two-phase nanocomposite structure. Structural investiga-tions lead to a growth zone model that accounts for the different nanostructures. Investigations on model systems using nanoscale multilayers show that in this materials system the absence of a major hardness enhancement, characteristic e.g. for TiN/Si3N4, can be understood in terms of epitaxy and elastic properties of the single phase components. The addition of oxygen to form $Al(Si)N_{1-x}O_x$ causes, similar to silicon addition, grain refinement and a gradual disappearance of the columnar structure with increasing oxygen content. Despite very high oxygen concentrations up to 20 at% O hardness values of 25 Gpa are reached. The properties of these coatings will be presented and underlying mechanisms will be discussed.

9:20am **B5-1-6 Corrosion Resistance and Hardness of Nb-Si-N Coatings Deposited by Dual Magnetron Sputtering**, ***G. Ramírez*** *(enggiova@hotmail.com), S.E. Rodil, S. Muhl, L. Huerta,* Universidad Nacional Autonoma de Mexico*, E. Camps, L. Escobar-Alarcón*, Instituto Nacional de Investigaciones Nucleares, Mexico

In this work, we prepared thin films of Nb-Si-N using two separate magnetrons, where one target was Si and the other Nb. The atmosphere was a variable mixture of argon and nitrogen. The film composition and structure was modified by varying the power of the two magnetrons independently. For the Si target, the rf source was varied between 40-200 W and for the Nb target, we tested dc powers between 100-300 W. The aim of the study was to find deposition conditions that lead to a dense hard microstructure presenting both high hardness and corrosion resistance, in a similar fashion as the nc-TiN/a-SiN_x phases reported by different authors. The films were characterized by X-ray photoelectron spectroscopy to obtain the composition and the chemical bonding characteristics. Similarly, Raman spectroscopy was used to identify the bonding characteristics and the presence of isolated silicon phases. The corrosion resistance was evaluated for films deposited on two different steels using dc and ac electrochemical techniques. The dc techniques include potentyodynamic polarization and polarization resistance, data that were analyzed using the Tafel method. Meanwhile, electrochemical impedance spectroscopy as a function of the immersion time up to 72 hours was used to evaluate the stability of the coatings and electronic equivalent circuits were used to model the variations of the coatings parameters in time. The results of the different characterization techniques were correlated to the deposition conditions and the films composition.

9:40am **B5-1-7 Quaternary-Phase Coatings in the Cr-WC-N System**, ***M.J. Walock*** *(mwalock@uab.edu),* University of Alabama, Birmingham*, I. Rahil,* Arts et Metiers ParisTech, France*, Y. Zou,* University of Alabama, Birmingham*, C. Nouveau,* Arts et Metiers ParisTech, France*, A.V. Stanishevsky*, University of Alabama, Birmingham

Binary tungsten carbide films can be smooth, hard crystalline materials, but with low fracture toughness. Tungsten nitride films are frequently harder, but are more brittle. Chromium nitride films have excellent wear and oxidation resistance, but often develop a porous columnar structure with low hardness. The composites of these binary compounds offer a possibility to tailor the material for a desired combination of properties. However, little is known about ternary and quaternary thin-film systems based on these compounds. To this end, we have used reactive RF-magnetron sputtering with Cr and WC targets to form ternary and quaternary thin-film coatings (film thicknesses from 1 to 2 microns), with an argon/ nitrogen working gas. The films were deposited onto Si, Ti, CoCr, WC, and high-speed steel substrates at a substrate temperature below 500 K. The structural and mechanical properties of the resulting coatings have been characterized with XRD, XPS, AFM, SEM/ EDX, and nanoindentation. Depending on the deposition conditions, the XRD, XPS, and EDX results indicate the presence of the binary (W2C and WC1-x), ternary (WC-N and Cr-WC), and quaternary (Cr-WC-N) phases. Our SEM and AFM results show smooth films for the tertiary and quaternary compounds. The mixed binary phase W2C and WC1-x films demonstrated nanoindentation hardness above 40 GPa, but they partially delaminated from the majority of the substrates. All ternary compositions (WC-N and WC-Cr systems) tested to date have shown strong adhesion to the substrates, but the hardness was in the range of 12 – 20 GPa. However, the hardness values for some films with Cr-WC-N composition (Cr/W ratio ranges from 1.4 to 2.8:1) were measured in excess of 35 GPa. The formation of a nanocrystalline (grain size 5-8 nm) nanocomposite (i.e. more than one pure phase present) material was suggested on the basis XRD and XPS data. These results combined with low roughness (RMS 1.1 – 1.5 nm) and high adhesion make these quaternary thin-film coatings a promising material for demanding applications such as cutting tools, friction pairs, and intermediate layers for deposition of micro- and nanocrystalline diamond coatings.

This work has been supported by the U.S. National Science Foundation (DMR-0806521, DMR-0922910) and the Regional Council of Burgundy, France.

10:00am **B5-1-8 Self-Organized ZrN/Si_3N_4 Lamellar Growth During Reactive Dual Magnetron Sputtering of $Zr_{1-x}Si_xN_y$ Thin Films at High Temperature**, ***N. Ghafoor*** *(naugh@ifm.liu.se), K. Yuan, J. Birch, J. Jensen, L. Hultman, M. Odén,* Linköping University, Sweden*, J. Wen,* University of Illinois at Urbana- Champaign*, I. Petrov*, University of Illinois at Urbana-Champaign

In the field of superhard nanocomposites the research has focus on introducing new multifunctional materials as well as on the understandings of the structural complexity of the nanocomposites which boost their functionality, such as hardness, thermal stability, and corrosion resistance. Here we present an experimental study on $Zr_{1-x}Si_xN_y$ ($0 \leq x \leq 1$; $1 \leq y \leq 1.22$) alloys synthesized by reactive magnetron sputter deposition onto single-crystal MgO(001) and Al_2O_3(0001) substrates at 800°C that allows for phase separation during growth and hence make possible to design the structure of the internal interfaces by controlling the composition. For this high temperature, epitaxial growth allows incorporation of as much as 10 at.% of Si in ZrN, which enhances oxidation resistance and thermal stability of the films up to 1000°C, while retaining its superhard nature. The structure of $Zr_{0.8}Si_{0.2}N$ films constitutes 3-5 nm thick lamellas that extend in the growth direction with a strong (002) texture. It is revealed by lattice resolved z-contrast transmission electron microscopy imaging that the lamellas consist of ZrN and amorphous Si_3N_4 separated by a possible crystalline SiN_x: Zr tissue phase.

10:20am **B5-1-9 Modulation Structure and Mechanical Properties of W/ZrB_2 Multilayers**, *G.Q. Liu, Y.B. Kang,* ***D.J. Li*** *(dejunli@mail.tjnu.edu.cn), X.Y. Deng*, Tianjin Normal University, China

Nanoscale multilayers made of borides, nitrides, and carbides, exhibiting desired mechanical properties, have been developed and applied to various kinds of industries for the past decades. In this study, we worked with W/ZrB nanoscale multilayers coatings. Tungsten, as a high atomic-number and refractory material, has been widely applied in applications such as wear- or corrosion-resistant components in high-temperature and high-vacuum environments due to its excellent mechanical, thermal and electrical properties. The refractory compound ZrB also has a high hardness, high melting point, high electrical conductivity and excellent corrosion resistance. Because W and ZrB have different crystal structures, we expect little mutual intermixing of both nanolayers at elevated temperatures and hence preserve the high-temperature tribological performance. Several different types of transition metal nitrides, borides, and carbides multilayered coatings, such as W/NbN, Mo/NbN, AlN/VN, AlN/TiN, TiN/TiB_2, TiB_2/TiC, TiN/SiN*x*, have been explored. For the W/ZrB_2 multilayers addressed in this work, studying the influences of various growth parameters will help us determine their microstructure and the related mechanical properties.

In our previous works (Appl. Phys. Lett. 91 (2007) 251908, Surf. Coat. Technol. 201 (2007) 6812, J. Vac. Sc. Technol. B25 (2007) L11, J. Vac. Sci. Technol. A24 (2006) 966), we have specifically achieved some insight into the relation between the growth parameters and the microstructure and mechanical properties of lots of multilayers such as CrN/ZrN, ZrC/ZrB_2, ZrN/TiAlN, ZrN/W_2N. Over 30 GPa hardenss with desired fracture resistance has been observed in these multilayer systems. In this work, W/ZrB_2 nanoscale multilayers were deposited on silicon by magnetron sputtering at room temperature. The multilayered modulation structure and mechanical properties of the W / ZrB multilayers were studied using SEM, XRD, surface profiler and nanoindenter. The mechanical properties of the multilayers were controlled by modulation periods (Λ) ranging from 9.5 to 40 nm and modulation ratios (t_w:t_{ZrB2}) from 1:1 to 1:9. All of the multilayers with clear sharp interfaces revealed higher hardness and elastic modulus than the rule-of-mixtures value for monolithic W and ZrB_2 coatings. The maximum hardness of 41.5 GPa and critical load of 62.5 mN could be obtained for the multilayer with a Λ of 30 nm and t_w:t_{ZrB2} of 1:3 . The polycrystalline and multilayered modulation structures were directly responsible for the enhanced mechanical properties.

10:40am **B5-1-10 Growth and Properties of Cr_2GeC Epitaxial Nanolaminated Thin Films**, ***P. Eklund*** *(perek@ifm.liu.se),* Linköping University, Sweden, *M. Bugnet, M. Jaouen, S. Dubois, C. Tromas, T. Cabioc'h*, University of Poitiers, France

The $M_{n+1}AX_n$ phases (n = 1 – 3, or 'MAX phases') are a group of ternary carbides and nitrides (X) of transition metals (M) interleaved with a group 12-16 element (A) [1]. Although a relatively little researched member of the MAX-phase family, Cr_2GeC exhibits a number of traits that render it interesting from a fundamental-research point of view, such as its reported thermal expansion coefficient which is the highest of the known MAX phases, and its reported anomalously high density of states at the Fermi level. Because of these intriguing observations and the limited amount of studies available, we are interested in Cr_2GeC. For synthesis of this phase, thin-film growth is a potentially important approach because of the relative ease with which numerous MAX phases can be epitaxially grown, often as single crystals. Here, we report growth of epitaxial phase-pure Cr_2GeC onto Al_2O_3(0001) both directly and using a TiN(111) seed layer. The use of a seed layer results in fewer defects as evidenced by the rocking curve full width at half maximum. For optimized composition, phase-pure epitaxial Cr_2GeC can be grown at temperatures above 700°C. This enables determination of mechanical and electrical properties. Increased Ge or C content results in film containing additional impurity phases such as $Cr_5Ge_3C_x$ and pure Ge segregated on the surface. A reduction in temperature yields polycrystalline growth of Cr_2GeC in the temperature range 500 – 650°C.

[1] See review: P. Eklund et al Thin Solid Films 518 1851 2010

11:00am **B5-1-12 In-Situ Characterisation of Microstructure Evolution in $Ti_{1-x}Al_xN$ Coatings During Annealing**, ***Ch. Wuestefeld*** *(wuestefeld@ww.tu-freiberg.de), D. Rafaja, V. Klemm, M. Dopita, M. Motylenko,* TU Bergakademie Freiberg, Germany, *C. Baehtz,* Forschungszentrum Dresden-Rossendorf, Germany, *C. Michotte,* CERATIZIT, Luxembourg, *M. Kathrein*, CERATIZIT, Austria

Hardness and high-temperature stability of hard coatings are indirectly controlled by their microstructure induced by the deposition process, as the initial microstructure strongly affects the kinetics of microstructure changes at elevated temperatures. Thus, the development of the microstructure at elevated temperatures is an important topic for $Ti_{1-x}Al_xN$ coatings which can be used in machining applications. In this study, the development of microstructure in $Ti_{1-x}Al_xN$ coatings at elevated temperatures was investigated using in-situ synchrotron high temperature glancing angle X-ray diffraction (HT-GAXRD) experiments and related to the original microstructure of the coatings, which was modified via the titanium to aluminium ratio and the bias voltage.

The Ti:Al ratio in the coatings varied between 60:40 and 33:67; the bias voltage ranged from -40 to -120 V. The in-situ synchrotron HT-GAXRD experiments were done at 450°C, 650°C and 850°C. After each annealing step, the coatings were cooled to 100°C and an additional GAXRD measurement was performed in order to seek for the spinodal decomposition of metastable fcc-(Ti,Al)N.

From the analysis of the GAXRD pattern, the phase composition as well as the macroscopic lattice strain and the stress-free lattice parameter of the fcc-(Ti,Al)N phase were determined for all investigated temperatures. At 850°C AlN segregated from fcc-(Ti,Al)N and formed c-AlN and w-AlN. It was found that for the same coating composition the ratio between the individual phases present in the coating after annealing at 850°C was different in the coatings deposited at -40 V, -80 V and -120 V. This effect of the initial microstructure, which was adjusted by the bias voltage during CAE deposition, on the phase evolution during annealing will be related to the results from GAXRD and transmission electron microscopy.

11:20am **B5-1-13 Laminated Structure in the Internal Oxidation of Ta-Ru Coatings**, ***Y.-I. Chen*** *(yichen@mail.ntou.edu.tw), S.-M. Chen*, National Taiwan Ocean University, Taiwan

During the application of refractory alloy coatings for protective purpose at high temperature under oxygen containing atmospheres, the internal oxidation phenomenon has been observed and explored. The characteristic of the internal oxidation zone is a laminated structure with alternative oxygen-rich and deficient layers stacked with a general orientation. The forming conditions has been proposed, i.e., one of the elements should be relatively noble, the coatings exhibit an orientated columnar structure in the as-deposited state, and the inward diffusion of oxygen is faster than the out-diffusion of the constituents of the coatings. In this study, Ta-Ru coatings were prepared with various rotating speeds of substrate and sputtering powers in the deposition processes, and then annealed at 600°C in a 50 ppm O_2-N_2 atmosphere. The periods of laminated layers were examined by transmission electron microscopy. We also investigated the surface roughness and mechanical properties for the internally oxidized coatings.

11:40am **B5-1-11 Nanostructured Superhard Films Ti-Hf-Si-N, their Properties and Structure**, ***D. Pogrebnjak*** *(apogrebnjak@simp.sumy.ua),* Sumy State University, Ukraine, *M. Beresnev,* Kharkov National University, Ukraine, *P.V. Konarski,* Tele and Radio Research Institute, Poland, *V. Uglov, F. Komartov,* Belarus State University, Belarus, *M.V. Kaverin,* Sumy Institute for Surface Modification, Ukraine, *D.A. Kolesnikov,* Belgorod State University, Russia, *V. Grudnitskiy,* Kharkov National University, Ukraine, *N.A. Makhmudov,* Samarkand Branch of Tashkent Institute of Information, Uzbekistan, *M.V. Il'yashenko, G.V. Kirik*, Sumy State University, Ukraine

Using vacuum-arc source with HF discharge, superhard nanocomposite films of 1.05 to 1.2 µm thickness were fabricated. Their thickness depended on the bias potential on the substrates and N pressure in a chamber. It was found that the film hardness was ≥ 42 GPa and elastic modulus was E = 490 ± 10 GPa, nanograin size being 5 to 35nm. It was demonstrated that depending on the substrate bias potential, ratio of α-H_5S_4, nc-$HfSi_2$ and nc-TiN or (Ti,Hf)N phases changed. Using SIMS, RBS, EDS with SEM analysis, the films stoichiometry and concentration profiles over depth were measured. Analyzing the film cross-section, we found good quality of the films, very good adhesion to the steel 3 substrates, pores and columnar structures were not observed.

XRD and TEM with micro-diffraction were applied to determine sizes of nanograins of the above mentioned phases. 200°C to 600°C annealing in vacuum demonstrated that a hardness increased almost by a factor of 15 to 17% (48 to 52 GPa), i.e. an effect of self-hardening due to a process of spinodal phase segregation along grain interfaces was observed. Annealing at higher than 1100°C temperature resulted in formation of an oxide layer of 120 to 140 nm thickness at the film surface.

The work was funded by the NAS project of Ukraine – Nanosystems, Nanocomposites, and Nanotechniques.

Tribology and Mechanical Behavior of Coatings and Thin Films
Room: California - Session E2-1

Mechanical Properties and Adhesion
Moderator: M.-T. Lin, National Chung Hsing University & Chaoyang University of Technology, J. Michler, Empa

8:00am **E2-1-1 Theoretical Model Developed for the Pop-In Arising in the Thin Solids Films and Its Testification by Nanoindentations**, ***J.-F. Lin*** *(jflin@mail.ncku.edu.tw), C.-F. Han*, National Cheng Kung University, Taiwan **INVITED**

In the present study, the indentation depth corresponding to the pop-in arising in the thin solids film is caused by the delaminations and stress-induced phase transformations. This load-depth behavior gives a clue that the occurrence of pop-in is perhaps related to the buckling of the thin solids film which had already delaminated from the substrate. The membrane theory was first applied to develop the internal compression stress as a function of the normal load and the film thickness. This indentation depth of buckling predicted by the present model is quite close to the pop-in depth obtained from experimental results. This characteristic reveals that the present model is developed successfully to predict the pop-in depth of a specimen; and the pop-in is created due to the buckling of the composite film under a compression stress.

The stress and strain relationships expressed in terms of nanoindentation force and depth are applied to identify the phase transitions due to stress-induced crystallizations at different indentation depths. The further provision of the function of electrical contact resistance (ECR) in the present indentations system plus the aids of the diagrams of Gibbs free energy and the Raman spectra allow to be more clear and complete to track the paths of phase transition. The predictions of the critical stress and strain corresponding to some phase transitions by the present model are proved to have good consistence with the experimental results appearing a noticeable turning. The borders for different phase transitions arising in the loading/unloading process can be determined in the stress-strain diagram. The loading/unloading rate is of importance to the phase species created in the nanoindentation process and the critical stress and strain forming in phase transition.

8:40am **E2-1-3 Time Resolved Mechanical Surface Testing and Subsequent Physical Analysis**, ***N. Schwarzer*** *(n.schwarzer@siomec.de)*, Saxonian Institute of Surface Mechanics, Germany

Within sufficiently long time scales and depending on the temperature all solid materials show to a certain extent time dependent mechanical behavior. There are many different models to describe this effect, but none of which is sufficiently and generally applicable to the problem of analyzing mechanical surface tests like indentation and scratch in a proper and physical manner. The way out of this dilemma usually is to perform the tests fast enough in order to reduce the influence of the time dependency of certain mechanical parameters like Young's modulus and yield strength in order to apply the classical none-time dependent analyzing techniques.

However, this bypass has its limits

a) with respect to the materials it could be properly applied to

b) because it explicitly excludes the time dependency of the material properties, which is a great disadvantage if exactly this dependency shall be discussed

Thus, a new method is required providing the means for taking time into account generally and in an applicable manner. In principle, such a method is already at hand and its extension to time dependency is rather straight forward. It is called "the concept of the effectively shaped indenter" [1].

Within the talk it will be demonstrated how the concept has to be adapted not only to take time, even load rate into account, but also to become applicable for layered materials and multiaxial indentation tests.

[1] A. Bolshakov, W.C. Oliver, and G.M. Pharr, MRS Symp. Proc 356, p 675 (1995)

9:00am **E2-1-4 Mechanical Stress Effect on the Formation of Copper-Tin Intermetallic Thin Films**, ***M.-T. Lin*** *(mingtlin@nchu.edu.tw), C.-C. Yang, S.-N. Li, T.-C. Chen, C.-M. Chen*, National Chung Hsing University & Chaoyang University of Technology, Taiwan

In microelectronics, a mechanical reliable lead free solder thin film plays a very important role both in device reliability and environmental friendly. In order to obtain better understanding of mechanical properties on the effect of stress state related to interfacial Cu-Sn IMC thin layer growth, custom design four point bend experiments had been conduct. 250 micron thick, 4 inch double polished silicon wafers were cut into strips with 27mm in length and 5mm in width as test samples. A very thin adhesion layer was deposited on the silicon substrate using sputtering then 10 um thick copper layer was deposited using electroplating method and 35 um tin layer was continue deposited on top of the copper film. During the experiment, a set of samples were put into furnace at 200℃ and relatively low levels of in-plane bending stress were applied on the samples under tension, compressive and no stress. The results on intermetallic formation affected by different stress levels (20MPa, 30MPa and 45MPa) and different reflow time were presented. Each thickness of different phases (Cu_3Sn) and (Cu_6Sn_5) could be observed clearly in scanning electron microscope images. Both of tension and compression stress would affect the Cu-Sn intermetallic formation. The thickness of intermetallic layer was increased when sample under both compression stress and tension stress. The growth rate of Cu-Sn IMC layer was relatively enhanced by compression bending stress than tension stress and no stress. We hypothesize that the observed IMC thickness increasing is related to straining of the underlying lattice at the diffusion interface.

9:20am **E2-1-5 What Qualifies a Well Adherent Cr-Based Adhesion Layer for Diamond-Like Carbon Coating Systems?**, ***J. Schaufler*** *(jens.schaufler@ww.uni-erlangen.de), C. Schmid, G. Yuang, M. Göken, K. Durst*, University Erlangen-Nuremberg, Germany

The adhesion strength of industrial Diamond-like Carbon (DLC) coatings is a crucial factor for the performance of the coated components in high load automotive applications. On an industrial scale metallic adhesion layers are frequently used to achieve a certain interfacial strength between the DLC coating and the steel substrates. However, details concerning the correlation between the microstructure, the chemical gradients and the load bearing capacity in terms of interfacial strength of the adhesion layers are not fully understood. In this work Cr-based adhesion layers with different interfacial strength ranging from excellent to poor were investigated in terms of the microstructure, the chemical gradients and their resistance against interfacial failure. From Energy Filtered TEM analysis clear differences in the microstructure and the chemical gradients are found for the two systems. The local structure nicely correlates with the local hardness and Young's modulus, determined on low angle cross sections of the coating systems using nanoindentation. In addition, SEM in-situ bending tests were performed on FIB milled DLC bending beams. By varying the dimensions of the beams, focused investigations on the interfaces of the DLC coating systems with different adhesion strengths can be performed, allowing a quantification of the interfacial strength. Herewith, basic design microstructural based design principles for well adherent Cr-based adhesion layer for DLC coating systems can be obtained.

9:40am **E2-1-6 Evidence of Vacuum Below Buckling Structures**, ***E. Dion*** *(eloi.dion@univ-poitiers.fr), C. Coupeau, J. Colin, J. Grilhe*, Université de Poitiers, France

Thin films and coatings are widely used for their functional properties that strongly depend on their mechanical behaviour and stability. During the elaboration process by physical vapor deposition methods, high internal compression stresses can develop and may then result to failure by delamination and buckling. A plethora of buckling patterns has been observed such as straight-sided wrinkles, circular blisters or telephone cord structures. During the past decade, the buckling phenomenon has been extensively studied in the framework of the Föppl-Von Karman theory of thin plates assuming no pressure mismatch between the lower (inside) and the upper (outside) parts of the buckled films.

It is the purpose of this work to investigate the pressure level inside the buckles. In this context, straight-sided wrinkles have been first induced on a 400 nm nickel thin film by a uni-axial compression of the polycarbonate substrate. To investigate the pressure effect, some closed and airtight wrinkles have been selected and analyzed by atomic force microscopy (AFM). Wrinkles have been cut by a focus ion beam (FIB) technique and then re-analyzed by AFM. An increase of 20 nm of the maximal deflection has been observed after the FIB opening process. This experimental result suggests the presence of a low vacuum environment inside the buckle, between the film and the substrate. This behaviour is discussed in the framework of the Föppl-Von Karman theory of thin plates.

10:00am **E2-1-7 Investigation of the Mechanical Properties of DLC-Coatings by Means of Nanoindentation and It's Modelling**, ***A. Gies*** *(astrid.gies@oerlikon.com),* OC Oerlikon Balzers AG, Liechtenstein*, N. Schwarzer,* Saxonian Institute of Surface Mechanics, Germany*, J. Becker, H. Rudigier*, OC Oerlikon Balzers AG, Liechtenstein

Diamond like Carbon – coatings are used in the automotive industry since more than 15 years now. This is 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. In order to choose a coating system which is adapted to a tribological application, one has to consider the whole tribological system comprising the coated substrate, the counter body and eventually present lubricants. After that, the mechanical coating properties, for example coating hardness, yield strength, adhesion, Young's modulus and intrinsic stress, have to be adjusted to the tribological system.

In this work, multiaxial nanoindentation and it's modelling has been used in order to determine the mechanical properties of DLC-coatings and to predict the behaviour of different DLC-coating systems in various mixed-load applications.

In a first step, vertical and lateral nanoindentation has been carried out during coating development. This allowed us to determine the mechanical properties of different coatings as well as to calculate the coating behaviour for different loading cases in order to identify critical areas in the coating and potential for improvement.

In a second step, vertical and lateral nanoindentation and it's modelling was carried out on a DLC-coated component from the automotive industry which showed sometimes good and sometimes poor performance in a real industrial tribological application. In this case and for the first time we were able to physically quantify the failure of a coating system by a real multiaxial, 3-dimensional nanoindentation test and it's modelling.

10:20am **E2-1-8 Fracture Behavior of Hard Multilayered Thin Films on Soft Substrates**, *C.G. Oliva,* Politecnico di Torino, Italy*, R. Ghisleni, R. Raghavan,* Empa, Switzerland*, D. Ugues,* Politecnico di Torino, Italy*, **J. Michler** (Johann.Michler@empa.ch)*, Empa, Switzerland

Compositionally graded and nanostructured thin films not only provide new technological opportunities, but are also interesting from a scientific perspective. Deliberate design of such advanced thin films has revealed superior and unique combinations of mechanical properties, such as high hardness, toughness, wear resistance etc.

In this study, the fracture behavior of (Cr,Al)N/a-Si_3N_4 and (Ti,Al)N/a-Si_3N_4 multilayered thin films deposited by PVD on steel substrates is compared to the fracture behavior of the corresponding monolayers using the following methodologies. In particular, crack patterns formed by subjecting the thin film-substrate system to four-point bending and spherical indentation are analyzed in terms of crack density and equilibrium crack spacing. Complementary experiments have been conducted in-situ SEM to study the crack propagation sequence along the cross-section of the thin films to elucidate whether the cracks originate at the film surface or interface. Values of fracture strength estimated using both methodologies are compared for both cases. Finally, novel methodologies such as in-situ SEM compression and tension of micro-pillars and micro-beams respectively, FIB machined within the film have also been attempted to study the fracture behavior and estimate the fracture strength of the films in order to minimize the influence of deformation of the substrate. Thus, this study provides novel insights not only into the crack patterns and propagation sequence of multilayered thin films, but also suggests the advantages and disadvantages of the novel methodologies used to estimate the fracture strength.

10:40am **E2-1-9 Correcting Time Dependent Displacement Effects in Nanoindentation Analysis**, ***M.I. Davies** (emxmd1@nottingham.ac.uk),* Univeristy of Nottingham, UK*, N. Schwarzer,* Saxonian Institute of Surface Mechanics, Germany*, B. Beake,* Micro Materials Ltd, UK*, N.M. Everitt*, University of Nottingham

Instrumented nanoindentation is now a commonly used tool in assessing the properties of materials for a wide range of applications. Analysis of nanoindentation data is typically carried out using the methods popularised by Oliver and Pharr, with Young's modulus and hardness determined by a power law fit to the unloading data of the load displacement plot. One of the key limitations of this analysis technique is that it does not allow consideration of time dependent deformation mechanisms such as creep or visco-elastic behavior exhibited by some materials. Hence if testing such materials, experimentalists find Young's modulus values dependent on the experimental unloading rate.

Conventional nanoindentation techniques use a fast unloading rate in order to minimise the influence of time dependent deformation on calculated Young's modulus. Such techniques have been used on two representative samples - a visco-elastic polymer and gold, tested at room temperature and higher (creep) temperatures respectively. Oliver and Pharr analysis of this data returns acceptable Young's moduli but the results still exhibit unloading rate dependence. Additionally, failure to account for time dependent depth change can lead to physically unrealistic fitting constants in the power law (m>2), calling into question the validity of the fit.

Results using a new analysis method which allows determination of the time dependent contributions to the Nanoindentation depth will be presented. This enables calculation of a Young's modulus independent of the unloading rate and with physically meaningful fitting constants in the power law. The technique also provides estimates for the stress field in the indented region during unloading.

11:00am **E2-1-10 Measuring Substrate-Independent Young's Modulus of Thin Films***, **J. Hay** (jenny.hay@agilent.com)*, Agilent Technologies

Substrate influence is a common problem when using instrumented indentation (also known as nano-indentation) to evaluate the elastic modulus of thin films. Many have proposed models in order to be able to extract the film modulus (E_f) from the measured substrate-affected modulus, assuming that the film thickness (t) and substrate modulus (E_s) are known. Existing analytic models work well if the film is more compliant than the substrate. However, no analytic model accurately predicts response when the modulus of the film is more than double the modulus of the substrate. In this work, a new analytic model is proposed. Using finite-element analysis, this new model is shown to be able to accurately determine film modulus (E_f) over the domain $0.1 < E_f/E_s < 10$. Finally, the new model is employed to determine the Young's modulus of thin chromium-nitride coatings on steel.

11:20am **E2-1-11 Interfacial Indentation Test of FeB/Fe_2B Coatings**, *M.A. Doñu-Ruiz, I.E. Campos-Silva (icampos@ipn.mx), J. Martinez-Trinidad, **G. Rodriguez-Castro**, E. Hernandez-Sanchez*, Instituto Politécnico Nacional, Mexico

The boriding process enhances mechanical and chemical properties at the surface of steels through the formation a Fe_2B coating or FeB/Fe_2B coatings. The thickness of the coating formed (known as the case depth), which affects the mechanical and chemical behavior of borided steels, depends on the boriding temperature, the treatment time and the boron potential that surrounds the surface sample. Based on the formal theory of boride growth in different steels, the formation of the FeB borided phase results from the transformation of Fe_2B crystals at the outermost part of the sample due to the high boron potential at the surface. When treatment times and temperatures are increased, FeB regions grow from compact and oriented crystals of Fe_2B and become much deeper. The layers grow preferentially in the (002) plane, thereby increasing the mechanical stresses at the FeB/Fe_2B interface due to lattice distortions in this zone.

For this reason, the present study estimated the adhesion of the FeB/Fe_2B coating formed at the surface of AISI 316 borided steel by means of interfacial indentation test. This technique is used to create and propagate a crack in the FeB/Fe_2B interface, and defining the apparent fracture toughness, which can represent the adhesion and the mechanical support of the aforementioned interface. First, the boriding process was carried out at the surface of AISI 316 steels by developing the powder-pack method, at temperatures of 1123, 1173, 1223 and 1273 K with 2,4,6,8 and 10 h of exposure. Mechanical properties like Young modulus and hardness were obtained by depth-sensing nanoindentation technique for each surface layer. Also, Vickers microindentation fracture technique was used to generate microcracks at the FeB/Fe_2B interface with different indentation loads. The applied loads, crack lengths generated from the corners of the indentations, the Young modulus, and hardness values were set as the experimental parameters for determining the apparent fracture toughness of the FeB/Fe_2B interface.

Considering the set of experimental parameters and the depth of the FeB layer, the apparent fracture toughness for the FeB/Fe_2B interface is in the range of 3.69 to 4.31 MPa m ^{½}.

11:40am **E2-1-12 Indentation Size Effect on Fe_2B/Substrate Interface***, I.E. Campos-Silva (icampos@ipn.mx), **E. Hernandez-Sanchez**,* Instituto Politécnico Nacional, Mexico*, M. Ortiz-Domínguez,* Instituto Politecnico Nacional, Mexico*, A. Rodriguez-Pulido, G. Rodriguez-Castro*, Instituto Politécnico Nacional, Mexico

This study evaluated the indentation size effect on Fe_2B/substrate interface applying the Berkovich nanoindentation technique. First, the Fe_2B layers were obtained at the surface of AISI 1018 borided steels by developing the powder-pack boriding method. The treatment was carried out at temperatures of 1193, 1243 and 1273 K with 4, 6 and 8 h of exposure times for each temperature. The boriding of AISI 1018 steel results in the formation of saw-toothed Fe_2B surface layers. The formation of a jagged boride coating interface can be attributed to the enhanced growth at the tips of the coating fingers, due to locally high stress fields and lattice distortions. Thus, the mechanical properties achieved at the tips of the boride layer are of great importance in the behavior of borided steel.

Applied loads in the range of 10 to 500 mN were employed to characterize the hardness in the tips of the Fe_2B/substrate interface for the different conditions of boriding process. The results showed that the measured hardness depends crucially on the applied load, which indicated the influence of the indentation size effect (ISE). The load dependence of hardness was analyzed by using the classical power law approach, a proportional specimen resistance (PSR) model, a modified proportional specimen resistance (MPSR) model, and elastic recovery model. The true hardness in the tips of the Fe_2B/substrate interface was obtained for each model for the set of experimental parameters whose values are similar between the empirical equations adopted in these models. Finally, the nanoindentation technique was used to estimate the state of residual stresses in the critical zone of the Fe_2B/substrate interface.

New Horizons in Coatings and Thin Films
Room: Sunset - Session F1-1

Nanomaterials, Nanofabrication, and Diagnostics
Moderator: S. Kodambaka, University of California at Los Angels, Y.A. Gonzalvo, Hiden Analytical

8:00am **F1-1-1 Ordered ZnO/AZO/PAM Nanowire Arrays Prepared by Seed Layer Assisted Electrochemical Deposition**, ***Y.-M. Shen***, *C.-H. Pan,* National Cheng Kung University, Taiwan, *S.-C. Wang,* Southern Taiwan University, Taiwan, *J.-L. Huang (jlh888@mail.ncku.edu.tw)*, National Cheng Kung University, Taiwan

Zinc oxide nanowire is a n-type semiconductor which exhibits wide band gap (3.3 eV) and high bonding energy (~60 meV). It has attracted great attention because of its specific optical and electric properties. In this work, AZO (Al-doped in ZnO) seed layer was prepared on the back side of PAM substrate by spin coating and annealing in vacuum at 400°C. The average sheet resistance of 5-layers AZO films was 129.66 Ω/sq. Zinc oxide in order arrays mediated by high aspect ratio and order pores array AZO/PAM was synthesized. The ZnO nanowire array was prepared by 3-electrode electrochemical deposition in $ZnSO_4$ and H_2O_2 solution at various deposition potential (-0.8 ~ -1.2 V/SCE) and temperature (25~80°C). The microstructure and chemical composition of AZO seed layer and ZnO/AZO/PAM nanowire arrays were characterized by field emission scanning electron microscopy (FE-SEM), X-ray diffraction (XRD), and Energy dispersive spectrometer (EDS), respectively. The interface between ZnO and AZO was analyzed by high resolution transmission electron microscopy (HR-TEM) and selected area electron diffraction pattern (SAED). The photoluminescence spectra (PL) and Hall effect measurement were employed to analyze the luminescent properties and carrier concentration of ZnO/AZO/PAM nanowire arrays. The results indicated that the ZnO nanowire arrays were assembled into the nanochannel of porous alumina template with diameter of 120~140 nm. The crystalline structure of single ZnO nanowire was depended on AZO seed layer. The nucleation and growth process of ZnO/AZO/PAM nanowires were interpreted by seed layer assisted growth mechanism.

8:20am **F1-1-2 Hierarchical and Core-Shell ZnO/TiO_2 Photocatalytic Heterostructures**, ***J. Migas***, *D. Stone, L. Wang, M.E. McCarroll, S.M. Aouadi (saouadi@physics.siu.edu)*, Southern Illinois University, Carbondale

ZnO/TiO_2 hierarchical heterostructures were created as potentially effective photocatalysts to degrade organic pollutants into more environmentally friendly chemical species. ZnO/TiO_2 heterostructures, combining two of the most effective photocatalysts in the literature, were synthesized using a two-step route that consists of the hydrothermal growth of ZnO nanowires followed by the deposition of TiO_2 using unbalanced magnetron sputtering. The synthesis conditions were altered in order to control the growth process of TiO_2. The morphology of the synthesized heterostructures was evaluated using scanning electron microscopy (SEM) revealing that the growth process of TiO_2 may be controlled to produce hierarchical and core-shell structures. The crystal structure and the optical and chemical properties were determined by means of transmission electron microscopy (TEM), x-ray diffraction (XRD), and spectroscopic ellipsometry (SE). Lastly, the photodegradation of Rhodamine 6G was investigated. Enhanced catalytic activity of the hierarchical structures was found to be due to the increased contact surface area and to the enhanced interfacial charge transfer mechanism at the junction between ZnO and TiO_2.

8:40am **F1-1-3 Photo-Degradation Behavior of N-Doped TiO_2 Nanotubes Prepared by Anodic Oxidation and Nitrogen Implantation**, ***J. Li*** *(lijl@nimte.ac.cn), F. Huang, Q.-J. Xue*, CAS Ningbo Institute of Materials Technology and Engineering, China

Nitrogen-doped TiO_2 nanotubes are fabricated on Ti_6Al_4V sheets via anodic oxidation followed by nitrogen implantation. Highly regular nanotubes, roughly 80 nm in inner diameter and 16 nm in wall thickness, form selectively in the region of the dominant phase (a) of the Ti_6Al_4V sheet. Post implantation annealing up to 650°C obtains a mixture of anatase with a small fraction of rutile. X-ray photoelectron spectroscopy (XPS) studies reveal that the doped nitrogen exists in three forms: β–N, N–Ti–O, and γ-N. Nitrogen doping extends the TiO_2 photo-response into the visible light region of 400-600 nm. A higher photo-degradation rate is further identified for the Ti_6Al_4V sheets covered N-doped TiO_2 nanotubes in subsequent tests.

9:00am **F1-1-4 Low Temperature Growth Mechanisms of Vertically Aligned Carbon Nanofibers (CNFs) and Carbon Nanotubes (CNTs) by RF-PECVD**, ***H. Wang***, *J.J. Moore (jjmoore@mines.edu)*, Colorado School of Mines

Using radio frequency-plasma enhanced chemical vapor deposition (RF-PECVD) method, different CNFs and CNTs were synthesized at low temperature. Base growth vertical turbostratic CNFs were grown using sputtering 8 nm amorphous Ni thin film catalyst on Si substrates at a temperature of 150°C. Tip growth vertical platelet graphite nanofibers (PGNFs) were grown using Ni nanocatalysts in 8 nm Ni films at 180°C. By introduction of hydrogen tip growth vertical multi-walled carbon nanotubes (MWCNTs) were also produced at 180°C using FeNi nanocatalysts in 8 nm FeNi films on glass substrates. Low temperature growth mechanisms of CNFs and CNTs in RF-PECVD were discussed based on plasma physics, catalysts structure, substrate characteristics and temperature, and types of gases. In comparison to the most widely used thermal CVD (T-CVD) method, in which its synthesis temperature was 550-850°C for CNFs and CNTs growth, RF-PECVD had a huge advantage in low temperature growth of CNFs and CNTs and control of other deposition parameters.

9:20am **F1-1-5 Inkjet-Printed Carbon Nanotube Films**, ***A.R. Hopkins*** *(alan.r.hopkins@aero.org), D.C. Straw*, The Aerospace Corporation

Due to their remarkable mechanical properties, single walled carbon nanotubes (“SWNTs”) are expected to eventually revolutionize structural designs of both spacecraft and air vehicles with great expectations in reducing the overall weight of these applications. As these carbon nanotubes are considered anisotropic nanoparticles with an extreme aspect ratio, they exhibit most of their remarkable properties, such as their extraordinary tensile strength (~200 GPa) in a single direction: along the tube axis. The achievement of uniform alignment is therefore a crucial condition in order to exploit these SWNT materials as potential nano-reinforcment materials for spacecraft applications. This work is aimed at development of a technique to allow a non-contact deposition and organization of SWNTs using an ink-jet spray technique to build up three dimensional (3D) structures with greater strength and toughness than possible by use of composites or monolithic materials such as steel or aluminum. We report the successful formulation of two single walled carbon nanotube (SWNT) inks which yielded a consistent, homogenous printing pattern and possessed the requisite viscosities needed for flow through the microcapillary nozzles of the ink-jet printer with fairly modest drying times.

9:40am **F1-1-6 Super-Hydrophobic Surfaces via Synthesis of Vertically Aligned Carbon Nanotube Arrays on Aluminum-Iron Matrix**, *B. Baykal, G. Kucukayan (kgokce@bilkent.edu.tr),* ***E. Bengu***, Bilkent University, Turkey

We explored the wetting behavior of water droplets on vertically aligned carbon nanotube arrays (VANTA) of varying film density, film thickness and alignment orientation. The carbon nanotube (CNT) arrays (or *forests*) were synthesized with a 3 inch tube furnace through chemical vapor deposition (CVD). The synthesis environment includes the mixture of flowing ethanol, argon, and hydrogen gases at a temperature ranging from 600-750°C. Dilute aqueous solutions (5 mmol l^{-1}) of iron (III) nitrate and aluminum (III) nitrate have been applied on oxidized Si (100) substrates (approximately 10mm X 10mm) in an alternating fashion with the help of a micro-pipette. These nitrate solution treated substrates were dried at room temperature, and then loaded onto a quartz boat and placed into the load-lock of the tube furnace for processing. The pre-treatment procedure includes changing applied catalyst layer and base layer concentrations separately. Some of the CNT forests synthesized in this study showed super-hydrophobic behavior upon testing with deionized water, where contact angles (CA) measured were in excess of 150°. Dynamic CA measurement experiments were also performed upto 30 minutes. The results indicated that some CNT forest samples preserved their super-hydrophobic character for an extended period of exposure to the water droplet. Some retained a CA above 150° even after 30 minutes of exposure.

We investigated the effect of film density, film thickness and orientation on the measured CA and the rate of change in the CA. Graph 1-4 indicates the change in the CA for CNT array films synthesized using different pre treatment parameters. Our studies indicated an optimum CNT film density and tube length for optimizing the dynamic behavior of these surfaces. Hence, we found that synthesis parameters and catalysis application methodology may significantly affect hydrophobic properties of these CNT forests.

10:00am **F1-1-7 Fabrication of Nanoimprint Molds by Sub-Micron Sphere Lithography**, ***S. Portal*** *(sabineportal@hotmail.com), C. Corbella, E. Cabrera, V.-M. Freire, E. Pascual, J.-L. Andújar, E. Bertran*, Universitat de Barcelona, Spain

Monodisperse silica sub-micron particles (150 to 600 nm) were synthesized by sol-gel process. They were assembled on silicon wafers by Langmuir-Blodgett method to produce hexagonal structured monolayers. The periodic hexagonal pattern was transferred onto the underlying substrate by colloidal lithography, which consisted in ion beam etching of the monolayer at normal or oblique incidence. The resulting substrate surface showed periodic patterns consisting in nano-pillars whose orientation depended on the etching angle. For its performance as nanoimprint mold, the patterned surface was coated with an amorphous carbon film with fluorine (a-C:H:F) by plasma-enhanced chemical vapor deposition (PECVD). The size and the compactness of the pillars depended on the initial silica particle monolayer and could be controlled by the sol-gel and Langmuir-Blodgett deposition conditions. The pattern of the molds was replicated on polymer and soft surfaces (PMMA, silica gel) by nanoimprint lithography. Both the molds and the patterned polymers were characterized, before and after nanoimprinting, by SEM, AFM, wettability measurements (contact angle) and friction coefficient (nanotribometer).These patterns show tuned and direction-dependent surface properties of interest in photovoltaic, polarimetry and self-cleaning applications.

10:20am **F1-1-9 Gas Sensors with Porous Three-Dimentional Framework Using TiO_2/Polymer Double-Shell Hollow Microsphere**, ***C.-J. Chang*** *(changcj@fcu.edu.tw), C.-K. Lin,* Feng Chia University, Taiwan*, C.-C. Chen,* National United University, Taiwan*, C.-Y. Chen, E.H. Kuo*, Feng Chia University, Taiwan

Double-shell hollow spheres were prepared by encapsulating the polymeric hollow spheres with TiO_2 shells. T he ratio of the TiO_2 shell thickness to the diameter of the double-shell hollow microsphere can be tuned by changing the precursor concentration and the diameter of polymeric hollow microspheres. Porous thin-film gas sensor was prepared by coating the double-shell hollow sphere dispersion and the removal of inner polymer shell. We examined the gas sensing properties of porous films consisting of packed hollow microspheres with porous TiO_2 walls. The response properties of the sensors toward NO_2 depend on TiO_2 shell thickness, film thickness and three-dimentional porous structure of TiO_2 films. These films showed enhanced gas sensitivity compared with TiO_2 thin film sensor deposited on untreated substrates. Such improvement in sensitivity results from the porous architecture of the hollow microsphere films which not only increase the active surface area but also promotes the gas diffusion.

10:40am **F1-1-10 Abnormal Retention Characteristics of $NiSi_2/SiN_X$ Compound Nanocrystal Memory at Elevated Temperature**, ***Y.-T. Chen*** *(u9223005@ems.ndhu.edu.tw)*, National Sun Yat-sen University, Taiwan

Nanocrystals (NCs) and SONOS nonvolatile memory (NVM) are the promising candidates for the next generation of flash memory since the discrete storage nodes can effectively alleviate the charge leakage from storage layer during scaling down.

We have previously reported the fabrication of $NiSi_2/SiN_x$ compound nanocrystal (CNC) memory to combine the advantages of nanocrystal and SONOS memory. And the enhanced retention characteristics over control sample ($NiSi_2$ nanocrystal memory) are clarified to be due to the compound tunnel barrier and nitride traps.

In this paper, the retention characteristics of above nanocrystal memory are systematically measured, especially at elevated temperature aiming at the long term storage performance. The retention characteristics of both devices degrade at 350K, and the difference of charge decay rate between CNC memory and control sample is larger than that of room temperature. At 400K, the charge decay rate of control sample continues to increase due to the stimulated leakage mechanism, however, the retention window of CNC memory increases at the first thousand seconds and then reduces.

The stored charges in nitride traps are easier to be stimulated to the energy band of nitride at elevated temperature and then transfer to $NiSi_x$. Since the area of $NiSi_x$ nanocrystal ($\sim1.2\times10^{-13}cm^{-2}$) is much larger than the capture cross section of nitride ($10^{-16}\sim10^{-15}cm^{-2}$), the shift of flat-band voltage will increase when the stored charges transferred from nitride traps to $NiSi_x$ nanocrystals. And it's also confirmed by the retention measurement with different programming voltage. It indicates that the long term storage performance of CNC memory is considerably improved due to the compound nanocrystal of $NiSi_2$ and SiN_x.

11:00am **F1-1-11 A Novel Fabrication Technique for Free Standing Nickel Nanowires and their Possible Applications***, M. Urgen (urgen@itu.edu.tr),* ***F.B. Bayata****, N.S. Solak*, Istanbul Technical University, Turkey

Free standing nickel nanowires supported by a nickel base film has been produced in this work by nickel electrodeposition on pore bottom activated aluminium anodic oxide (AAO) structures. The AAO films were prepared by anodization of pure aluminum and then this porous structure was exposed to a novel pore bottom activation process based on zincating. By means of this process, electrodeposition within the pores by direct current became possible without the need to other processes that are conventionally used, such as metallic aluminium etching, pore bottom dissolution and vacuum metallization. In order to form supporting layer for nanowire arrays, nickel electrodeposition process has been maintained until a thick metallic layer is formed on the nanowire structures. After removing AAO template, easily handled free standing nickel nanowire arrays which are perpendicular to nickel film surface have been achieved.

These free standing nickel nanowires with high specific surface area have shown relatively high enhancement ability, good reproducibility, long term stability as a surface enhanced Raman active material and high conversion efficiency for dry reforming of natural gas as a catalyst. Since nickel/nickel oxides have been intensively developed to act as an alternative electrode material for supercapacitors, the free standing nickel nanowires produced in this work are also considered as promising supercapacitor electrode materials owing to their high electrochemical activity.

New Horizons in Coatings and Thin Films
Room: Royal Palm 1-3 - Session F5

New Oxynitride Coatings
Moderator: W. Kalss, Oerlikon Balzers, S. Ulrich, Karlsruhe Institute of Technology (KIT)

8:00am **F5-1 Oxynitride Coatings - Opportunities and Challenges from an Industrial Perspective**, ***J. Sjölén*** *(jacob.sjolen@secotools.com),* Seco Tools AB, Sweden*, A. Khatibi, L. Hultman*, Linköping University, Sweden **INVITED**

The development of wear resistant coatings produced by different PVD techniques has mainly been focused on metal-nitride and metal-carbide coatings, such as (Ti,Al)N, (Cr,Al)N, Ti(C,N) and (Ti,Si)N etc. However, during the recent years there has been a tremendous progress in the attempts to produce crystalline metal-oxide coatings, such as $(Cr,Al)_2O_3$, especially by using cathodic arc evaporation. Challenges, such as target poisoning and insulating anodes have been overcome, opening up for a completely new group of materials. By the combination of nitride and oxide coating processes, a new dimension in the material space has been opened, giving us metal-oxy-nitrides. This presentation concerns coatings such as (Ti,Al)(O,N) and (Cr,Al)(O,N) deposited onto WC-Co-substrates using cathodic arc evaporation. Results for coating structure, analyzed by SEM, XRD, TEM, etc., and mechanical properties, analyzed by nanoindentation and metal cutting tests will be presented as a function of the O/N ratio. A unique advantage of the highly ionized plasmas combined with the relatively low deposition temperatures in the cathodic arc processes is that the energy of the impinging species cause collision cascades in the lattice that makes it possible to quench solid solutions and metastable compounds. These coatings have shown improved metal cutting performance with enhanced tool life in both turning and milling applications.

8:40am **F5-3 Deposition and High Temperature Stability of Reactively Magnetron Sputtered Al-Cr-O and Al-Cr-O-N Thin Films**, ***D. Diechle****,* Karlsruhe Institute of Technology, Germany*, A. Cavaleiro,* Coimbra University, Portugal*, H. Leiste,* Karlsruhe Institute of Technology, Germany*, V. Schier,* Walter AG, Tübingen, Germany*, M. Stueber (michael.stueber@kit.edu), S. Ulrich*, Karlsruhe Institute of Technology, Germany

PVD coatings for high performance applications such as protective coatings for metal cutting require outstanding properties including high hardness, chemical inertness and high temperature stability. In the last decade the synthesis of hard Al-O and related protective thin films attracted large scientific interest and such coatings were successfully introduced in industrial production processes.

We present a combinatorial approach for the synthesis of ternary Al-Cr-O and quaternary Al-Cr-O-N solid solution strengthened thin films, grown in α-phase structure, by reactive r.f. magnetron sputtering in argon-oxygen-nitrogen atmospheres. The deposition experiments were carried out with a laboratory scale Leybold Z 550 PVD machine by sputtering from a segmented Al-Cr target at non-equilibrium conditions. The substrate temperature during deposition was adjusted to 500°C and the r.f. substrate bias was varied from zero up to -300 V. The metastable thin films were characterized by determining the Vickers micro hardness, the residual stress, the chemical composition by EPMA, the structure by XRD and the microstructure by SEM and TEM.

This paper addresses further the high temperature stability of the nanocrystalline α-Al_2O_3 based thin films. The structure of selected Al-Cr-O solid solution strengthened thin films was analyzed during HTXRD and after annealing in ambient air from 500°C up to 1400°C. The Al-Cr-O thin films revealed a decomposition of the single α-phase into a dual phase microstructure of an Al-rich and a Cr-rich α-phase. According to the Al_2O_3-Cr_2O_3 phase diagram, the decomposition temperature varied between 1200°C and 1300°C as a function of the coatings chemical composition.

9:00am **F5-4 Synthesis of the Al-Cr-O-N Coatings by Reactive Cathodic Arc Evaporation**, ***D. Kurapov*** *(denis.kurapov@oerlikon.com), H. Rudigier, T. Bachmann,* OC Oerlikon Balzers AG, Liechtenstein, *M. Doebeli*, Ion Beam Physics, ETH Zürich, Switzerland

This work reports on the correlation between deposition parameters, chemical composition, crystal structure, mechanical properties and cutting performance of Al-Cr-O-N coatings produced by reactive cathodic arc evaporation. The coatings have been synthesized using Al_xCr_{1-x} alloyed targets where x varies from 0 to 0.85. The reactive gas mixture was adjusted in a way to obtain coatings with composition varying from AlCrN to $(Al,Cr)_2O_3$. The chemical composition of the coatings was investigated by means of Rutherford backscattering spectroscopy (RBS). The evolution of the crystallographic structure as a function of chemical composition was studied by X-ray diffraction (XRD). Based on the results of RBS and XRD analysis we propose formation of the oxide coatings with cubic crystal structure if the ratio of oxygen atoms to metal atoms during the deposition is close to one. The oxide coatings with the cubic structure exhibit the highest deposition rate, the highest hardness as well as significantly improved tool life as compared to (Al,Cr)N and $(Al,Cr)_2O_3$ coatings.

9:20am **F5-5 Effect of Heat Treatment on the Structural Properties of LARC-Deposited AlCr-Based Oxynitride Coatings**, *H. Najafi (hossein.najafi@epfl.ch), A. Karimi,* EPFL, Switzerland, *P. Dessarzin,* ***M. Morstein***, Platit AG, Switzerland

In this work we focus on the influence of oxygen content on the properties of cathodic arc-deposited $AlCr(O_xN_{1-x})$ coatings. The samples were prepared in a mixture of O_2 and N_2 at 550°C using lateral rotating arc cathodes (LARC) technology and a pulsed bias voltage. The obtained coatings were characterized by various techniques including XRD, SIMS, SEM, TEM, pin-on-disk tests and nanoindentation.

The diffraction results show that the samples can be classified in three groups with respect to their oxygen content, x. For the first group of samples with $x \leq 0.6$, single-phase films with *fcc* lattice are obtained despite the large proportion of oxygen. In the second group, composite coatings consisting of a mixture of α-$(Al,Cr)_2O_3$ with corundum structure and (Al,Cr)(O,N) with cubic structure are achieved within a range of oxygen from $0.6 < x \leq 0.95$, as confirmed by XRD and TEM. The third group is formed by coatings with $x > 0.95$, where a well-crystalline α-$(Al,Cr)_2O_3$ corundum phase is observed. In all three groups, coatings heat-treated for 1h at 1000°C in argon environment show enhanced crystallinity and kept their structure except for those close to the threshold of the first group ($x \approx 0.6$), where a huge difference between as-deposited and heat-treated states was observed. Our results indicate that these single-phase oxynitrides are metastable and after heat treatment convert to a composite from equal volume fractions of nitride and oxide. This behaviour was attributed to the presence of a sufficient quantity of oxygen in the coatings to enable local formation of oxide lattice during annealing.

The characteristics of the $AlCr(O_xN_{1-x})$ arc-PVD coatings are compared to both chemically equivalent and silicon-doped pulsed DC magnetron sputtered layers, and friction and wear for the different series were studied at both ambient and high temperatures. The low wear rates observed for the oxynitride coatings suggest their suitability for turning and milling applications, which will be demonstrated by cutting test examples.

9:40am **F5-8 Dedicated Oxynitride Coating Systems for Heavy Machinable Materials**, *P. Mahr,* ***H. Frank*** *(H.Frank@gfe-net.de), S. Reich*, GFE Schmalkaden e.V., Germany

Conventional hard coatings are used to reduce wear during production processes. But normally these coatings are not applicable for systems with high processes temperatures e.g. in machining heavy machinable materials. Oxynitride coatings show a better chemical and thermal stability and furthermore oxynitride structures can be used to reduce adhesion effects and build-up edges.

Deposition of oxynitride hard coatings was realized with an arc-PVD process by use of an oxygen-nitrogen gaseous mixture. For a stabilized and reproducible deposition process without micro arcs, an adapted coating hardware and optimized coating procedure were used. To determine the optimal process design, several parameters of the arc-PVD-process were varied: the material system (Zr-O-N; Cr-Al-O-N), the coating structure (gradient, multilayer, block), the pre- and post-treatment and the process condition (current, pressure, hf-pulsed or constant bias …). The results of optimization the coating process are oxynitride coating systems with improved coating properties and a higher thermal stability.

Applicability of the developed coating systems are demonstrated in several investigations in machin-ing heavy machinable materials. In various analyses an increase in tool life of oxynitride coated tools at higher cutting speed could be proved. This shows the applicability of the developed oxynitride coating systems to improve the efficiency of cutting processes.

10:00am **F5-9 Fabrication and Optical Performance of Zirconium Oxynitride Coatings**, ***C.V. Ramana*** *(rvchintalapalle@utep.edu), I.C. Fernandez,* University of Texas at El Paso, *A.L. Campbell*, Wright-Patterson Air Force Base (WPAFB)

Zirconium oxide (ZrO_2) exhibits excellent optical properties such as high refractive index, large band gap, low optical loss, high transparency in the visible and near-infrared regions, and high dielectric constant. However, ZrO_2 is UV-light sensitive. In addition, interfacial reactions during thin-film growth suppress the effective dielectric constant and degrade the optical performances. The present work was performed on ZrO_xN_y thin films to effectively alter the electronic structure by the method of nitridation, which well-known to suppress the interfacial reactions. ZrOxNy thin films were produced by magnetron-sputter deposition under the reactive pressure of nitrogen and oxygen. The effect of nitrogen/oxygen flow rate on the structure and optical properties of ZrO_xN_y thin films was investigated and compared with that of ZrO_2. The optical measurements of ZrO_2 films show a very high optical transmission with a band gap of 5 eV. The optical absorption measurements on ZrOxNy thin films grown at various reactive nitrogen pressures indicate a progressive shift from insulating to semiconductor behavior. The corresponding changes in the profiles of index of refraction were also remarkably distinct. The results indicate that tailoring the electronic structure and optical constants of ZrO_xN_y thin films to meet the requirements of visible-light functionality can be achieved by carefully controlling the reactive pressure. The results will be presented and discussed in detail.

10:20am **F5-10 Characterization of Nanostructured Hydrophobic Zirconium Oxynitride Coatings Deposited by RF Magnetron Sputtering**, *S.K. Rawal (sushant2713@gmail.com), A.K. Chawla, V. Chawla, R. Jayaganthan,* ***R. Chandra***, Indian Institute of Technology, Roorkee, India

The aim of this work is to develop zirconium oxynitride coatings by RF magnetron sputtering on silicon substrates. The film properties were analyzed as a function of oxygen partial pressure in two different inert gas atmospheres namely argon and helium. At low oxygen partial pressure, Zr_2ON_2 and m-ZrO_2 phases are present as observed from the structural characterization done by X-ray diffraction. The surface morphology was investigated by AFM. The proportion of metalloid content rises with increase in oxygen partial pressure which was determined by FE-SEM/EDS. The thickness of the film was measured by surface profiler and varies inversely with oxygen partial pressure. The films deposited are hydrophobic and the contact angle was measured by contact angle measuring system. Higher surface roughness and contact angle values are observed at low oxygen partial pressure. The surface energy of films was calculated by two methods: Owens–Wendt's geometric mean and Wu's harmonic mean approach. The elevated surface energy values were observed with increase in oxygen partial pressure. The stress measurements of the deposited films were done by $\sin^2\psi$ X-ray diffraction method which depends on the variation of Zr_2ON_2 and m-ZrO_2 phases.

Applications, Manufacturing, and Equipment
Room: Royal Palm 4-6 - Session G1

Innovations in Surface Coatings and Treatments
Moderator: A. Leyland, University of Sheffield, R. Cremer, KCS Europe

8:00am **G1-1 Electrical Measurement of Contamination Films in Plasma Reactors**, ***B.P. O'Shaughnessy*** *(breandan81@gmail.com), S.H. Jang,* University of Texas at Dallas, *J.S. Lee,* DMS, *G.S. Lee*, University of Texas at Dallas

A novel means of contamination monitoring in plasma etching and deposition chambers is presented. Electrical measurements and digital signal processing (DSP) are applied to the measurement of relative thickness of films deposited on a probe during industrial etching processes. Etching and cleaning in a commercially available PlasmaTherm etching reactor are monitored in this way. The efficacy of O2 and SF6 cleaning is verified using these results.

8:20am **G1-2 Hierarchical Homo- and Hetero-Structures Produced using Unbalanced Magnetron Sputtering Techniques**, ***S.M. Aouadi*** *(saouadi@physics.siu.edu), B. Sirota, D. Stone, L. Wang, M.E. McCarroll*, Southern Illinois University, Carbondale

Hierarchical nanostructures that consist of various combinations of metal oxides semiconductors (TiO_2, ZnO, V_2O_5, etc.) were synthesized using the unbalanced magnetron sputtering processes on Si and glass substrates. These structures were created to be used primarily as photocatalysts to degrade pollutants in water and air but may be used for other applications that include solar energy harvesting. The crystal structure and the morphology of the nanostructures were evaluated using x-ray diffraction, scanning electron microscopy, and transmission electron microscopy. These properties were evaluated as a function of deposition conditions such as power to the targets, substrate temperature, oxygen partial pressure, and substrate bias. Finally, the performance of these materials was investigated by evaluating the photoluminescence spectra of these materials and the degradation characteristics of various dyes.

8:40am **G1-4 Synthesis, Interface Engineering, and Applications of Cubic Boron Nitride Films**, ***W.J. Zhang*** *(apwjzh@cityu.edu.hk), B. He, Q. Ye, Y. Yang, I. Bello, S.T. Lee*, City University of Hong Kong **INVITED**

Cubic BN (cBN) has a set of extreme properties similar or even superior to diamond, which makes cBN a very promising material for fabrication of cutting tools, thermal, optical, and high-temperature and high-frequency electronic devices. Cubic BN is a synthetic material, and the study on the synthesis of cBN by high pressure high temperature (HPHT) method started in the early 1960s. Cubic BN films have also been prepared by a variety of ion-assisted physical vapor deposition (PVD) methods. The bombardment of deposited films by energetic species (tens to hundreds of eV) is, however, inevitably accompanied with a significant build-up of compressive stress (5-20 GPa) and leads to the nanocrystalline nature and delamination of the films with a thickness larger than 200 nm. Recent success in the growth of cBN films by chemical vapor deposition (CVD) methods based on fluorine chemistry results in considerable progresses in improving crystallinity, thickness, and adhesion of cBN films. This presentation aims to discuss the major issues hindering cBN films for practical applications, and review the recent progress in the nucleation, growth, and characterization techniques of cBN films. It describes various successful approaches in the interface engineering and growth techniques in increasing film thickness, improving crystallinity, and tuning the electrical properties of cBN films. New developments of cBN films in the applications of mechanical, electronic, and optoelectronic devices will also be addressed.

9:20am **G1-6 Solution-Based Diamond-Like Carbon Coatings**, ***V.Z. Poenitzsch*** *(vicky.poenitzsch@swri.org), C. Ellis-Terrel, R. Wei, K. Coulter*, Southwest Research Institute

Southwest Research Institute has identified and demonstrated, at a proof of concept level, an innovative method of fabricating diamond-like carbon (DLC) coatings that involves chemical synthesis of hydrocarbon polymers possessing diamond-like structure at the atomic level and subsequent use of pyrolysis to convert the polymers to diamond-like carbon (s-DLC). The low-temperature, atmospheric, and solution-based processing allows for coating substrates previously considered impractical or impossible due to their size, geometry, or incompatibility with vacuum processes. Further, the properties of the films may be tuned by adjusting the precursor chemistry to control the sp^2, sp^3 and H content. The chemical composition, microstructure, and properties of the s-DLC coatings were examined with and compared to those of traditional DLC using FTIR and Raman spectroscopy, electron energy loss spectroscopy (EELS), scanning electron microscopy (SEM), electrical impedance, and nanoindentation measurements. In this presentation, an overview of the synthesis, application, and performance of the s-DLC coatings will be given with a specific focus on areas for further development.

9:40am **G1-7 Microstructure and Corrosion Behavior of Magnetron Sputtering Ni-P-Based Alloy Thin Films**, ***F.-B. Wu*** *(fbwu@nuu.edu.tw), C.-C. Wu, Y.-C. Hsiao*, National United University, Taiwan

The Ni-P thin film is widely used for surface protective coating in versatile applications, especially for anti-corrosion layer. The alloying elements are frequently doped to form Ni-P-based alloy thin films with enhanced properties. In this work alloying species, including Al, W, and Ru, which are characterized as light weight, refractory, and noble metals, are incorporated through magnetron sputtering technique. The 350°C as-deposited Ni-P-based film exhibits an amorphous/nanocrystalline feature. With higher treatment temperatures, Ni-P compounds, such as $Ni_{12}P_5$, Ni_5P_2 and Ni_3P, are observed for ternary Ni-P-based films. The alloying elements show a strong effect on suppression of Ni-P phase transformation at 350°C. At elevated temperatures, W dissolves into Ni to form the Ni(W) phase for the Ni-P-W coating. Meanwhile, Ni_3Al compound precipitates in the Ni-P-Al film. The Ni-P-Ru film shows an inert electrochemical response under potentiodynamic scanning test as compared to other alloy films. The effect of deposition temperature on corrosion resistance is also analyzed. The corrosion resistance decreases significantly with deposition temperature. The amorphous/nanocrystalline microstructure feature is beneficial to the Ni-P-based alloy films. The influence of alloying elements and phase transformation on electrochemical response of the ternary Ni-P-based films is analyzed.

10:00am **G1-8 An Investigation into the Effect of Triode Plasma Oxidation (TPO) on the Properties of Ti-6Al-4V**, ***S. Banfield*** *(sarah.banfield@tecvac.com),* Tecvac Ltd and University of Sheffield, UK, *J.C. Avelar-Batista Wilson,* Tecvac Ltd, UK, *G. Cassar, A. Leyland, A. Matthews,* University of Sheffield, UK, *J. Housden*, Tecvac Ltd, UK

Improving the poor tribological properties of titanium alloys has been the subject of extensive research for many years. A number of oxidation processes have been developed for that purpose. In this study, surface hardening of Ti-6Al-4V is achieved by triode plasma oxidation (TPO) which differs from conventional diode plasma treatments through the use of a third electrode; a negatively biased tungsten filament to enhance the ionisation levels in the plasma. The resultant surface generally consists of a top oxide layer with an oxygen diffusion zone lying immediately underneath it. The effects of process parameters such as substrate temperature, current density and oxygen partial pressure are investigated. Surface hardness measurements at various indentation loads were carried out on all TPO-treated samples to assess the changes in hardness with depth across the diffusion layer. The hardness profiles obtained confirmed the gradual decrease in surface hardness with depth and provided a rough estimate of the thickness of the hardened layer produced. Ball-on-plate reciprocating sliding wear data and glancing angle XRD analysis of the oxidised samples are also presented. The results indicate that a harder and deeper case is achieved both at high substrate temperature and high oxygen partial pressure. Furthermore XRD data show that the substrate temperature significantly affects the structure of the oxide layer produced. All TPO-treated samples also exhibit better wear performance compared to the untreated material.

10:20am **G1-10 Interfacial Reaction of $Sn_{3.0}Ag_{0.5}Cu$ Solder with novel $Ni_{-x}Zn$ Under Bump Metallization**, ***H.-M. Lin***, *J.-G. Duh (jgd@mx.nthu.edu.tw)*, National Tsing Hua University, Taiwan

A novel Ni-xZn under bump metallization (UBM) design was provided by magnetron sputtering to improve the conventional Ni metallization. In flip chip technology many efforts have been focused on suppression of both intermetallic compounds (IMCs) formation and UBM consumption rates. In this study, the formation and growth of Sn3.0Ag0.5Cu (SAC305) solder joint with Ni-xZn UBM were evaluated with a field-emission scanning electron microscopy (FE-SEM). Further, more the IMCs interfacial reactions were analyzed by a field emission electron probe microanalyzer (FE-EPMA) to evaluate the composition re-distribution. After reflow and aging, Zn elements might slow down the IMC formation and growth in these solder joints with Ni-xZn UBM. These beneficial observations were attributed to the effect of Zn, which played a role of interdiffusion barrier between Ni and Sn. A possible mechanism for the growth, formation, and phase transformation in the related interfacial reaction was discussed and proposed.

10:40am **G1-11 A Novel Preparation of Sn,Sb-O_{2-x} Coatings by Pulsed Fiber Laser Annealing**, ***C.-M. Wang**,* National Cheng Kung University, Taiwan*, C.-C. Huang, H.-T. Lin,* Cheng Shiu University, Taiwan*, J.-L. Huang (jlh888@mail.ncku.edu.tw)*, National Cheng Kung University, Taiwan

A novel method was used for antimony doped into tin oxide to form Sn,Sb-O_{2-x}. The Sb/ SnO_2 multilayer films were prepared by ion beam sputtering and RF magnetron sputtering deposition technology separately. The as deposited films were treated by UV 355 nm pulsed laser for the assistance of Sb-ion driven into SnO_2 to form antimony-doped structure.

Sn,Sb-O_{2-x} films have 45% resistivity decrease and over 90% transparent compared with non-doped SnO_2 thin films. The majority carrier concentration showed over 20% improvement at the laser power peak 50 mJ, 30 Hz condition. As the laser power increasing, the majority carrier amounts dropped gradually. The Sb content was decreased as laser power over 50 mJ because of Sb evaporation after high temperature laser ablation. The as deposited films surface morphology was observed by atomic focus microscope (AFM). The results showed roughness of laser treated films were worse than untreated films and some crystallization formed on the surface.

11:00am **G1-12 An analysis of the Temperature-Induced Supersaturation Effects on Structure and Properties of Sono-Electrodeposited Copper Thin Films**, ***A. Mallik** (archananitrkl@gmail.com), B.C. Ray*, National Institute of Technology, India

The effects of ultrasound and temperature on the nucleation mechanism, structure and properties of electrodeposited copper thin films on aluminum were studied using cyclic voltammetry (CV), X-ray diffraction (XRD), scanning electron microscopy (SEM) and atomic force microscopy (AFM) techniques. It was found that deposition without ultrasound (silent) showed a mixed kinetics control while sonicated system was dominantly charge transfer control. Films were crystalline in structure. The deposits from the doubly activated bath have the distinct mushroom like morphologies, while in silent conditions there was a transition of morphology from dendritic structures to spherical grains with decrease in deposition temperature. Further, the addition of sonication environment has lead to substantial variations of thermal and mechanical properties of the copper thin films. There was a significant change in the variation of energy absorbed for films that deposited at different bath temperatures. The observed hardness values of the films were higher than the conventional polycrystalline copper. Further the soft films were found to have good wear properties. Thus, the beneficial sonication effect on deposits may be effortlessly and suitably tailored depending on the requirement, which holds a great promise for the future.

11:20am **G1-9 The Stratified - Equiaxed Microstructure Transition of 316L Coatings by Low Pressure Plasma Spraying**, ***D.-M. Yang**, B.-H. Tian, Y. Gao (tianbohan@yahoo.cn)*, The Thermal Spraying Center of Dalian Maritime University, China

The equiaxed microstructure of 316L stainless steel coatings has been successfully deposited by low pressure plasma spraying (LPPS), compared with the stratified microstructure prepared by other thermal spraying technologies previously. In this article, the coatings were prepared by changing of plasma currents from 500 to 700A and spraying distance from 250 to 450mm and preheating substrate from 300 to 900°C. The results indicated that the equiaxed coatings were determined by the power inputted to the plasma jets, the temperature of the preheating substrate, and spraying distance. The equiaxed coatings were not obtained under selected spraying distance and substrate temperature when the plasma current was below 500A . After increasing the power of plasma jet, some equiaxed grains were found between lamellar boundaries when the substract was preheated to 600°C around and fine equiaxed grains without lamellar boundaries were formed at about 900°C .

11:40am **G1-3 The Titanium Oxide Film for Vascular Stent Modification**, ***Y.X. Leng** (yxleng@263.net)*, Southwest Jiaotong University, China

Vascular stent has been an effective therapy for coronary artery disease. 316L stainless steel and 605L CoCrMo are the popular materials used to make stent due to their excellent mechanical property. But restenosis is a big challenge to the further application of vascular stent in biomedical field. Drug eluting stents (DES) have been shown to be effective in decreasing restenosis to a low level. However until now the complications of thrombosis for DES have still remained to some extent, even if anticoagulants have been taken by patients. It has been pointed out that the stent material, which will contact with blood when DES drug layer completely eluted, might be a main factor in influencing the propensity of thrombosis. To decrease thrombosis generation rate, surface modification techniques are extensively employed to improve the biocompatibility of stent materials. It is necessary to put an inorganic film with good blood compatibility for a long time between the stent and the drug. In this way, not only thrombosis but also releasing of toxic ions from stent will be reduced. In the work described in this paper, Ti–O film was deposited on coronary stents. The investigation of the behavior of mechanical compatibility, corrosion resistance and blood compatibility of the Ti–O film coated stent were performed. The results showed that the Drug eluting stents (DES) with Ti-O film pre-coated had lower restenosis and thrombosis generation, comparing with DES without Ti-O film.

Coatings for Microelectronics and Active Devices
Room: Tiki Pavilion - Session TS6

Coatings for Microelectronics and Active Devices
Moderator: S.J. Bull, Newcastle University, U. Helmersson, Linköping University

8:00am **TS6-1 Improvement of Resistance Switching Behavior by Localizing Filament with Si Injection WO_X Switching Layer**, ***Y.E. Syu** (syuyongen@gmail.com)*, National Sun Yat-Sen University, Taiwan

Metal-insulator-metal (MIM) structures with transition metal oxide (TMO) are typically used to implement resistance random access memory (RRAM) device. The specific structures in this paper are TiN/WO_x/Pt and TiN/$WSiO_x$/Pt. A constant voltage forming method is used to induce repeatable bipolar resistance switching behavior. Comparing with the TiN/WO_x/Pt structure, the TiN/$WSiO_x$/Pt device exhibits excellent characteristic with good endurance of more than 10^5 times, long retention time of 10^4 s in 125℃ and more stable in resistance switching state. Furthermore, the switching mechanism is investigated by current-voltage (IV) curve fitting and material analysis. From the experiment result, the conductive path of the TiN/WO_x/Pt RRAM device is disorder due to its filament formed everywhere in the switching layer. In addition, the switching behavior in the TiN/$WSiO_x$/Pt device is regard as point electric filed by localizing filament between the interface of top electrode and insulator. The TiN/$WSiO_x$/Pt device presents a highly stable and excellent memory feature for developing next generation nonvolatile memories.

8:20am **TS6-2 Mechanism and Characteristic Studies of Resistive Switching Effects on a Thin FeO_x-Transition Layer of the TiN/SiO_2/FeO_x/Fe Structure by Thermal Annealing Treatments**, ***Y.-F. Chang**, C.-Y. Chang (cyc@mail.nctu.edu.tw),* National Chiao Tung University, Taiwan*, T.-C. Chang*, National Sun Yat-Sen University, Taiwan

Thermal annealing effects and mechanism studies on the resistive switching characteristics of a thin FeO_x-transition layer were demonstrated by a TiN/SiO_2/FeO_x/Fe structure, including bipolar switching behaviors, statistics of set and reset electrical characteristics, and retention. Increase of the thermal budget on the structure shrinks both the operation voltage and variation as well as improves the device operation stability and power dissipation. Cross-section image, crystallinity and composition analyses of the transition layer were examined by tunneling electron microscope, X-ray diffraction and X-ray photon-emission spectra depth profiles, respectively. In addition, the FeO_x-contained structure switching mechanism was also studied by statistics of the electrical parameter results. Retention property at room temperature and 85ºC keeps both resistance states over 6×10^4 sec, providing the potential for nonvolatile memory applications.

8:40am **TS6-3 Integration of Nickel Silicides in VLSI Circuits: A Mateirals Science Perspective**, ***P. Desjardins** (Patrick.Desjardins@polymtl.ca)*, Ecole Polytechnique, Montreal, Canada **INVITED**

Silicides formed by the thermally-induced solid-state reaction of a transition metal with Si are widely used in CMOS technology to reduce sheet and contact resistances at poly-Si gates and at implanted contacts. As technology progress allows for the fabrication of continuously smaller devices, roughness and Si consumption become critical issues for contact materials. While $CoSi_2$ still dominates in industrial applications, NiSi, which results in both a smoother contact with less silicon consumption and a lower resistivity, is now used in high-performance circuits. We have utilized a combination of in situ synchrotron x-ray diffraction and ex situ reciprocal space mapping and transmission electron microscopy analyses to characterize the thermally-induced reaction of thin Ni films with Si substrates. Whereas early studies of that solid-state reaction reported the sequential appearance of phases with increasing Si content, the use of sophisticated probes reveals that several highly-textured phases form simultaneously and coexist in thin-film systems. I also demonstrate that texture inheritance between phases, where little atomic motion is required for the transformation to occur, provides a low activation energy pathway which permits the formation of metastable phases in ultrathin systems. The implications of the observed reaction pathways and film microstructure on the integration of NiSi in advanced VLSI circuits are discussed with emphasis placed on the effects of dopants, alloying elements, and substrate orientation on reaction pathways and phase formation temperatures. I conclude by discussing potential technological limitations of NiSi and approaches to circumvent them.

9:20am **TS6-5 Resistive SwitchingCharacteristics of Ytterbium Oxide Thin Film for Nonvolatile Memory Application**, ***H.-C. Tseng*** *(d982030010@student.nsysu.edu.tw)*, National Sun Yat-sen University, Taiwan

This paper studies the effect between a positive and a negative forming process on resistive switching characteristics of Pt/Yb_2O_3/TiN RRAM device. The polarity of the forming process can determine the transition mechanism, including bipolar and unipolar. The bipolar behaviors exist after positive forming process. Contrarily, the unipolar behaviors exist after negative forming process. Furthermore, the bipolar switching characteristics of Pt/ Yb_2O_3/TiN device can be affected by using reverse polarity forming treatment. Not only the set and reset voltage can be reduced, but also the on/off ratio can be improved by using the additional reverse polarity forming treatment.

9:40am **TS6-11 Study of Micro-Imprint by Electroless Nickel Plating Method**, ***H.-T. Hsu***, *M.-J. Ho, T.-J. Yang (yangtj@fcu.edu.tw)*, Feng Chia University, Taiwan

Imprint lithography has drawn a lot of attention as one of the promising technologies for the transfer of nano/micro-patterns due to its simplicity, low cost and high throughput. Complex-shaped structures such as micro-channels, micro-trenches and non-flat patterns over large areas are commonly required for semiconductor industry. Electroless nickel (EN) plating process is much simpler than e-beam, X-ray lithography, and UV photolithography. The aims of this study are to evaluate the feasibility for the replication of micro-patterns by EN plating method and to examine the effect of additives on the surface morphology by scanning electron microscopy (SEM) and microhardness by nanoindentation. The micro-pattern with line-width 400 nm and pitch 800 nm on silicon substrate (24 mm x 24 mm) can be coated uniformly by EN plating. A blind hole structure of 200 nm in diameter and 300 nm in depth with SiO_2 sidewall of 400nm in thickness on 100 mm x 100 mm silicon substrate could be filled with EN. After removal of SiO_2 and silicon by 30% KOH aqueous solution, the imprinted columnar array of EN is clearly shown by SEM. Additions of saccharin and SDS wetting agent to EN plating solution are closely related to the smoothness of imprinted surface, but only slightly increases the microhardness of the coating from 6.303 GPa to 6.437 GPa with 15mN loading. Post-treatment of stress relaxation after EN plating is necessary to minimize potential hydrogen embrittlement adverse effect. Excellent pore-filling capability and step coverage of EN plating have been shown during micro-imprint.

10:00am **TS6-8 Effect of the Thermal Stability and Electrical Behavior of Nickel Silicide by using Nickel Nitride**, ***C.-T. Wu*** *(n2896101@mail.ncku.edu.tw), W.-H. Lee, C.-Y. Wu, S-A. Yan*, National Cheng-Kung University, Taiwan

Metal silicides have been widely used in ultralarge scale integrated (ULSI) circuits to reduce the contact resistance of source/drain (S/D) in complementary metal-oxide-semiconductor (CMOS) devices. Currently, the most commonly used silicides are $TiSi_2$ and $CoSi_2$. The $TiSi_2$, the transformation from the high resistivity C49 phase to the low resistivity C54 phase is nucleation limited, causing linewidth dependence of the sheet resistance for gate lines narrower than submicrometer dimension. Therefore, $CoSi_2$ and NiSi have emerged as the most promising candidates to replace C54-$TiSi_2$ phase in Self-Aligned Silicide (Salicide) technology.

Nickel mono-silicide (NiSi) with low sheet resistance (Rs), line-width independence and relatively low silicon consumption has received much attention in recent years. The main disadvantage of NiSi is low thermal stability. The formation of NiSi takes place around 350^{o}C, and the phase transition of NiSi to the high resistivity $NiSi_2$ phase occurs at over 700^{o}C, which limits its application. Nickel silicide agglomeration easily occurs at a temperature above 600^{o}C, and the related phase transformation $NiSi_2$ degrades device performance and gives rise to some reliability issues.

In this study, the effects of nickel nitride (NiN_x) capping layers on the formation of nickel silicide have been investigated. Using the NiN_x replace the capping layer (TiNx) with the anticipation that the resulting materials would be suitable for next-generation CMOS processes. Nickel silicide films using NiN_x (N ratio flow of 0~30 sccm) are used in an RTA process. They exhibit advanced thermal stability at 300-800^{o}C/30s, and inhibit surface agglomeration better than the TiN_x and non-capping layer nickel silicide. The diffraction peaks of the NiN_x films deposited with N_2 flow ratios rang from 10~20 sccm has a Ni_4N peak, when N_2 flow ratios rang from 25~30 sccm has a Ni_3N peak. The Ni_4N phase is inhibit surface roughness and thermal stability properties better than Ni_3N phase. The results of the Ni_4N remove rate faster than Ni_3N and NiSi and the thermal stability and inhibit surface agglomeration behavior still Ni_4N has better than Ni_3N on the nickel silicide. Final, the Tafel corrosion rate curves of the NiN_x (Ni_4N and Ni_3N) and nickel thin films in the H_2SO_4:H_2O_2=4:1 were investigated.

10:20am **TS6-9 Inkjet-Printed High-k Nanocomposite Dielectric Film for OTFT Applications**, ***C.-T. Liu*** *(n28981036@mail.ncku.edu.tw), W.-H. Lee, T.-L. Shih, H.-J. Yan*, National Cheng-Kung University, Taiwan

The preparation of nanocomposite as the gate insulating film was achieved by blending cross-linked Poly(4-vinylphenol) of polymer and high-k TiO_2 nano-particles to enhance the permittivity of the dielectric and reduce operating voltage of devices. In order to well disperse the TiO2 particles and increase doping concentration higher than 1 wt%, we utilize pearl mill to crumble the agglomerations and dispersant to stabilize the nano-particles in the polymer matrix for inks. In this paper, the dielectric film with the admixture was made by inkjet printing to avoid the photography process. By studying the characteristics of insulating films at different parameters of ink-jet printing, including voltage, frequency and waveform, we successfully printed dielectric layout, accomplishing the purpose of directly-patternable and low roughness after curing at 190°C, when the solid content of TiO_2 about 3 wt% in the ink. Finally, we realized a low leakage current density in the nanocomposite dielectric and high current ratio in the pentacene-TFTs device with top contact structure. These devices exhibited p-channel TFT characteristics with a high field-effect mobility (a saturation mobility of ~0.49 cm2V-1s-1) and a low voltage operation (<6 V), indicating that these NC-dielectric materials can be used in low-cost and high-performance printable electronics.

10:40am **TS6-10 Resistive Switching Characteristics of Gallium Oxide for Nonvolatile Memory Application**, ***J.-J. Huang*** *(m952030007@student.nsysu.edu.tw)*, National Sun Yat-Sen University, Taiwan

In this study, we fabricated the resistance random access memory (RRAM) of Ti/GaO_x/Pt structure and the device present a bipolar resistance switching characteristics. The gallium oxide of control sample was sputtered in Ar atmosphere, and demonstrates a bistable resistance ratio of about 2 orders by I-V sweeping. Additionally, the gallium oxide layer of proposed sample was sputtered in a mixed ambient of Ar and oxygen to increase the oxygen ion quantity, and the resistance ratio can be enhanced to 3 orders. Endurance and retention results indicate that the proposed memory device has excellent device reliability, and the multi-level phenomenon can be applied for multi-bit storage. The X-ray photoelectron spectroscopy (XPS) was employed to verify the influence of oxygen content on the resistance switching characteristic.

11:00am **TS6-6 Study of Sputter Deposited SiO_2/Co/Pt/SiO_2 Multilayers for Magnetic Storage**, ***R. Walia***, Indian Institute of Technology, Roorkee, India, *A.K. Chawla, R. Chandra (ramesfic@iitr.ernet.in), R. Jayaganthan*, Indian Institute of Technology Roorkee, India

Conventional Co alloy based recording media are unable to fulfill the requirement of high density magnetic recording up to 1 Tbit/ in^2 due to phenomenon like superparamagnetism. $L1_0$ CoPt is a potential candidate due to its large K_u value of 10^7 ergs/cm^3. The high K_u value of CoPt allows smaller and thermally stable grains (of size 3nm) against superparamagnetism[1]. Such small grain size is able to increase the areal density beyond 1 Tbit/ in^2. However, as deposited CoPt film shows fcc phase. To achieve the desired phase, high deposition temperature or postdeposition annealing at temperature higher than 600°C is required [2-4]. High deposition temperature increases the grain size which effectively reduces the signal-to-noise ratio. $L1_0$ CoPt–SiO_2 nanocomposite provides control the CoPt grain size and intergranular magnetic interaction [5]. However, the effects of SiO_2 addition on chemical ordering and magnetic properties of Co/Pt multilayers will be interesting to probe.

In this study we have prepared different set of thin films containing different number of multilayers of Co and Pt with SiO_2 as a buffer and capping layer on Si (100) substrates. Deposition were made in a custom built DC/RF sputtering chamber by varying number of multilayers of SiO_2 /Co/Pt/SiO_2. In each set of thin films thichkness of various layers were kept fixed while the number of multilayers were varied. Samples were annealded up to (400^{o}C -700^{o}C) in Ar atmosphere. Structural studies of these films were done by X-ray diffraction and Field Emission Scanning Electron Microscopy, Atomic Force Microscopy and Transmission Electron Microscopy while magnetic measurements were done by SQUID

(Superconducting Quantum Interference Device) magnetometer. Structural properties of as deposited thin films show the formation of fcc phase of CoPt nanoparticles while annealing at higher temperatue shows the change in the crystal structure. Magnetic Measurements show the high value of coercivity for both longitudinal as well as in perpendicular direction.

1. R. Sbiaa and S. N. Piramanayagam, Recent Patents on Nanotechnology **1**, 29 (2007).

2. Y. Xu, Z. G. Sun, Y. Qiang, and D. J. Sellmyer, J. Magn. Magn. Mater. **266**, 164 (2003).

3 O. Kitakami, Y. Shimada, K. Oikawa, H. Daimon, and K. Fukamichi, Appl. Phys. Lett. **78**, 1104 (2000).

4. C. Chen, O. Kitakami, S. Okamoto, and Y. Shimada, Appl. Phys. Lett. **76**, 3218 (2000).

5. C. Chen, O. Kitakami, S. Okamoto, and Y. Shimada, IEEE Trans. Magn. **35**, 3466 (1999).

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

Thermal and Environmental Barrier Coatings
Moderator: R. Wellman, Cranfield University, B.T. Hazel, Pratt & Whitney, R. Trice, Purdue University

1:30pm **A2-1-1 Effect of (CMAS-Assisted) Sintering under Service Conditions on the Thermo-Mechanical Stability of Plasma-Sprayed TBCs**, ***T.W. Clyne*** *(twc10@cam.ac.uk), M. Shinozaki*, Cambridge University, UK **INVITED**

Sintering-driven changes in the microstructure and properties of (zirconia-based) TBCs in gas turbines, occurring during service, can impair their thermo-mechanical stability. In particular, sintering can cause substantial increases in stiffness and reductions in strain tolerance. These changes can be accelerated by the presence of impurities that segregate to the grain boundaries, where they enhance the solid state diffusivity or, at sufficiently high concentrations, produce a vitreous (liquid) phase that can dramatically accelerate sintering. The impurities that are most likely to have such effects are sometimes termed CMAS (calcia-magnesia-alumina-silica), particularly when they have been deposited on the coating in the form of particulate ingested into the engine.

Attention will be focussed on plasma sprayed coatings, although most of the points made apply equally to PVD coatings. A model of the (solid state) sintering process [1] will be briefly outlined, based on the variational principle. Comparisons will be presented between theory and experiment, for shrinkage (dilatometry), surface area (BET) and thermal conductivity. The roles of surface (non-densifying) and grain boundary (densifying) diffusion will be highlighted.

Work will then be described in which specimens have been subjected to extended periods at (isothermal) high temperature (1200-1500˚C) and periodically quenched to room temperature using gas jets, with automatic monitoring of spallation events via a webcam. These specimens comprised partially stabilised zirconia (PSZ) coatings plasma sprayed onto relatively thick alumina substrates, with and without the subsequent surface addition of particulate designed to represent CMAS incorporation. Prior roughening of the alumina surface, via laser processing, was employed to ensure adequate interfacial toughness. The thermal misfit strain induced during cooling of such specimens has a magnitude (~15-20 millistrain) similar to that for PSZ on a superalloy substrate, although it is of opposite sign. Since little or no chemical reaction is expected between substrate and coating at these temperatures for a zirconia-alumina combination, any observed spallation is likely to have been promoted by changes occurring within the coating, such as sintering-induced stiffness enhancement. Experimental data will be presented concerning such observed spallation events, and conclusions drawn about the significance of sintering effects for TBC stability, with and without CMAS incorporation.

[1] A Cipitria, IO Golosnoy & TW Clyne, *A Sintering Model for Plasma Sprayed Zirconia TBCs*, Acta Mater., vol.**57** (2009) 980-1003.

2:10pm **A2-1-3 Degradation of YSZ Thermal Barrier Coatings by CMAS Infiltration**, ***V. Kolarik*** *(vladislav.kolarik@ict.fraunhofer.de), M.M. Juez-Lorenzo,* Fraunhofer ICT, Germany, *W. Stamm,* Siemens Power Generation, Germany*, H. Fietzek*, Fraunhofer ICT, Germany

Yttria partially stabilised zirconia (YSZ) is widely used for thermal barrier coatings (TBC) in power generation, deposited both by APS as well as by EB-PVD. Degradation by molten deposits, mostly calcium-magnesium-alumino-silicates, which enter the turbine from the environment and are known as CMAS, has been identified as a serious cause of failure. It infiltrates the pores and cracks, reacts with the YSZ and leads to its destabilisation. To understand better after which time does CMAS penetrate into which depth and react to which extent and to investigate potential protection against CMAS attack is the purpose of the current research work.

A model CMAS, composed in mol% from 38CaO, 6MgO, $5Al_2O_3$, $50SiO_2$ and $1Fe_2O_3$ ultra-milled, molten two times for 4 h at 1400°C and milled again, was deposited on the surface of an APS thermal barrier coating from commercial YSZ. The samples were exposed to 1100°C and 1150°C for 50h, 100h and 1000h in air and analysed by X-ray diffraction with micro-focus (µ-XRD) and by field emission SEM. Scanning the sample surface by µ-XRD from the unaffected area to the attacked area in steps of 200 µm reveals already after 50h considerable portions of the monoclinic phase in the CMAS attacked area. In micrographs however, this structural degradation is not visible while the infiltration by CMAS is observed. Performing a step-wise line scan by µ-XRD across the TBC in cross-section, the depth of the destabilisation was determined and compared to a CMAS-damaged TBC fragment from service, where the destabilisation reaches into a depth of up to 120 µm. Experiments with samples coated with alumina showed a reduction of the destabilisation by CMAS attack.

2:30pm **A2-1-4 The Effect of Volcanic Ash on Sintering of Plasma Sprayed Thermal Barrier Coatings**, ***M. Shinozaki*** *(ms660@cam.ac.uk), T.W. Clyne*, Cambridge University, UK

Vermiculite powder (~100 µm diameter) was selected as having a composition (42%O-36%Si-8%Mg-5%K-3%Al-3% Na-2.5%Fe-0.5%Ti) representative of volcanic ash. Its melting temperature is about 1330˚C. Selected loadings of this powder were introduced onto the surface of plasma sprayed YSZ coatings (detached from their substrates), either on one surface or on both surfaces. The mass of these additions, relative to that of the YSZ, was in the range 0.1 - 5.0%. A short heat treatment was initially given, designed to promote adhesion of the vermiculite particles, after which the exact loading was established via high precision weighing. The following measurements were then made, on samples that had been exposed for periods (up to 50 hours) at elevated temperature (up to 1500˚C):

• Composition profile measurements by EDX on transverse sections, to monitor the penetration (down grain boundaries) of species from the vermiculite

• XRD spectra from free surfaces, after serial sectioning, to monitor the vitreous phase (ie grain boundary phase) content as a function of depth, and also the possible formation of new crystalline phases

• Measurement of the average (in-plane) Young's modulus, by 4- point bend testing of samples "injected" with vermiculite on both sides, to monitor the progression of sintering

• Measurement of the curvature of samples "injected" with vermiculite on one side, to monitor differential sintering (provided it is occurring via mechanisms that generate a volume contraction)

These measurements were used to provide information about the effect of typical volcanic ash particulate on the acceleration of sintering. It is shown that there is potentially a highly significant effect, with associated impairment of thermal protection and thermo- mechanical stability. Finally, preliminary experiments have been carried out to measure the deposition efficiency of the vermiculite powder on (uncoated) blades within a small jet engine, under typical operating conditions. These studies included the effect of blade surface roughness, particle size and engine speed. While these efficiencies are often quite low, it is shown that, for relatively low ash cloud particulate burdens, the deposition rates could in some cases be in a range such that substantially accelerated sintering would be promoted.

2:50pm **A2-1-5 Mechanical Charactersation of Thermal Barrier Coatings After Thermal Treatments**, ***P. Xiao*** *(ping.xiao@manchester.ac.uk), X. Zhao, A. Shinmi, J. Liu, Y. Zhao, I. Shapiro*, University of Manchester, UK **INVITED**

Micro and Nano- indentation, a strain-to fail method, and a modified 4-point bending technique has been employed to study mechanical behaviour and to evaluate the interface toughness of thermal barrier coatings (TBCs) after thermal treatments. Meanwhile microstructure characterisation and impedance measurements have been carried out to examine sintering and phase transformation in TBCs. The bending and strain in TBCs leads to delamination in TBCs. The interfacial toughness increases first to a maximum after a initial thermal treatment, and then gradually decreases after further treatments. Meanwhile thermal treatments induced the phase transformation and densification of TBCs. The focus of this talk is to establish methods for mechanical and microstructure characterisation of TBCs.

3:30pm **A2-1-7 Interfacial Strength Measurement of Oxidized EB-PVD Thermal Barrier Coatings by the Laser Shock Adhesion Test (LASAT)**, ***G. Fabre*** *(gregory.fabre@mines-paristech.fr), V. Guipont, M. Jeandin,* Centre des Materiaux - Mines ParisTech, France*, A. Pasquet, J.Y. Guedou,* SNECMA Safran Group, France*, M. Boustie,* Institut PPRIME ENSMA, France*, F.L. Berthe*, PIMM ENSAM, France

Turbines for aircraft propulsion and power generation need Thermal Barrier Coatings (TBCs) which allow higher gas temperature and improve lifetime. The zirconia layer reduces surface temperature and oxidation damage is limited by the thermally grown oxide. However, during thermal cycling the coating can delaminate by crack nucleation, propagation, and coalescence phenomena.

In this study, the LAser Shock Adhesion Test (LASAT, Fig.1) was applied to EB-PVD TBCs with different aging periods of one-hour cycles at

1100°C. A high energy pulsed laser is focused on the superalloy substrate surface opposite to the zirconia coat. The compressive shock wave propagates through the TBC layers and is reflected in a tensile shock wave at the zirconia free surface. Increasing the laser energy deposited on the superalloy surface, the zirconia-(Ni,Pt)Al bond coat interface remains intact for low levels of laser energy and fails for high levels with possible coating spallation for highest levels. Two laser spallation methods have been used to discriminate specimens depending on their thermal cycling. For the conventional method, by determining the minimum laser energy ("LASAT threshold") necessary to crack interface, results proved that oxidation reduces the LASAT threshold and the corresponding measured interfacial strength. Features of the interfacial cracks were observed by SEM cross-sectional and top-surface views of laser shocked regions. For both specimens, the failure path (Fig.2) was located along the zirconia-alumina interface or within zirconia in instability sites as "pinched-off" regions. This failure morphology activated by laser shock was very similar to damage induced by crack nucleation and propagation under thermal cycling for this TBC system.

Due to large cracks at the alumina-zirconia interface and light transmitting properties of ceramic layers, optical response of TBCs changes and the interfacial damage generated by LASAT is directly detected by visual inspection (Fig.3). The change in TBC whiteness induced by failure allows the direct detection and measurement of the delamination crack front without cross-sectional observations. By plotting interfacial failure diameter versus deposited laser energy (graph 1), the decrease in crack resistance at the interface is demonstrated by the continuous gap of damage diameter between as-deposited and cycled specimens. A new LASAT method is established.

Further numerical FEM calculations of shock wave mechanics have been developed for TBCs to determine the interface stress level and simulate damaging phenomena. This work showed that LASAT is a powerful testing tool to investigate fracture resistance of TBCs.

3:50pm **A2-1-8 Observations of Ferroelastic Switching by Raman Spectroscopy**, ***A. Bolon***, *M. Gentleman (mgentleman@tamu.edu)*, Texas A&M University

Characterization and observations of ferroelastic switching have become increasingly important in the study of thermal barrier materials because of the important role they play in the high temperature toughness of tetragonal zirconia materials. In this paper we discuss the observations of ferroelastic domains in ceria-stabilized zirconia by confocal Raman spectroscopic mapping. Evidence of ferroelastic switching at the crack tip has been observed using this technique as well as measurements of the crystal orientation of individual grains. We will also discuss the use of this technique to complete measurements of coercive stress using a high temperature diamond anvil cell.

4:10pm **A2-1-9 Factors to Consider in Cyclic Oxidation Testing of Thermal Barrier Coatings with MCrAlY-Bondcoats**, ***D. Naumenko* *(d.naumenko@fz-juelich.de)*, *P. Song, L. Singheiser, W.J. Quadakkers***, Forschungszentrum Julich, Germany

Air plasma sprayed thermal barrier coatings (TBCs) with MCrAlY (M = Ni, Co) bondcoats on Ni-based superalloys were tested in laboratory air at 1000 and 1100°C under various temperature cyclic conditions. Metallographic cross-sections of the exposed specimens were studied by optical metallography and scanning electron microscopy (SEM). The analytical studies indicated that in all studied testing conditions TBC-failure was initiated in the convex regions at the alumina scale / bondcoat interface. The crack propagation through the TBC was found to be the major lifetime limiting step.

The lifetime of a given TBC-system was strongly affected by the testing parameters. The parameters of importance are hot and cold dwell times, exact cold dwell temperature and cooling rate, which all have an effect on the crack propagation rate in the TBC. The lifetimes are longer with longer hot dwells and slower cooling rates, whereas the extension can be as large as a factor of two to three, as compared to shorter dwells and higher cooling rates. Furthermore, specimen geometry and preparation procedure for the test were also found to have an effect on the TBC lifetime.

The presented results indicate that careful selection and exact definition of the specimen preparation and testing procedures are absolutely necessary for a reliable lifetime determination in one testing laboratory, comparison of data between different laboratories and extrapolation of laboratory results to lower coating application temperatures.

4:30pm **A2-1-11 Characterization of the Alumina Scale Formed on Coated and Uncoated Doped**, ***K.A. Unocic*** *(unocicka@ornl.gov)*, *B.A. Pint*, Oak Ridge National Laboratory

Doping of superalloys with oxygen active elements such as Y and La to improve oxidation performance has been widely reported. However, the mechanism by which the dopants improve TBC lifetime has not been clearly demonstrated. The alumina scale formed at 1100°C on two variants of Ni-base superalloy CMSX4 was analyzed with and without a MCrAlYHfSi bond coating using high-resolution scanning transmission electron microscopy. Analysis of the alumina grain boundaries in the uncoated specimens will determine if the Y and La levels in the substrate are sufficient to detect as segregants. The same analysis on coated versions of these substrates will determine if Ti and La from the superalloy can diffuse through the coating into the scale.

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

4:50pm **A2-1-12 Laser Cycling Exposure of Thermal Barrier Coatings on Copper Substrates**, ***J. Schloesser*** *(j.schloesser@tu-bs.de)*, *M. Bäker, J. Rösler*, Technische Universität Braunschweig, Germany

In rocket engine combustion chambers the cooling channels experience extremely high temperatures and environmental attack. Thermal and environmental protection can be provided by Thermal Barrier Coatings. Because of the good heat conduction the inner combustion liner is made of copper. The performance of a standard coating system for nickel based substrates is investigated on copper substrates.

To account for extremly high heating rates in reality, a laser-cycling set-up was developed to qualify different coating systems. This set-up consists of a high-power diode laser (3kW) and realizes temperatures up to 1500°C. Furthermore, it is possible to realize high thermal gradients inside the specimen with an additional cooling.

Failure mechanisms of the Thermal Barrier Coating systems are investigated with this set-up. In preliminary experiments the interface between bond coat and substrate fails which is also theoretically confirmed by FEM-simulation.

5:10pm **A2-1-13 Processing, Repairing and Cyclic Oxidation Behaviour of Sol-Gel Thermal Barrier Coatings**, *L. Pin,* Institut Clément Ader Mines Albi, France, *F. Ansart, J.-P. Bonino,* Cirimat Cnrs-Inpt-Ups Ensiacet, France, *Y. Le Maoult,* ***P. Lours*** *(lours@mines-albi.fr)*, Institut Clément Ader Mines Albi, France

The new promising and versatile sol-gel process has been proved to be efficient for depositing yttria-satbilised thermal barrier coatings (TBC) on top of multi-materials systems composed of superalloy substrates, NiPtAl bond coats and Al_2O_3

thermally grown oxides. Processing such TBC by the so-called dip-coating route results in either thin or thick, fairly adherent coatings showing non-oriented microstructures with randomly structured pore network. This specific microstructure confers to the barrier an optimum compromise between a satisfactory low thermal conductivity to properly insulate the system and a good lateral compliance to resist without fracture the thermo-mechanical stresses generated in service. After soft chemical processing has been completed, sintering of the TBC is ensured by a controlled heat treatment that generates the formation of a fairly regular surface crack network as a result of the bi-axial loading due to the ceramic shrinkage. Upon cyclic oxidation, the behaviour of the TBC strongly depends on the characteristics of the initial crack network that can further enhance under the detrimental effects of the thermomechanical stress generated by the cumulative cycles. Ultimately, the development of cracks that can perfectly connect to each other can provoke the detachment of individual yttria particles resulting in the onset for spallation and catastrophic failure of the TBC.

Focus is first placed on the influence of the heat treatment parameters such as the heating and cooling rates and the holding time at temperature, on the geometrical characteristics of the crack network that control its own behaviour under loading. Then, optimised TBCs are cyclically oxidised in a specially designed rig able to establish thermal gradient across the specimen thicknesses and to monitor *in situ* the surface evolution during the damaging cooling sequences of the cycles. The evolution of the degradation versus the number of 1 hour-cycles at 1100°C through the development of cracks and spalls is investigated using complementary approaches including SEM plus image analysis, laser interferometry and X-ray tomography. Finally the possibility to proceed to the colmatation of either the initial or the cyclic oxidation induced crack network is investigated as a mean to properly prepare TBC prior to thermal loading or to repair TBC after degradation.

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

Hard and Multifunctional Nano-Structured Coatings
Moderator: C.P. Mulligan, Benet Laboratories, US Army ARDEC, R. Sanjines, EPFL, P. Zeman, University of West Bohemia

1:30pm **B5-2-1 Wear-Resistant PTFE Based Nanocomposites**, ***T.A. Blanchet*** *(blanct@rpi.edu), S.S. Kandanur*, Rensselaer Polytechnic Institute **INVITED**

Polytetrafluoroethylene is known for low friction, however high wear rates ~10^{-3} mm^3/Nm have stymied PTFE as a bearing material. Conventionally, hard micron-scale fillers have been added to PTFE to yield composites typically two orders of magnitude more wear-resistant. Defying mechanisms hypothesized from microcomposite observations, some PTFE nanocomposites now display not only comparable but, particularly in the case of alpha phase alumina nanofiller, lower wear rates to ~10^{-7} mm^3/Nm. The goal of this research is thus to better understand PTFE nanocomposite wear resistance mechanism through studying effects of various parameters (filler size, weight fraction, dispersion technique, countersurface roughness and chemistry) on wear of alumina-PTFE composites.

With 5 wt % alpha phase alumina nanoparticles (40 or 80nm) against polished steel, wear rates ~10^{-7} mm^3/Nm were measured, four orders of magnitude lower than unfilled PTFE and two orders of magnitude lower than with microparticles (0.5 or 20um). For alumina-PTFE microcomposites wear rate gradually increased towards that of unfilled PTFE as filler content was reduced, whereas alumina-PTFE nanocomposite maintained ~10^{-7} mm^3/Nm wear rate to as low as 0.32 wt % before reverting towards the rapid wear rate of unfilled PTFE. Lightly-filled alumina-PTFE nanocomposites depend upon low countersurface roughness for such low wear rate, and at a critical value of increasing roughness the wear rate transitioned to ~10^{-5} mm^3/Nm. Nanocomposites of higher filler content maintained wear resistance to higher roughness before such transition. At extremely high roughness Ra = 6-8um, nanocomposites at all filler contents increased in wear rate to ~10^{-4} mm^3/Nm.

Among other observations, alumina-PTFE nanocomposite wear resistance was not changed by instead sliding against CoCr or alumina countersurfaces. Wear resistance of alpha alumina-PTFE nanocomposite was also greater than that provided by several other nanofillers investigated, including alumina of other phases, by at least two orders of magnitude. Finally, in the presence of water alumina-PTFE nanocomposite was observed to lose this wear resistance, with wear rates approaching that of unfilled PTFE.

Countersurfaces of low wearing nanocomposites revealed thin uniform transfer films. It is hypothesized that alpha phase alumina's influence on matrix PTFE is heightened by the higher surface-to-volume ratio, augmenting its intrinsic wear characteristic while forming thinner transfer films via increase ability to fibrillate. The low ~10^{-7} mm^3/Nm wear rate is considered a consequence of slowed removal rates of better-adhered thinner transfer films.

2:10pm **B5-2-3 Comparison of Different Bionic Structures Coated with CrAlN**, *W. Tillmann (wolfgang.tillmann@udo.edu),* ***J. Herper***, Technische Universität Dortmund, Germany

The reduction of friction and wear is an important goal for the extension of the tool life in many industrial applications. Especially the forming and cutting industry is very interested in new techniques in order to improve the tribological behavior of the tool surfaces.

Biomimetics is a very promising approach where biological surfaces or phenomena are used to optimize technical components. The "Lotus Effect" is the most popular example, whereby the surface is made water- and dirt-repellent. Taking a closer look at nature, it can be noticed that many different natural surfaces have adapted perfectly to their environment in order to meet the respective requirements. Especially because of its excellent frictional behavior, the skin of many insects has the potential to be transferred onto technical surfaces. In this paper the surface structures of different beetles were investigated. Thereby, the main objective is the combination of nature-adapted surface patterns with wear-resistant near-netshape PVD-coatings.

A substrate composed of high speed steel material 1.3343 was structured by means of milling. The shells of dung and scarabaeus beetles served as patterns for the structurization of the surfaces. Afterwards a CrAlN multilayer coating system was deposited with the aid of magnetron sputtering.

To compare the mechanical and tribological properties, the structured and coated surfaces were analyzed by a nanoindenter, a ball-on-disc-tester as well as a scanning electron microscope.

2:30pm **B5-2-4 Surface Modification of Nanostructured NiTi Shape Memory Alloy Thin Films Using Various Passivation Layers by dc Magnetron Sputtering**, *N. Choudhary,* ***D. Kaur*** *(dkaurfph@iitr.ernet.in)*, Indian Institute of Technology Roorkee, India

NiTi based shape memory alloy (SMA) thin films have been recognized as promising and high performance materials in the field of biomedical and microelectromechanical systems (MEMS) applications due to their unique superelasticity and shape memory effect. However, the materials are vulnerable to surface corrosion, unsatisfactory mechanical and tribiological performances and biological reliability. The present study explored the insitu deposition of hard and adherent nanocrystalline protective coatings on NiTi thin films prepared by dc magnetron sputtering to improve the surface, mechanical and corrosion properties of NiTi thin films without sacrificing the phase transformation effect. Further the interfaces between a Silicon substrate and a NiTi thin film is also an important place where reaction between both these materials occurs during high temperature deposition. By controlling the chemical reaction, the interface can provide strong bonding and the reaction does not proceed excessively. In the present study a buffer layer of hard TiN was provided to control the diffusion at the interface. Following heterostructures were prepared; TiN/NiTi/TiN/Si, ZrN/NiTi/TiN/Si, CrN/NiTi/TiN/Si and TiAlN/NiTi/TiN/Si by dc magnetron sputtering technique. The structural, electrical, and mechanical studies of these heterostructures were performed and the results were compared. Nanoindentation studies were performed at room temperature to determine the hardness and reduced modulus. Surface modified NiTi thin films were found to exhibit high hardness, high elastic modulus and thereby better wear resistance as compared to pure NiTi films.

2:50pm **B5-2-6 Mechanical Properties, Tribological and Corrosion Resistance Evaluation of Cathodic Arc Deposited ZrN/CrN Multilayer Coatings**, *S.-F. Chen,* National Taiwan University of Science and Technology, Taiwan, ***J.-W. Lee*** *(jefflee@mail.mcut.edu.tw),* Mingchi University of Technology, Taiwan, *S.-H. Huang,* National Chiao Tung University, Taiwan, *C.-J. Wang,* National Taiwan University of Science and Technology, Taiwan, *T.-E. Hsieh,* National Chiao Tung University, Taiwan, *Y.-C. Chan, H.-W. Chen, J.-G. Duh,* National Tsing Hua University, Taiwan, *J.-W. Chen*, Gigastorage Corporation

Five nanostructured CrN/ZrN multilayer coatings were deposited periodically by the cathode arc deposition system. The bilayer periods of CrN/ZrN multilayer coating were controlled ranging from 8 to 30 nm. On the other hand, the thickness ratios of CrN to ZrN layer were changed for several multilayer coatings as comparison. The crystalline structure of multilayer coatings was determined 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. A nanoindenter, scratch tester and pin-on-disk wear tests were used to evaluate the hardness, adhesion and tribological properties of thin films, respectively. Electrochemical tests in 3.5 wt.% NaCl aqueous solution were performed to evaluate the corrosion resistance of multilayered coatings. It was found that the hardness, tribological and corrosion resistance were strongly influenced by the bilayer period and thickness ratios of CrN to ZrN layer of the CrN/ZrN multilayer coatings.

3:10pm **B5-2-7 High Temperature Crystallisation of Cr_2AlC MAX-Phase Coatings Sputter-Deposited at Room Temperature**, ***J.S. Colligon*** *(J.Colligon@mmu.ac.uk), O. Crisan, P. Dobrosz, V. Vishnyakov*, Manchester Metropolitan University, UK

Chromium Aluminium Carbide, which belongs to so named MAX-phases, has been deposited by ion sputtering from combined elemental targets onto Silicon and Stainless Steel at room and elevated temperature of the substrate. The material was annealed at 700°C in air for 20 min. Material composition was determined by Energy dispersive and Wave dispersive X-Ray (EDX and WDX) Analysis. The crystallinity of the films was accessed by X-Ray Diffraction (XRD) and Raman spectroscopy. As- deposited and annealed films are homogeneous and dense over large areas. Negligible, below 1 at %, traces of Oxygen are detected by WDX in as-deposited films which are predominantly amorphous. Raman spectra of as-deposited films show characteristic but not well structured MAX-phase bands in the region of 100-400 cm^{-1} and broad amorphous Carbon D-band. After annealing Cr_2AlC single-phase is well-formed, with small traces of oxides or other phases (occurring, in the 5% error range), as estimated from the Rietveld-type refinement of the XRD patterns of the samples. It is evident that the oxides are mostly confined to the surface layers. The MAX-phase region in the Raman spectra becomes well structured and shows good correspondence to crystallinity. Surprisingly, Carbon also develops a G-band signature and this probably indicates presence of some carbon nano-clustering in the system. It is possible that the nanoclustering is only happening in the oxidised top layers. It is thought that this carbon can be partially responsible for the low friction coefficient of the Cr_2AlC phase. Ion assistance during film deposition shows significant preferential sputtering of Carbon, which can be explained on the basis of weak incorporation of carbon into the growing amorphous film and indicates that magnetron sputtering from stoichiometric targets in the presence of even small ion assistance from the plasma will lead to carbon depletion in the deposited film.

The results for coatings formed using ion beams are designed as a first step towards optimisation of the synthesis procedures that will be required for production of large area samples in view of the potential industrial applications of MAX phase materials.

3:30pm **B5-2-8 Recent Advances in Transition Metal Nitride–Based Nanostructured Hard and Superhard Coatings**, ***H.C. Barshilia*** *(harish@nal.res.in), K.S. Rajam*, NAL, Bangalore, India **INVITED**

Current research problems in surface coating technology include development of various thin coatings with exotic properties as part of an effort to modify the surfaces of a variety of engineering materials at lower cost. The role of coatings as a surface modification technique has grown significantly in recent years for applications in cutting tool, automobile, aerospace, biomedical, and other industrial sectors, since they can impart specific properties such as high hardness, high wear resistance, etc. to a surface. Binary and ternary transition metal nitride/carbide coatings with hardness in the range of 20-35 GPa have been widely used as protective hard coatings to increase the lifetime of various engineering components. However, for most of the technological applications, it is desirable to develop a coating with a combination of properties such as high hardness, high fracture toughness, high oxidation and corrosion resistance, etc. In this direction, in recent years, great advances have been made in the field of nanostructured coatings with improved properties using nano-scale engineering. In particular, transition metal nitride-based nanolayered multilayer coatings and nanocomposite coatings have emerged as novel superhard coatings (hardness > 40 GPa), which can operate across multiple extreme environments. Both nanolayered multilayer coatings and nanocomposite coatings provide enormous flexibility in choice of materials and, therefore, provide an opportunity to design novel coating properties. In this paper, we describe the state-of-the-art in the deposition and characterization of transition metal nitride-based nanolayered multilayer coatings and nanocomposite coatings. Various physical vapor deposition techniques used for the preparation of the nanostructured superhard coatings are described, in brief. It is shown that reactive magnetron sputtering is a promising technique for the deposition of these coatings on small engineering components. However, development of these coatings on large scale and deposition at production scale at affordable cost still needs considerable efforts. We discuss in detail the growth process, microstructure, mechanical and tribological properties, oxidation resistance and thermal stability, and corrosion resistance of sputter deposited transition metal nitride nanostructured coatings. We also present the potential applications of the transition metal nitride nanostructured superhard coatings.

4:10pm **B5-2-12 Comparison of Superhard and Superelastic Ti-Based Nanocomposite Erosion Resistant Coatings on Ti-6Al-4V Substrates Prepared by PECVD**, *S. Hassani,* ***E. Bousser****, S. Guruvenket, D. Li, J. Klemberg-Sapieha (jsapieha@polymtl.ca), L. Martinu*, Ecole Polytechnique de Montreal, Canada

Enhanced tribological erosion resistant coatings require high toughness. This can be obtained by an appropriate combination of hardness and elasticity that allows one to optimize energy dissipation during particle impact.

In the present work we investigated two types of coating systems deposited on Ti-6Al-4V substrates and prepared by Plasma Enhanced Chemical Vapor Deposition (PECVD), namely (A) superhard Ti-Si-C-N multilayer coatings consisting of TiN, (nanocomposite) nc-TiN/a-SiN_x and nc-TiCN/a-SiCN, and (B) hard superelastic Ti-Si-C multilayer systems consisting of a sputter deposited chromium adhesive layer followed by the deposition of a-SiC:H and nc-TiC/a-SiC:H/a-C:H films.

The Ti-Si-C-N multilayer architecture (A) provided an effective (composite) hardness of 5000HV 0.05, and very high resistance to plastic deformation and elastic resilience, expressed by H^3/E_r^2 and H^2/E_r ratios, respectively.

The Ti-Si-C multilayer coatings (B) exhibited an unusual but highly desirable combination of hardness, low friction, and high elastic strain to failure with a ratio $H/E_r > 0.2$, thus exceeding the superelastic threshold.

Both coating systems resulted in a significant improvement of erosion resistance compared to the bare Ti-6Al-4V substrate. Under conditions simulating compressor blades in aircraft engine, the erosion resistance was improved by a factor of 50.

4:30pm **B5-2-10 Effects of Nanostructure Formation on the Fundamental Physical Properties of Epitaxial $Hf_{1-x}Al_xN(001)$ Alloys**, ***B.M. Howe*** *(brandonhowe@gmail.com),* University of Illinois at Urbana-Champaign*, T.W.H. Oates,* ISAS, Germany*, S.A. Puttnam,* Air Force Research Laboratory*, J. Wen,* University of Illinois at Urbana- Champaign*, M.R. Sardela, Jr.,* Frederick-Seitz Materials Research Laboratory*, A.A. Voevodin,* Air Force Research Laboratory*, H. Arwin,* Linköping University, Sweden*, J.E. Greene,* University of Illinois at Urbana-Champaign*, L. Hultman,* Linköping University, Sweden*, I. Petrov*, University of Illinois at Urbana-Champaign

Transition metal nitrides (TMN) are well known to have a remarkable range of unique physical properties and thus find their place in a variety of applications. By employing highly kinetically-limited growth techniques including low growth temperatures and high-flux, low-energy ion bombardment during film growth, metastable TMN alloys can be synthesized and have shown to exhibit novel and exotic physical properties. The most famous example is $Ti_{1-x}Al_xN$; many have reported drastically enhanced hardness, elevated oxidation resistance, age-hardening behavior, as well as the ability to tune the reflectance of optical coatings. Many of these properties are often accompanied by the formation of self-organized nanostructures due to the onset of spinodal decomposition. However, very little has been reported on the ability to control the nanostructure formation and as a result, the systematic effects of nanostructure on the bulk fundamental physical properties of TMN alloys are relatively unknown. Here, we report on an investigation into the effects of nanostructure formation on the optical, electronic, and thermal transport, as well as elastic properties of high-quality $Hf_{1-x}Al_xN(001)$ single crystal layers using ellipsometry, temperature-dependent hall effect, picosecond probe acoustic and thermal transport measurements, in combination with advanced HR-TEM and STEM techniques. The layers were grown on MgO(001) by reactive magnetron co-sputter deposition. Films with $0 \le x \le 0.17$ are random $Hf_{1-x}Al_xN$ solid solutions with moderate changes in film properties. The onset of spinodal decomposition with $x > 0.17$, as indicated by the observation of 3D-nanoscale composition modulations using HR-STEM, results in abrupt changes in the thermal and optical properties, while gradual changes occur in the electronic properties. For instance, the thermal conductivity drops over an order of magnitude while the effective carrier concentration maintains values $>10^{22}$ cm^{-3}. Dielectric functions are determined for all compositions $0 \le x \le 0.54$ using ellipsometry at various degrees of incidence and simultaneously well fit using a combination of Drude-Lorentz behavior and a Bruggeman effective medium approximation. These fits suggest a percolated network of spherical metallic particles exists in a semiconducting medium with $0.24 \le x \le 0.32$, while films with $x \ge 0.37$ fall below the percolation limit, and carrier localization is observed (using electronic transport measurements). Comparisons are made with changes in film properties and those observed using advanced HR-TEM and HR-STEM techniques.

Tribology and Mechanical Behavior of Coatings and Thin Films
Room: California - Session E2-2

Mechanical Properties and Adhesion
Moderator: M.-T. Lin, National Chung Hsing University & Chaoyang University of Technology, J. Michler, Empa

1:30pm **E2-2-1 Fatigue Damage in Ultra Thin Cu Films**, ***C.A. Volkert*** *(volkert@ump.gwdg.de), C. Trinks*, Institute for Materials Physics, University of Göttingen, Germany **INVITED**

It has recently been observed that thin metal films exhibit completely different fatigue behavior than thicker films and large grained bulk samples. The thin films show much higher fatigue resistance and the typical fatigue damage that is observed in bulk materials, such as extrusions and complex dislocation structures, is replaced by interface cracks and isolated dislocations. These observations indicate reduced plasticity in the thin films and is likely a manifestation of their increased strength. Up until now, studies have focused on Cu films on polyimide with film thicknesses down to 50 nm. Here, a new method for fatigue testing is introduced based on free resonance of a film-coated cantilever in an AFM, which allows fatigue testing of high quality films with thicknesses down to 20 nm and to cycle numbers as high as 10^{11}. Using this method, the high cycle fatigue behavior of very thin films has been systematically investigated in the regime where dislocations are hindered and fatigue damage is dominated by interfaces. The evolution of fatigue damage as a function of film thickness and strain amplitude will be reported as well as the effect of cyclic loading on grain growth.

2:10pm **E2-2-3 Strain-Rate Sensitivity of Strength in Macro-to-Micro-to-Nano Crystalline Nickel***, R.T. Humphrey,* ***A.F. Jankowski*** *(alan.jankowski@ttu.edu)*, Texas Tech University

The strain-rate sensitivity of strength is a key parameter to evaluate the deformation of crystalline materials. It is widely reported that many metals strengthen with increasing strain rate, wherein an increase in the strain-rate sensitivity exponent occurs as the grain size decreases. The strain-rate sensitivity exponent as evaluated from a power-law relationship between yield strength and strain rate is thought to increase when the deformation mechanisms change. As an increase in the strain-rate occurs, strengthening is attributable to alloy content, then to dislocation activity, and finally to an increase in effective mass – also known as the phonon drag regime. We will evaluate the behavior of nickel over eight-orders of magnitude change in strain rate to determine if the change in strain-rate exponent is affected by the scale of the grain size from the macro- to micro- to nano- scale range as the strain rate increases. In this study, tensile testing is used to measure the strain-rate dependence of the tensile strength on the grain size in crystalline nickel foils. Similarly, micro-scratch testing is used to determine the strain-rate dependence of the scratch hardness variation with scratch velocity. Results for these two test methods are compiled for strain rates that range from 10^{-5} to 10^{3} sec^{-1}. It is found that these mechanical test results can be directly compared, and the increase in strain rate sensitivity exponent with increasing strain rate is slower for nanocrystalline than for microcrystalline nickel.

This work was supported by the J.W. Wright Endowment for Mechanical Engineering at Texas Tech University.

2:30pm **E2-2-4 Strain Rate Effects on Coated Surfaces' Response and their Film Fatigue Fracture: An Investigation by a Novel Impact Tester with Modulated Repetitive Force***,* ***K.-D. Bouzakis*** *(bouzakis@eng.auth.gr), G. Maliaris, S. Makrimallakis*, Aristoteles University of Thessaloniki, Greece, CERTH, Greece & IPT, Germany

For investigating the effect of strain rate on the surface response and film fatigue fracture of coated specimens subjected to cyclic impact loads, an impact tester was developed, facilitating the impact force modulation concerning its signal pattern. This device consists of a high rigidity base, a linear drive supported by appropriate electronic equipment and a piezoelectric actuator, for generating the impact force. In this way, impact loads with sinusoidal, triangular or trapezoidal patterns, at adjustable frequencies and impact durations can be applied. By the developed impact tester, experimental results were obtained, revealing the effect of the strain rate on film fatigue fracture induced by the coated specimens dynamic surface response. The surface response depends among others, on the substrate and coating strain, strain rate properties. These properties were quantified via an analytical FEM-supported procedure for describing the coated specimen deformation during the impact test. Based on these data, the critical strain, strain rate combinations leading to film fatigue fracture developed at various impact force signal patterns were determined.

2:50pm **E2-2-5 Microstructural Analysis of the Failure Mechanisms of Amorphous Carbon Coating Systems in Load-Scanning Tests***,* ***H. Hetzner*** *(hetzner@mfk.uni-erlangen.de), J. Schaufler, S. Tremmel, K. Durst, S. Wartzack*, University Erlangen-Nuremberg, Germany

Combining a low friction coefficient and good wear resistance, amorphous carbon coatings offer very attractive tribological properties. However, their load-carrying capacity and overload capability are more limited compared to other hard coatings and this still prevents their use in higher loaded applications like rolling bearing raceways or forming tools. The mechanical failure of amorphous carbon coating systems is most often attributed to the high residual stresses and low cracking resistance of the functional carbon layer. But the stress states and fracture behavior of metallic and ceramic adhesion and interlayers as well as the interfaces may also play an important role. Thus, it is necessary to understand the mechanical behavior of the whole coating-substrate system under application-oriented conditions in order to locate and eliminate the weak spots.

In the present study the failure mechanisms of different amorphous carbon coating systems deposited on cold work tool steel in dry sliding contact against uncoated cold work tool steel were investigated. The coating-substrate systems were subjected to a tribological model test on a load-scanning test rig under medium to high loading conditions. The test setup consists of two crossed cylindrical specimens that are forced to slide reciprocally against each other while the normal load is gradually increased. The test kinematics results in a straight contact path along the cylinder where each point corresponds to a specific loading condition. In addition to the normal load, the number of load cycles and the surface roughness of the uncoated counter body were varied in the tests.

The contact paths of the tested specimens were investigated with atomic force microscopy and scanning electron microscopy in terms of wear and damage of the surface. Furthermore, focused ion beam techniques were used for in-situ material removal in order to prepare micrometer scale cross sections of surface areas showing damage indications. This allowed for the directed study of subsurface failure mechanisms like crack propagation and decohesion of coating interfaces.

In addition to the physical tests finite element simulations of the loaded coating-substrate systems were performed in order to determine the stress conditions that are responsible for the initiation of the observed failure mechanisms.

3:10pm **E2-2-6 A Route to Avoid Thermo-Mechanical Fatigue Damage in Al Thin Films***, W. Heinz,* ***G. Dehm*** *(gerhard.dehm@mu-leoben.at)*, Montanuniversität Leoben, Austria

Cyclic compressive and tensile stresses occur in metallic films and interconnects applied in sensors and microelectronic devices when exposed to temperature changes. The stresses are induced by differences in the thermal expansion coefficients of the adjacent materials. Repeated cycling leads to damage evolution and, eventually, to failure. In this study we report on a successful strategy how to avoid thermal stress induced fatigue damage. We analysed the deformation structures of 0.2 to 2 µm thick Al films subjected to thermal cycling between 100°C and 450°C up to 10000 times. The investigations reveal that a reduction in film thickness or controlling the Al texture and the Al/substrate interface structure can be used to prevent thermo-mechanical fatigue damage. The findings are explained by orientation dependent plasticity and differences in dislocation mechanisms for different interface structures, and less accumulated plastic strain for thinner films. The approach is expected to apply in general for metallic films on substrates.

3:30pm **E2-2-7 Evaluation of Mechanical Properties in Cu Thin Films Under Various Substrate Conditions by Molecular Dynamics Simulation***, J.-C. Huang (Jc-huang@mail.tnu.edu.tw),* ***Y.-C. Liao***, Tungnan University, Taiwan

For thin films deposition, surface roughness and substrate temperature control many important physical and chemical properties. Additionally, more and more researches in the thin films growth greatly emphasize the nanoscale characterization with simulation. This paper mainly aim to study the nanoscale mechanical properties of Cu thin films deposited on monocrystalline silicon substrates with various surface roughness at elevated temperatures by molecular dynamics (MD). To investigate the adhesion under different interface roughness, the single-crystal Cu thin films deposited on silicon substrates were tested in nano-tensile, and the strength of Cu thin films was also discussed. To sum up, the surface roughness of substrate could directly affect the thin films morphology and the adhesion between coatings and substrates. Moreover, the substrate temperatures and thickness of single-crystal Cu films may cause significant variation in adhesion.

3:50pm **E2-2-8 Comparison Titanium and Zirconia Dental Implants' Stress Analysis Using Finite Element Method***, R. Yesildal,* ***F. Karabudak*** *(filizkbudak@atauni.edu.tr), M.P. Yildirim, F. Bayindir*, Ataturk University, Turkey

The purpose of this study was to use three-dimensional finite element analysis (FEM) to analyze stress distributions patterns in implant restorations made of titanium and zirconia. Two three dimensional (3-D) FEM models of a mandibular incisor implants were modelled surrounded by cortical and cancellous bone. For first model; Ti-6Al-4V for implant fixture and abutment , yttrium tetragonal zirkonium polycrystal (Y-TZP) for zirconium framework, feldsphatic porcelain for superstructure material; for second model; Y-TZP for implant fixture, abutment and zirconium framework, feldsphatic porcelain for superstructure material are used. Two implants and their superstructures were modeled using CAD software Pro/Engineer and the mandibular is modelled using MIMICS software. Two solid models of mandibular incisors transferred to mesh model in FEM (ANSYS) to analyze. No important difference is observed in resolved stresses between implant–abutment-crown combinations, thus, zirconia implant may be viable alternative for esthetic region.

4:10pm **E2-2-9 Effect of Nitrogen Flow Ratio on Microstructure and Property of Ta-Ti-N Thin Film by Reactive Sputtering of Ta-Ti Target***, C.-K. Chung (ckchung@mail.ncku.edu.tw),* ***N.-W. Chang****, T.-S. Chen*, National Cheng Kung University, Taiwan

Binary transition-metal nitride coatings of tantalum nitride (TaN) and titanium nitride (TiN) have been extensively studied for the mechanical and microelectronics application due to high hardness and low resistivity. It is of thus interest to study the combination of both TaN and TiN properties for the promising application. In this paper, the effect of nitrogen flow ratio on the evolution of microstructure, hardness and resistivity of the promising Ta-Ti-N thin films has been investigated using reactive magnetron sputtering of the Ta-Ti alloy target. The Ta-Ti-N thin films were deposited on Si(100) substrates at differ ent nitrogen flow ratios (FN_2% = FN_2/(FAr+FN_2) x 100%) of 0-20%. The microstructure, morphology, composition, bonding, hardness and resistivity of films were measured by grazing incident angle X-ray diffraction (GIXRD), atomic force microscopy, energy dispersive spectrometry, X-ray photoelectron spectroscopy, nanoindentation and four-point probe, respectively . GIXRD results showed that the Ti-Ta alloys formed at 0 FN_2% were polycrystalline with the merged bcc α-Ta and bcc β-Ti crystal structure. Increasing FN_2% resulted in the increased nitrogen content and Ta/Ti ratio in Ta-Ti-N films as well as nitrogen-doped α-Ta (α-Ta(N)) and NaCl-type (Ta,Ti)N (c-(Ta,Ti)N) structure. The hardness of Ta-Ti-N films initial increased with FN_2% then decreased at high FN_2% while the resistivity continuously increased with FN_2%. A appropriate FN_2% is good for the formation of Ta-Ti-N film with much enhanced hardness and low resistivity for the novel coating application. The relationship between the process, microstructure and property was further discussed and established.

4:30pm **E2-2-10 Mechanical Properties of Vapor Deposited Polyimide**, ***R. Chow*** *(chow3@llnl.gov), M. Schmidt*, Lawrence Livermore National Laboratory

The mechanical properties of vapor-deposited polyimide (VDP) coatings were determined as a function of the cure temperature. Monomers of PMDA and ODA were evaporated from separate sources to coat various metalized and alumina surfaces. A stoichiometric coating was defined by the absence of compositional defects induced by excessive monomer concentrations. The coatings were cured for 2 hrs at temperatures from 150°C to 400°C. The hardness and derived modulus of elasticity were determined from nano-indentation measurements. The coating adhesion was measured [1] from surfaces with and without an application of an adhesion promoter. The adhesion of the VDP was compared to wet-cast Kapton [2] and Parylene-C [3] coatings deposited on the same surfaces.

This work (LLNL-ABS-430771) performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

References

ASTM standard 5179, Standard Test Method for Measuring Adhesion of Organic Coatings to Plastic Substrates by Direct Tensile Testing.

S.C. Lee, F.C. Tai, C.H. Wei, and J.I Yu, ATR-FTIR and Nanoindentation Measurements of PMDA-ODA Polyimide Film under Different Curing Temperature, Materials Transactions, v 48, n 6 (2007), 1554-1557

Xylene Polymers, *Encyclopedia of Polymer Science and Engineering*, v 17, 2nd edition (1989) John Wiley & Sons, Inc.

4:50pm **E2-2-11 Elastic Properties of Metastable $Mo_{1-x}Si_x$ Alloys: A Brillouin Light Scattering Study**, ***P. Djemia*** *(djemia@univ-paris13.fr)*, Université Paris, France*, A. Fillon, G. Abadias, A. Michel, C. Jaouen*, University of Poitiers, France

Elastic properties of MoSi alloy films have been investigated by the Brillouin light scattering technique thanks to the analysis of the surface acoustic waves in the film on substrate. A transition from crystalline to amorphous state is observed for a Si content, x = 0.20. This transition is accompanied by different modifications of the elastic constants, namely, C_{11}, C_{33}, C_{12}, C_{13} and C_{44}. A more pronounced softening of the shear elastic C_{44} constant from 110 Gpa to 60 Gpa is observed from pure molydenum to this critical threshold. The longitudinal constants C_{11} or C_{33} have experienced a softening from 420 Gpa to 300 Gpa whereas C_{12} or C_{13} constants have not shown modification in this range of Si concentration. An intrinsic consequence of the high supersaturation of MoSi alloys is the development of an important lattice instability. In the amorphous state, the evolution of the elastic properties exhibits two distinct behaviors depending on the electronic properties of the amorphous alloys.

5:10pm **E2-2-12 The Effect of Film Thickness Variations in Periodic Cracking: Shear Lag Analysis and Experiments**, ***AA. Taylor*** *(aidan.a.taylor@gmail.com)*, Erich Schmid Institute, Austria*, V. Edlmayr*, Montanuniversität Leoben, Austria*, R. Raj*, University of Colorado-Boulder*, G. Dehm*, Montanuniversität Leoben, Austria

Periodic cracking experiments are frequently used in the assessment of interface quality in brittle film/compliant substrate systems. Through these techniques it is possible to extract a quantitative measure of interface shear strength and therefore assess the mechanical suitability of these systems for application. The influence of film thickness inhomogeneities on the crack spacing is assessed in this study. While film thickness inhomogeneities are always present in thin film systems, only nominal thickness values have been considered up to this point. By defining two separate regimes of film thickness variation, roughness and unevenness, defined in relation to the crack spacing, the influence of such variation on the data is analysed. The results of this analysis are then considered in reference to a model system of an amorphous alumina film on a copper substrate (Al_xO_y/Cu). A further means of analysing the data produced by such periodic cracking experiments is presented and its application to the Al_xO_y/Cu system is demonstrated. This crack neighbour ratio analysis validates the application of a shear lag approximation in determining interface properties for such systems.

5:30pm **E2-2-13 Optimized Adhesion Strength of TiSiN Films Deposited by a Combination of DC and RF Sputtering**, ***A.R. Bushroa*** *(bushroa@um.edu.my), H.H. Masjuki, M.R. Muhamad,* University of Malaya, Malaysia*, B. Beake*, Micro Materials Ltd, UK

This paper outlines the experimental studies of adhesion strength of TiSiN films deposited using a combination of direct current (DC) and radio frequency (RF) PVD magnetron sputtering (DR-PVD) on high speed steel (HSS) substrates. An L9 Taguchi orthogonal array was used to conduct the design of experiment for finding the optimum process parameters. Four process parameters, namely, RF power, DC power, Nitrogen to Argon (N2/Ar) gas ratio and the deposition time have been considered. Pareto analysis of variance on the micro scratch of the coating has shown that amongst the variables, RF power has the significant influence on the adhesion strength of the TiSiN films. The surface structure, morphology and composition of films of selected samples have been studied under scanning electron microscopy (SEM), energy dispersed x-ray techniques (EDX) and x-ray diffraction (XRD). The results indicate that higher adhesion strength is achieved using RF power of 100 W, DC power of 500 W, N_2/Ar ratio of 1:2.5 and a deposition time of 6 hours. Subsequent optimization has resulted in the increase of the adhesion strength value from 177 mN, signifying a tremendous improvement of 747.46%.

New Horizons in Coatings and Thin Films
Room: Sunset - Session F1-2

Nanomaterials, Nanofabrication, and Diagnostics
Moderator: S. Kodambaka, University of California at Los Angels, Y.A. Gonzalvo, Hiden Analytical

1:30pm **F1-2-1 Fabrication of Aluminum Nanodot Assisted Growth of Nanoroots for Application in Amorphous/Crystalline Silicon Composite Thin Film Solar Cells**, ***B. Newton***, *H.K. Mohammed, H. Abu-Safe, S.Q. Yu, H.A. Naseem (hanaseem@uark.edu)*, University of Arkansas

The high absorption coefficient of amorphous silicon and the superb transport properties of crystalline silicon are combined in a newly proposed composite thin film solar cell comprising of crystalline nanoroots formed by metal nanodot assisted crystallization of amorphous silicon. The nanodots and nanoroots enhance light trapping through surface plasmon generation and absorption for highly stable low cost high efficiency solar cells. Aluminum nanodots were created utilizing a standardized method of deposition through an array of nanometer holes created in a sacrificial silicon dioxide template that was deposited onto a film of amorphous silicon. Aluminum was then deposited using sputtering on an amorphous silicon film supported on a <100> crystalline silicon substrate. The aluminum nanodots were then annealed at temperatures ranging from 200 to 450°C. The growth characteristics of nanoroots were analyzed using ESEM and TEM.

1:50pm **F1-2-2 Platinum Doped Molybdenum Oxide Nanowires Alcohol Gas Sensor by Atomic Layer Deposition**, ***C.-C. Chang***, National Tsing Hua University, Taiwan*, H.-C. Shih (hcshih@mx.nthu.edu.tw)*, Chinese Culture University, Taiwan

The molybdenum trioxide (MoO_3) nanowires were prepared by thermal chemical vapor deposition through a two-step evaporation process and distributed on a p-type Si (100) substrate from molybdenum trioxide powders at 900^{o}C. These obtained nanowires were deposited the platinum nanoparticles by atomic layer deposition (ALD), the morphology, crystal and alcohol gas sensing properties of undoped and platinum doped MoO_3 nanowires were investigated. The MoO_3 nanowires were rod-like shape and the diameter were approximately 10-500 nm and several hundreds of nanometers in length. Gas sensors base on updoped, 0.5 wt% and 1.0 wt% platinum-doped MoO_3 were fabricated. The MoO_3 nanowire gas sensor showed a reversible response to alcohol gas at an operating temperature of RT-250^{o}C. The sensor response increased with increasing Pt concentration. The results demonstrated that Pd doping improved the sensor response and lowered the operating temperature at which the sensor response was maximized.

2:10pm **F1-2-3 Nanorods, Nanopipes, Nanosmiles**, ***D. Gall*** *(galld@rpi.edu)*, Rensselaer Polytechnic Institute **INVITED**

Atomic shadowing during physical vapor deposition causes exacerbated growth of surface protrusions and leads to a chaotic 3D layer growth, which can result in the development of well-separated nanorods, nanosprings, or nanopipes, which are surprisingly regular and have potential applications ranging from fuel cell electrodes and pressure sensors to self-lubricating coatings and nanoactuation. Glancing angle deposition (GLAD) causes particularly strong atomic shadowing and can be used to systematically investigate the effect of shadowing on the morphological evolution. These extremely rough layers cannot be described as a chaotic perturbation from a flat surface. However, using a model which describes them as a nanorod array with an average rod width that follows power law scaling results in experimental curves where all metals converge on a single master curve which exhibits a discontinuity at 20% of the melting point, associated with a transition from a 2D to a 3D island growth mode, and a single homologous activation energy of 2.46 for surface diffusion on curved nanorod growth fronts, which is applicable to all metals at all temperatures. Also, under extreme shadowing conditions, the conventional structure zone model is simplified as there is a direct transition from an underdense (zone I) to a dense (zone III) structure at ~50% of the melting point.

2:50pm **F1-2-5 Effects of Temperature and Pulse Mode on Nanoporous Anodic Aluminum Oxide Film by Potentiostatic Anodization**, *C.-K. Chung (ckchung@mail.ncku.edu.tw)*, ***M.-W. Liao***, *H.-C. Chang*, National Cheng Kung University, Taiwan

Conventional anodic aluminum oxide (AAO) templates were performed using potentiostatic method of direct current anodization (DCA) at low temperature (0-10°C) to avoid dissolution effect. Recently, pulse anodization (PA) has been used to improve quality of AAO films and we have demonstrated the reversed current occurred randomly from PA approach could be effectively suppressed by hybrid pulse anodization (HPA) at room temperature. In this article, the effects of temperature and pulse mode on AAO films have been investigated in terms of joule heat and burning phenomenon. Two-step anodization in 0.3 M oxalic acid was performed for fabricating AAO films by different pulse modes of HPA, PA and DCA at temperatures of 5-25°C. In addition, the voltage was applied in the range of 30-40 V in order to further verify effect of pulse modes. The morphology, pore size and oxide thickness of AAO films were characterized by high resolution field emission scanning electron microscope (HR-FESEM). The pore size distribution of AAO films can be quantitative analyzed by image processing from SEM images. The uniformity of nanopore size distribution by HPA is better than PA and DCA at relatively high room temperature due to the low joule heat to diminish the dissolution of burning. The pore size of AAO films is related to temperature and voltage and used for varied nanostructure application.

3:10pm **F1-2-7 Epitaxial Si Layer Formed on ZrB_2 Thin Films - Silicene?**, *A. Fleurence, R. Friedlein, Y. Wang, F. Bussolotti,* ***Y. Yamada-Takamura*** *(yukikoyt@jaist.ac.jp)*, School of Materials Science, JAIST, Japan

Silicene, which is a two-dimensional sheet of silicon, is increasingly attracting interests owing to the success of graphene - its carbon counterpart. Similarly, massless fermions may occur as suggested in a recent theoretical study [1]. Here, we demonstrate that a two-dimensional, ordered Si layer can be prepared through surface segregation on a metallic film grown epitaxially on Si(111).

Zirconium diboride (ZrB_2) is a metallic ceramics with a high melting point. Thin films with a high purity and crystallinity can be grown on Si(111) through thermal decomposition of $Zr(BH_4)_4$ molecules under optimized conditions [2]. We have recently obtained predominantly single-crystalline films [3] with an epitaxial relationship of ZrB_2(0001)//Si(111) and ZrB_2[1-100]//Si[11-2]. Natural oxides formed on the film upon exposure to air could be removed by heating in ultrahigh vacuum. The oxide-free film surface shows a ZrB_2(0001)-(2×2) reconstruction. Scanning Tunneling Microscopy (STM) imaging on this surface shows that the atomically-flat ZrB_2(0001) terraces are uniformly covered with periodic stripes of two types of (2×2) domains having domain boundaries along ZrB_2<11-20> directions and domain width equivalent to four to five (2×2) half unit cells. The observation of Zr-related surface states by Angle-Resolved Ultraviolet Photoelectron Spectroscopy (ARUPS) proofs that the top-most hexagonal close-packed Zr layer remains intact in spite of the (2×2) reconstruction [3]. Both Zr- and Si-related electronic states follow the (2×2) symmetry showing that the electronic subsystems are not independent from each other. Surface-sensitive core-level photoelectron spectroscopy performed using a photon energy of 130 eV identifies Si atoms in different chemical states that are either in contact with Zr atoms or not. Further details of the relationship between the electronic structure of this epitaxial Si layer on metallic ZrB_2(0001) thin film and the atomistic structure will be discussed.

References:

[1] S. Cahangirov, M. Topsakal, E. Aktuerk, H. Sahin, and S. Ciraci, Phys. Rev. Lett. 102, 236804 (2009).

[2] C. W. Hu, A. V. G. Chizmeshya, J. Tolle, J. Kouvetakis, and I. S. T. Tsong, J. Cryst. Growth 267, 554 (2004).

[3] Y. Yamada-Takamura, F. Bussolotti, A. Fleurence, S. Bera, and R. Friedlein, Appl. Phys. Lett. 97, 073109 (2010).

3:30pm **F1-2-8 Synthesis of Bioactive $NaHTi_3O_7$ Films on Ti-Coated Si by a Hydrothermal - Galvanic Couple Method**, ***C.-J. Yang***, *L.-S. Chao,* National Chung Hsing University, Taiwan, *Y.-C. Chieh,* Hsiuping Institute of Technology, Taiwan, *F.-H. Lu (fhlu@dragon.nchu.edu.tw)*, National Chung Hsing University, Taiwan

The bioactive $NaHTi_3O_7$ films were synthesized on Ti-coated Si substrates below 100ºC by a novel hydrothermal-galvanic couple (HT-GC) method. A hydrothermal (HT) method was also conducted for comparison. The thickness of obtained $NaHTi_3O_7$ films synthesized by the HT-GC method was much higher than that prepared by the HT method in 4M NaOH solutions at 80ºC for 2hr. This indicates that the hydrothermal method aided by a galvanic couple setup could enhance significantly the growth rate of the films. The obtained $NaHTi_3O_7$ films exhibited nano-network structures and their pore sizes within the network increased with the NaOH concentration and the reaction temperature, as well as the reaction time . I n simulated body fluid solutions, calcium phosphate-based products were formed on the $NaHTi_3O_7$ films, suggesting that the films have great potentials in biomaterial applications.

3:50pm **F1-2-9 Amorphous Phases and Crystallization Behaviour of Sputtered $Fe_{1-x}C_x$ Films with x Ranging between 0.32 and 0.50**, ***E. Bauer-Grosse*** *(elizabeth.grosse@ijl.nancy-universite.fr)*, Nancy-University, France, *G. Le Caër*, Universite de Rennes, France

Iron-carbon and iron-carbon based alloys , which are of great importance from both fundamental and applied points of view, have triggered a wealth of publications which are most often devoted to studies of crystalline alloys with nanosized, ultra-fine or micron-sized grains. A full knowledge of the Fe-C system requires further to investigate and characterize amorphous Fe-C alloys which are known to exist in a wide concentration range. Sputtered $Fe_{1-x}C_x$ amorphous films were for instance found to exist for a carbon content x ranging between 0.19 and 0.50. These amorphous alloys can be prepared either as thin films or as powders, for instance when they are synthesized by mechanical alloying. The Fe-C amorphous alloys are interesting in their own for their peculiar structure, which depends on the carbon content, and for their intrinsic physical properties. Further, they are sources of new metastable carbides which are formed during their crystallization. The present work addresses the characterization of the carbon-richest $Fe_{1-x}C_x$ films (x > 0.32) with a special attention dedicated to $Fe_{0.55}C_{0.45}$. Electron probe microanalysis was used to determine the carbon content. As-sputtered amorphous films were characterized by Mössbauer spectrometry, X-ray and/or electron diffraction. Their thermal stability was studied by differential scanning calorimetry. The products of crystallization were identified both from Mössbauer spectra and from X-ray diffraction patterns. Crystallization was followed in situ using a hot stage transmission electron microscopy. For any carbon content in the range 0.32-0.50, the Mössbauer hyperfine parameters are observed to remain constant while the main crystallization product is identified to be the Fe_7C_3 carbide. These results indicate that, for x > 0.32, the amorphous films are composed of two phases: one Fe-rich metallic Fe-C phase, with a carbon content close to 0.3, and an amorphous carbon phase deprived of iron. The composition of the metallic phase remains essentially constant when the carbon content increases. Then, it is the increase of the fraction of the amorphous carbon phase which accomodates the carbon content increase. According to the carbon content, amorphous Fe-C films may be looked at as nanocomposites formed by two components, a metallic amorphous one and an amorphous carbon one, whose proportions can be controlled by a choice of the carbon content.

4:10pm **F1-2-11 Frost Reduction on the Micro/Nano Structured Superhydrophobic Aluminium Surface**, ***C.-T. Yang*** *(ctyang@mail.sju.edu.tw)*, *C.-H. Lan*, St. John's University, Taiwan

In refrigeration system, the heat transfer performance of evaporator is decreased when the fins covered with frost. The defrosting process is time and energy consumptions. The modification of superhydrophobic thin film on the aluminum fin surface could prevent the condensate water drop staying on the surface and so reduce the frost deposition. In order to modify the aluminum surface to be superhydrophobic, a thin film of micro/nano structure was coated by sol-gel process. The Tetraethoxysilane(TEOS) and Methyltrimethoxysilane (METMS) were employed and mixed with micro/nano silica particles to function like the lotus leaf. Those silane couple agents also provided the bonding force between aluminum and silica particles. The water contact angle of original untreated aluminum surface is 85 degrees. The best one after modification can reach 163 degrees. The SEM images tell that the more nano particles used, the more roughness the surface was, which the contact angle enhancement can be explained by Cassie-Baxter model. In order to understand how the wettability affects the frost deposition, the aluminum plate samples were placed in the refrigerator cold chamber and hot water was used to speed up the frosting process. After a period of time the samples were weighed by digital scale. The results show that the higher contact angle the surface had, the less frost deposition on surface happened. Compare to untreated aluminum plate, the frost deposition is only half when the contact angle is 163 degrees. For the long term (7 hours) frosting running, the frost reduction ability is decreased. Because when the superhydrophobic film was covered with frost, the high contact angle state cannot persist.

4:30pm **F1-2-12 Micro/Nanostructured Surfaces of a-C:H:F Films with Anisotropic Properties***, C. Corbella (corbella@ub.edu),* ***V.-M. Freire****, S. Portal, G. Oncins, E. Bertran, J.-L. Andújar*, Universitat de Barcelona, Spain

Amorphous hydrogenated carbon films with fluorine (a-C:H:F) with special surface properties have been fabricated by combining lithography techniques and plasma deposition. First, silicon wafers were patterned either by laser lithography or by colloidal lithography with silica nanospheres. Both techniques generated micro/nanotextures showing in-plane anisotropy on the surface. After that, the samples were coated by a-C:H:F thin films by pulsed-DC plasma-enhanced chemical vapor deposition using CH4 and CHF3 as precursors. Structural and morphological studies were carried out by scanning electron microscopy (SEM) and atomic force microscopy (AFM). The surface properties evidenced the formed anisotropy, as shown by the directional dependences of wettability and friction coefficient. Wettability, which was measured by water contact angle, showed an anisotropic chararacter evidenced by the elongated shape of the wetting drops. Superhydrophobicity was achieved on the preferential direction of the pattern. The tribological properties of the samples were also influenced by the in-plane anisotropy, as measured with a nanotribometer and an AFM operating in contact mode. Differences in friction coefficient and wear rate as a function of scan direction, load and contact area are discussed. Silica nanoparticles were arranged on the micropatterns to test their performance as self-assembly surfaces. These samples find applications where hard coatings with anisotropic properties are required, e.g. microelectromechanical devices (MEMs), microfluidics and patterned surfaces for biomedicine.

4:50pm **F1-2-13 Correlation Between Plasma and Properties of Cr_2AlC MAX Phase Coatings***,* ***C. Leyens*** *(christoph.leyens@tu-dresden.de), O. Schroeter, R. Basu*, Technische Universität Dresden, Germany

Cr_2AlC has recently been studied as a MAX phase coating due to its excellent thermo-mechanical properties resulting from its inherent nano-laminated structure. In the present paper the correlation between plasma characteristics during sputtering and the resulting coating properties will be shown. A sintered Cr_2AlC powder target was used for high power impulse magnetron sputtering (HIPIMS) or conventional DC magnetron sputtering. HIPIMS sputtering was performed at different pressures and at different pulse power levels; the effect of process parameters on the plasma was investigated by a quadrupole mass spectrometer. Plasma composition as well as amount and energies of single and double charged ions were analyzed. Moreover, the structure, the morphology and selected properties of the coatings were investigated. The Cr_2AlC coatings were single MAX phase; coating morphology and internal stress state were varied by using different bias voltages. Depending on the process parameters, the Cr_2AlC MAX phase coatings showed high adhesion in scratch test and very good plastic performance.

New Horizons in Coatings and Thin Films
Room: Royal Palm 1-3 - Session F2-1

High Power Impulse Magnetron Sputtering
Moderator: R. Bandorf, Fraunhofer IST, J. Sapieha, Ecole Polytechnique de Montreal

1:30pm **F2-1-1 High Power Pulsed Magnetron Sputtering: a Review of Magnetron Ion Sputtering***,* ***J. Alami*** *(jonesalami@hotmail.com),* Sulzer Metaplas, Germany*, K. Sarakinos,* Linköping University, Sweden*, K. Konstantinidis*, CIRMAP, University of Mons, Belgium **INVITED**

A main parts of a typical sputtering apparatus are a power supply, a sputter target sitting inside a vacuum chamber, a substrate powered by a bias power supply. Understanding of each of the consisting parts limitations and capabilities is of high importance to the coating developer, which is even more the case when HPPMS technology is used. HPPMS and HIPIMS are acronyms of an emerging sputtering technology that has gained substantial interest among academics and industrials alike. HPPMS (HIPIMS) which stands for high power (im)pulsed magnetron sputtering is a physical vapor deposition technique in which the power is applied to the target in low-duty-cycle pulses (< 10%) and low frequency (< 10 kHz). As a result, pulsed target power densities of several kW cm^{-2} are obtained. The HPPMS mode of operation results in generation of a large number of charged particles in the plasma, including electrons, ions, and multi-fold charged ions. The dynamics of such plasma have been especially studied with regards to the high ionization degree of the sputtered atoms, their charge, and their transport route as they are expanding away from the sputter-target. A number of studies have utilized the abnormal plasma dynamics observed in the HPPMS plasma in order to grow dense and smooth coatings on flat and complex-shaped substrates. They found that HPPMS provides new and parameters to control the deposition process, tailor the properties and optimize the performance of elemental and compound films.

In the present review paper, an attempt is made at demonstrating the main features of HPPMS by trying to find the red-line through the more-than-250 publications on the subject. In order to do this, the power supply types in the market are reviewed. This is followed by a short description of the type of magnetrons needed for the HPPMS operation. Finally, examples of coatings deposited by HPPMS are given and the benefits of using this technique are highlighted.

2:10pm **F2-1-3 A Two-Zone Model for High-Power Pulsed Magnetron Sputtering Discharges***,* ***T. Kozak*** *(kozakt@kfy.zcu.cz), A.D. Pajdarova*, University of West Bohemia, Czech Republic

We present a two-zone non-stationary model of a high-power pulsed magnetron sputtering discharge. The model splits the magnetron discharge into two zones, namely the high density plasma ring above the target racetrack including a target sheath and the bulk plasma region between the plasma ring and the substrate. By solving the particle and energy conservation equations for these two zones, the model makes it possible to evaluate time evolutions of the averaged process gas and target material neutral and ion densities, as well as the fluxes of these particles to the target and substrate during a pulse period. Consequently, the target and substrate current density waveforms, together with the effective electron temperature, can be calculated. In addition, the important deposition characteristics, such as the deposition rate, the fraction of target material ions in the total ion flux to the substrate and the ionized fraction of target material atoms in the flux to the substrate can be evaluated. The geometric input parameters of the model are the vacuum chamber dimensions, the target-to-substrate distance, the target and substrate diameters and the plasma ring size (defined roughly by the geometry of the magnetic field). The main process input parameters are the process gas pressure, the magnetic field strength, the target voltage waveform during a pulse period and the repetition frequency of the pulses. Furthermore, additional material parameters, such as the sputtering yields, the secondary electron emission coefficients, the ionization and excitation cross-sections for the process gas and target material must be provided. The effects of various process parameters on the discharge and deposition characteristics were examined. The model predictions were compared with the experimental results obtained for two different high-power pulsed magnetron systems.[1,2] It was shown that the model provides a good qualitative picture of the complicated processes determining the sputtering and deposition mechanisms in the high-power pulsed magnetron discharges investigated.

[1]A.D. Pajdarova, J. Vlcek, P. Kudlacek and J. Lukas: *Electron energy distributions and plasma parameters in high-power pulsed magnetron sputtering discharges*, Plasma Sources Sci. Technol. **18**, 025008 (2009).

[2]A. Anders, J. Andersson and A. Ehiasarian: *High power impulse magnetron sputtering: Current-voltage-time characteristics indicate the onset of sustained self-sputtering*, J. Appl. Phys. **102**, 113303 (2007); Erratum: J. Appl. Phys. **103**, 039901 (2008).

2:30pm **F2-1-4 Temporal Evolution of the Radial Plasma Emission Profile in HIPIMS Plasma Discharge***,* ***A. Hecimovic*** *(ante.hecimovic@rub.de), T. de los Arcos, M. Böke, J. Winter*, Institute for Experimental Physics II, Ruhr-Universität Bochum, Germany

High power impulse magnetron sputtering (HIPIMS) is a plasma vapour deposition technique used for deposition of dense coatings. HIPIMS utilizes short pulses of high power delivered to the target in order to generate a high amount of metal ions. Ion densities are two orders of magnitude higher compared to DC magnetron sputtering with the same average power. The dynamic of the plasma generation and the transport of metal particles during and after the pulse have not been fully understood. In order to contribute to better understanding of the dynamics of the HIPIMS plasma discharge time and wavelength resolved measurements of the light emitted from the plasma have been performed.

Sideway photos of the HIPIMS plasma have been recorded using Charge Coupled Device (CCD) camera with gate width of 5 μs. For each photo Abel inversion has been performed to compute the radial emission profile of the plasma. Bandpass interference filters were used to isolate desired wavelength in order to observe lines of Ti^0, Ti^{1+}, Ar^0 and Ar^{1+} particles in HIPIMS plasma discharge with Titanium (Ti) target in Ar atmosphere. Result is the temporal evolution of radial emission profile of both metal and gas atoms and singly charged ions.

Work funded by Deutsche Forschungsgemeinschaft (DFG) within SFB-TR 87 project.

2:50pm **F2-1-5 The Influence of Pulse Arrangement and Off-Time Between Positive and Negative Pulse in Bipolar HIPIMS**, ***R. Bandorf*** *(ralf.bandorf@ist.fraunhofer.de), M. Reschke, H. Gerdes, G. Bräuer*, Fraunhofer IST, Germany

Besides conventional unipolar high power impulse sputtering (HIPIMS) the bipolar mode is offering additional degrees of freedom, especially in case of reactive sputtering. For oxides improvement of process stability and coating quality is reported using bipolar mode instead of unipolar.

In this paper we investigated the influence of the used pulse arrangement on the resuting voltage-current response at the target, as well as the plasma and the film properties. For basic investigation pure titanium without additional oxygen was investigated. The pulse on-time for positive and negative pulse were kept constant. The off-time between the positive and negative pulse was varied. From a symmetric arrangement of defined pulse and pause for positive and negative pulse the off-time separating positive and negative pulse was shortened to a minimum pause of 20µs. From nearly no influence the peak current was modified and got unsymmetric when bringing positive and negative pulse close together. The remaining ions form the positive pulse led to faster ignition of the negative pulse. The correlated OES spectra, deposition rates, and film structure is investigated.

3:10pm **F2-1-6 A Study on the Deposition Rate of Modulated Pulse Power (MPP) Magnetron Sputtering of Metallic Thin Films**, ***J. Lin*** *(jlin@mines.edu), J.J. Moore,* Colorado School of Mines*, W.D. Sproul*, USA Reactive Sputtering, INC

As a variation of high power pulsed magnetron sputtering technique, modulated pulse power (MPP) magnetron sputtering has shown the possibility to achieve a high deposition rate and a high degree of ionization of the sputtered material at the same time. In this study, we have investigated the influence of themagnetic field strength on the deposition rate of different metal films (Cr, Ti, Al, Cu, etc,) and plasma properties using the MPP technique in a closed field unbalanced magnetron sputtering system. The MPP deposition rates have been compared to those obtained from the films deposited by direct current magnetron sputtering (DCMS) under the same experimental conditions. The time averaged ion energy and mass distributions of the positive ions at different magnetic field strength s were compared using an electrostatic quadrupole plasma mass spectrometer. The effects of the repetition rate, peak target current (power) and pulse length on the MPP deposition rate have also been investigated. It was found that both DCMS and MPP depositions showed an increase in the deposition rates as the magnetic field strength decreased under the same experimental conditions. The MPP deposition rate can generally achieve more than 70-80% of the DCMS rate for different metal film depositions. In many cases, the MPP deposition rate exceeded the DCMS rate in the right power, magnetic field strength and pulsing conditions . The magnetic field strength also showed a strong effect on the ion energy and mass distributions . Additionally, the microstructure and mechanical properties of the films deposited at different magnetron field strength will also be reported.

3:30pm **F2-1-7 The Effect of Various Deposition Parameters on the Phase of Tantalum Thick Films Deposited by Modulated Pulse Power Magnetron Sputtering**, ***S. Myers****, J. Lin, J.J. Moore (jjmoore@mines.edu),* Colorado School of Mines, *W.D. Sproul,* Reactive Sputtering, Inc.*, S. Lee*, US Army ARDEC Benet Labs

Tantalum thin films exhibit two crystalline phases, α (body-centered-cubic) and β (metastable tetragonal). α is the phase commonly found in bulk tantalum, which exhibits good ductility, high melting temperature, and low resistivity. β, however, has high resistivity, high hardness, yet is very brittle. Thus, α is typically preferred for wear and corrosion resistant applications. In this study, modulated pulse power (MPP) magnetron sputtering was used to deposit thin and thick tantalum coatings to determine the effect of several deposition parameters, such as target power (1-3 kW), working pressure (3 – 10 mTorr), substrate-to-target distance (60 – 165 mm), and negative substrate bias (0 – -150 V) on the phase control without substrate heating and post annealing process. The phase, microstructure, and mechanical properties of the coatings were characterized using X-ray diffraction, scanning electron microscopy, micro scratch test and nanoindentation.

3:50pm **F2-1-8 Control of the Magnetic Field for HiPIMS Process Optimization**, *J. Capek, M. Hala, O. Zabeida,* ***J. Klemberg-Sapieha*** *(jsapieha@polymtl.ca), L. Martinu*, Ecole Polytechnique de Montreal, Canada

Deposition of coatings from highly ionized metal plasma makes HiPIMS a very attractive PVD technique. However, discharge operation in the metal-dominated HiPIMS mode and process stability is frequently affected by a combination of the magnetron configuration (size and magnetic field) and by the target conditions (e.g. material and thickness). In addition, target erosion is an important issue significantly affecting process reproducibility.

In the present work, we propose to stabilize the HiPIMS discharge by controlling the target magnetic field using metal spacers with different thicknesses in between the magnetron surface and the target. We demonstrate a straightforward discharge optimization and enhanced reproducibility, while using various metal target materials (such as Nb, Ta or Ti, and even semiconducting Si), and different levels of target erosion. We show the effect of such an approach on the magnetic field in front of the target, and on its consequences on the deposition rate, the coating properties, and the overall process optimization.

4:10pm **F2-1-9 TiAlN Coatings Grown by HIPIMS**, ***G. Greczynski*** *(grzgr@ifm.liu.se), J. Jensen, L. Hultman,* Linköping University, Sweden*, M. Johansson,* Seco Tools AB Fagersta, Sweden*, Ch. Schiffers*, CemeCon AG, Germany

$Ti_{1-x}Al_xN$ ($0\leq x\leq 1$) films have been prepared in an industrial scale coating unit by high power pulsed magnetron sputtering (HiPIMS/HPPMS) using three different sets of target configurations. First, elemental targets were co-sputtered in a hybrid HIPIMS-DCMS set up with one target (Al or Ti) operated exclusively in HIPIMS mode and the other target ran in the conventional DC magnetron sputtering (DCMS) regime. Second, films were deposited from a Ti-Al gradient target operated in HIPIMS mode. The Al content in the co-sputtered coatings was controlled by adjusting the average power of Ti and Al cathodes. A significant overrepresentation of Al was found (as compared to films produced exclusively by DCMS at the same power settings). This can be interpreted in terms of element-specific loss of deposition rate during HIPIMS processing, since Ti exhibits higher degree of ionization than Al (at the same average power and pulsing frequency), and in consequence a larger fraction of the sputter-ejected material is back-attracted to the target. The tilt-angle dependent XRD studies revealed that in the case of Ti-DC/Al-HIPIMS target configuration, the resulting films retained single phase NaCl crystal structure up to x=0.62 and the first traces of the hexagonal phase were detected at x=0.645, close to the solubility limit of x=0.67. For the case of Al-DC/Ti-HIPIMS, the films contained hexagonal phase already at x=0.53, whereas coatings obtained from the gradient target constitute an intermediate case with the transition point at x=0.58. Common for all samples is the behavior of the interplanar distance d_{200} that shows first, a decrease with increasing Al content up to the critical concentration where the hexagonal phase was detected, and a plateau thereafter for further increasing molar fraction of Al. The results of nanoindentation hardness measurements are in good agreement with the evolution of the crystalline phase content indicated by XRD. Films grown from gradient target show relatively high compressive residual stresses ranging from -2 GPa up to -4 GPa. On contrary, Ti-DC/Al-HIPIMS samples are nearly stress-free and in the most interesting range of compositions ($0.55\leq x\leq 0.6$) exhibit residual stresses between -0.4 GPa and 0.2 GPa.

4:30pm **F2-1-10 Titanium Aluminum Nitride Sputtered using HIPIMS Technology**, ***M. Lechthaler*** *(markus.lechthaler@oerlikon.com), J. Weichart, O. Gstoehl*, OC Oerlikon Balzers AG, Liechtenstein

High Impact Power Impulse Magnetron Sputtering (HIPIMS) is a modern sputter technology with the potential to be industrially commercialized. Here, first results will be presented using this technology in an industrial-scaled Oerlikon Balzers deposition equipment which was modified and equipped with HIPIMS for R&D investigations. Within this study, a series of TiAlN coatings was deposited while applying a broad range of different deposition parameters. Basic films properties such as the deposition rate, the surface roughness, the hardness, the Young's modulus, and the film stress were determined to obtain a first categorization of these coatings and to make a comparison to established deposition technologies. In addition, the coating composition, the morphology and the structure of coatings are evaluated using X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray spectroscopy (EDX) in dependence of the different deposition parameters. Finally, lifetime machining investigations such as drilling and milling tests were conducted in order to evaluate as well the coating performance as the wear behavior. Potential applications of HIPIMS will be further discussed.

Applications, Manufacturing, and Equipment
Room: Royal Palm 4-6 - Session G6

Advances in Industrial PVD & CVD Deposition Equipment
Moderator: M. Rodmar, Sandvik Tooling Stockholm SE, K. Yamamoto, Kobe Steel Ltd.

1:30pm **G6-1 Current and Future Applications of HIPIMS**, ***Ch. Schiffers**, T. Leyendecker (Toni.Leyendecker@CemeCon.de), W. Kölker, S. Bolz*, CemeCon AG, Germany

HIPIMS has entered the industrial production in 2010. Thus the R&D efforts split into supporting the daily production of mostly nitride based films and the search for new application areas using more complex coatings as oxides.

The first commercial job coating HIPIMS film for cutting tools is been used for more than half a year when the ICMCTF 2011 takes place. This presentation will summarise the experiences of this first large scale use of HIPIMS: What advances of the HIPIMS coating machine are the result of this production use? What applications benefit most from this novel technique? What issues require intensified R&D? What about the economical aspects of HIPIMS? Is there a sensible return of investment for the user?

The world's dependency on fossil fuels and the related release of CO_2 are issues that need urgent answers. Fuel cells and batteries are a possible way out. Common to both is the need for dense oxides films on temperature sensitive substrates. A number of R&D groups are investigating HIPIMS for this. We will present the latest findings related to the deposition equipment and the process development of this ongoing project.

1:50pm **G6-2 Comparison of Hard Nitride Coatings Deposited by Industrial Scale AIP and HIPIMS Equipment**, ***K. Yamamoto** (yamamoto.kenji1@kobelco.com), S. Tanifuji, J. Munemasa, H. Nomura,* Kobe Steel Ltd., Japan, *R. Cremer*, KCS Europe, Germany

Cathodic arc discharge (CAD) is a high current – low voltage point discharge and characterized by a localized discharge that is large current of thermal electrons are emitted from small (10um square) cathode spots. Due to this unique discharge nature, a high degree of ionization of target materials, as well as high evaporation rate can be achieved. These characteristics make the CAD process very attractive for industrial application, in spite of the apparent drawback of CAD process that is MPs. On the other hand, conventional magnetron sputtering is a low current - high voltage planar discharge and the ionization of the target material is quite low, usually in the order of a few percent and the plasma is mainly consisting of gas ions. The HIPIMS process is also a planar discharge process like conventional sputtering. However, momentarily input power is approximately 3 orders magnitude higher and a number of reports indicate that significant amount of metal ions exist in the plasma. In spite of the apparent drawback of HIPIMS, the deposition rate, this process is gaining a lot of attention because it seems like that this process promises MPs free arc-like coatings which is critical for certain tribological applications.

Different types of nitride coatings including standard TiN and TiAlN were deposited by industrial arc ion plating (AIP), a new nearly droplet free arc technology, recently introduced by Kobe Steel and HIPIMS. TiAlN coatings deposited by the HIPIMS process show strong preferred (111) orientation and a relatively high hardness up to 35 GPa is obtained. Whereas AIP TiAlN coatings are is characterized by a moderate hardness up to 30 GPa and (200) or nearly random orientation at an equivalent substrate bias condition. Cross sectional TEM observations of both coatings revealed that HIPIMS coatings show smaller grain sizes compared to AIP coatings. High magnification image, many lattice defects can be observed for HIPIMS coating and is hardened by many atomic defects, possibly highly stressed.

In the presentation, a comparison between AIP, new nearly MP-free AIP and HIPIMS coating by different power supply, arc source and deposition conditions will be made not only from property of the coating but also from industrial perspective such as productivity and tribological performance.

2:10pm **G6-3 Hybrid PVD Industrial Deposition Equipment for R&D Purposes**, ***L. Peeters** (lpeeters@hauzer.nl), F. Papa, R. Tietema, T. Krug*, Hauzer Techno Coating, Netherlands

R&D centres are more and more developing in cooperation with the industry. Therefore the need for robust multi-functional R&D equipment with full scale industrial production potential has risen.

The Hauzer Flexicoat® 850 is a versatile machine with a modular set-up. The system is equipped with four interchangeable chamber walls, which means that the machines can be upgraded with new technology at any time. It is a hybrid machine, which can combine technologies such as arc, sputter, HIPIMS, HIPIMS$^+$, PACVD, dual magnetron sputtering and plasma-nitriding in one machine.

The machine is often used for developing tribological coatings in automotive markets and development of decorative and tool coatings. The combination of technologies is used to create multi-layers on products without breaking the vacuum between processes or to create multi-composite coatings.

Technologies will be discussed in combination with machine design and up-scaling of processes to industrial production levels. Furthermore a method for lowering development costs will be introduced. Special R&D cathodes will result in more flexibility and lower target material costs.

2:30pm **G6-4 Advantages of New Generation of Superior Arc Management Circuity**, *P. Ozimek, **W. Glazek** (Marta.Gryciuk@pl.huettinger.com), L. Zyskowski*, Huettinger Electronic Sp. Z o.o., Poland

Importance of the arc management in DC power supplies is getting new meaning as most advanced DC generators are more and more successful in sputtering highly arcing and difficult materials providing high deposition rate and economical benefits.

It has been developed as the answer to market demand to limit arc energy during an arc occurrence in sputtering. Industrial realization has been successfully employed in air cooled DC power supplies successful on the market for years already. Possibility of using DC power supplies for sputtering highly arcing materials is a result of this. It is a beginning of new age in magnetron sputtering technology. Further improvement and optimization by using more efficient water cooling and the fastest MOSFET transistors, results in the new generation of power supplies with state-of-the-art arc management parameters. Comparison of standard and state-of-the-art arc management solution in sputtering power supplies will be presented, along with experimental results for TCO materials.

2:50pm **G6-5 PVD Systems and Technology for Dedicated Hard Coatings: Challenges and Solutions**, ***J. Vetter** (joerg.vetter@sulzer.com), G. Erkens, J. Müller, J. Crummenauer*, Sulzer Metaplas GmbH, Germany **INVITED**

Increased loads (mechanical loads, thermal loads, etc.), longer life time, higher performance and thus higher productivity, reduction of weight and friction as well as the improvement of corrosion resistance are demanded for innovative tools and components to meet functional and decorative requirements. In particular, surface treatments and related coating technologies are selected in the day-to-day mass production of precision components in order to provide application specific surface solutions. Advanced coating systems offer multiple solutions to meet these demands. The four basic processes used for coating systems are: arc evaporation, magnetron sputtering, PA-CVD and nitriding. Some development streams have to be noticed: the arc evaporation process was progressively improved; the traditional magnetron sputtering is extended to the high current pulsed sputtering, PA-CVD mainly used for a-C.H:X coatings (X = Si, O …) has been upgraded to deposit high performance coatings; the duplex process plasma nitriding and PVD was introduced in industrial scale. Application tailored hybrid and duplex technologies provide the chance to synthesize the next generation of high performance PVD coatings. With the hybrid technology materials can be combined wisely nearly without limits.

The potentials of the advanced PVD-systems, the hybrid PVD technology and the duplex treatment will be illustrated. First coating solutions from latest approaches to hybrid processes that combine sputtering and arc technology as well as from duplex processing with a combination of nitriding and PVD will underline the leading edge technology presented.

3:30pm **G6-7 Laser-Arc-Module System Combined with a Novel Filtering Unit for Industrial ta-C Coating of Parts and Tools**, ***H.-J. Scheibe** (hans-joachim.scheibe@iws.fraunhofer.de),* Fraunhofer IWS, Germany*, M. Falz, Ma. Holzherr,* VTD Vakuumtechnik Dresden GmbH, Germany*, M. Leonhardt, A. Leson, C.-F. Meyer,* Fraunhofer IWS, Germany*, K.-D. Steinborn*, VTD Vakuumtechnik Dresden GmbH, Germany

Hydrogen-free tetrahedral amorphous carbon (ta-C) coatings are known to have extraordinary low-wear and low-friction properties. Therefore they are of increasing interest for sliding automotive and machinery components as well as tool applications. In contrast to the deposition of most other DLC and hard coatings, an efficient deposition of ta-C is only possible by vacuum-arc technologies, e.g. arc ion plating or pulsed arc deposition.

Two difficulties commonly are associated with the industrial deposition of ta-C by these technologies: (1) a limited control and long-term stability of the arc sources and (2) an emission of particles and droplets leading to a high coating roughness. By controlling the pulsed arc discharge by a laser

(Laser-Arc) an efficient tool for a long-term stable and efficient working carbon plasma source for ta-C deposition was obtained. The graphite cathode is designed as a rotating roll and placed in a separate source chamber (Laser-Arc-Module / LAM). This module is combined by an adapting flange with the industrial batch coater DREVA 600. A Q-switched Nd-YAG-Laser is used for the temporally and locally controlled arc-ignition while the ta-C deposition mainly originates from the pulsed arc discharge parameters. This combination of LAM with industrial coaters also opens new opportunities to design new generations of coating stacks incorporating super hard top-layers in combination with classical and proofed interface designs and hard coatings. In the final version the adapting flange is replaced by a novel filtering unit. Now, the industrial coating of parts and tools with smooth and virtually defect-free ta-C coatings becomes possible with this new equipment.

3:50pm **G6-8 InlineCoater™ 300: A New PVD System for Fast Research and High Volume Production**, *M. Samuelsson,* Linköping University, Sweden, *S. Åström, T. Joelsson, A. Flink, B. Wälivaara, N. Odelstam,* ***H. Ljungcrantz*** *(henrik@impactcoatings.se)*, Impact Coatings AB, Sweden

The InlineCoater 300 is a high yield multifunctional PVD deposition system equipped with four process chambers, including a load-lock with fast evacuation time (~20s). This, combined with high deposition rate coating sources, results in a system suitable to produce a high number of different coatings within a short time frame. The above allows using the system for development as well as up-scaling and high volume production, thus enabling a short industrialization process. Moreover, the system is generic and well suited both for different deposition techniques (e.g. arc evaporation, magnetron sputtering) and reactive processes.

The high capacity of the system has been demonstrated applying the concept of Design of Experiments (DOE). The material system used as a model system was the Ti-N-C, deposited by reactive cathodic arc evaporation. The parameters explored were: arc current, substrate bias voltage, partial pressures, and ratios of the reactive gases. In order to cover a relevant parameter space, more than 100 depositions was carried out within one day. The resulting coatings, which were grown to a thickness of approximately 1 µm were evaluated with respect to color, as defined by the L*a*b*-space.

The resulting model derived from the regression analysis of the measured L*a*b*-data was used to predict the full L*a*b*-space of the Ti-C-N-system with respect to the input parameters. The model could also be used for compensation of time-dependent drift, ensuring stability during a production cycle.

Post Deadline Discoveries and Innovations
Room: Tiki Pavilion - Session PD

Post Deadline Discoveries and Innovations
Moderator: G. Ramanath, Rensselaer Polytechnic Institute, S.J. Bull, Newcastle University

1:30pm **PD-1 Superhard Transition Metal Diboride Coatings**, ***V.A. Ravi*** *(vravi@csupomona.edu), A. Schissler, B. Harrison, A. Ly, J. Koch,* California State Polytechnic University, *A. Lech, R. Kaner*, University of California, Los Angeles

The diboride of the transition metal rhenium has been reported to have hardness values high enough to classify it as a superhard material and has been shown to scratch diamond. This superhard material has been synthesized in bulk form; however, the development of coatings of this material is still ongoing. Pack cementation techniques were implemented to form rhenium diboride coatings on rhenium substrates and a series of experiments are currently underway to examine the kinetics of rhenium diboride coating growth for several pack compositions. Thus far, coatings have been produced with thicknesses up to ~13 µm and Vickers microhardness values of up to ~43 GPa. X-ray diffraction was used to confirm the predominant phase as ReB_2. This talk will summarize the current status of the work on rhenium diborides; mention will also be made of the work underway on tungsten tetraboride coatings.

This work was supported by the National Science Foundation under Grant No. DMR 0805357

1:50pm **PD-2 Intelligent Self-Healing Corrosion Resistant Vanadia Coating of Flower-Like Morphology for AA2-24 and Novel Magnesium Alloys**, ***A.S. Hamdy*** *(asalam85@yahoo.com),* Max Planck Institute, Germany & King Fahd University, Saudia Arabia, *I. Doench, H. Möhwald*, Max Planck Institute, Germany

Environmentally acceptable vanadia based coatings of self-healing properties were developed for improving the corrosion protection performance of Aluminum Alloy 2024 and some newly developed magnesium alloys for possible application in automotive and aerospace industries. The optimum vanadia solution concentrations and pH that can offer the best corrosion resistance of aluminum or magnesium substrate in chloride containing solutions were measured by mean of electrochemical impedance spectroscopy and polarization techniques. A flower-like coating morphology of self healing properties was observed to improve the localized corrosion resistance in 3.5% NaCl solution. Surface morphology, composition and microstructure of vanadia conversion coatings were examined by AFM, XPS, SEM-EDS and macroscopic imaging techniques.

2:10pm **PD-3 Life Time Analysis of MCrAlY Coatings for Industrial Gas Turbine Blades (Calculational and Experimental Approach)**, ***P. Krukovsky*** *(kruk@i.kiev.ua),* Institute of Enbineeering Thermophysics, Ukraine, *K. Tadlya,* Institute of Engineering Thermophysics, Ukraine, *A. Rybnikov,* Polzunov Central Boiler and Turbine Institute, Russia, *V. Kolarik*, Fraunhofer ICT, Germany

A calculational and experimental approach was developed for life time analysis of MCrAlY coatings for industrial gas turbine blades. This approach based on a model that describes the main diffusion and oxidation processes within the coating-base metal system as well as experimental data for specimens after different short time exposures at different temperatures. In comparison with existing models the proposed model describes the interdiffusion zone between coating and base alloy. The model's adequacy to represent physical processes is provided by identifying model parameters from short-time experimental data for coating – base alloy systems. The measured Al concentration profiles were used as input values for model parameters estimation and a calculational prediction of the long term diffusion and oxidation behaviour of the coating was performed. The model, calculational and experimental approach as well as MCrAlY life time estimation results for 10000 h at 950°C are presented. These results were obtained with short time experimental data for Al concentration profiles across the coating thickness measured after 300 and 1000 h. The predicted and measured -phase content in the coating during oxidation for coating thickness 200 micron at 900, 950 and 1000 °C are presented too. The dissapearance of □-phase in the coating was assumed as the corrosion life time criterion.

2:30pm **PD-5 Development of Photonic Platforms from Hybrid Sol-Gel Thin Films**, ***M. Oubaha*** *(mohamed.oubaha@dcu.ie), R. Copperwhite, A. Gorin, C. McDonagh*, Dublin City University, Ireland

Over the past decade, integrated optoelectronic devices have gained increasing importance with the rising demand for higher lightwave transmission capacity. One technology that can aggressively address the increasing need for integration of electro-optical components into miniaturised systems is that of lightwave circuits (LWC) based on optical channel waveguides. The availability of LWCs on an industrial level would allow the direct integration of passive and active components such as parallel optical interconnects, Wavelength Division Multiplexer, Variable Optical Attenuators, Optical Switches, and Multianalyte Biosensors. The key components for facilitating the use of LWCs are suitable fabrication methods as well as advanced optical materials. In this paper, we show application of newly developed photocurable hybrid sol-gel materials to the fabrication of photonic devices for telecommunication, optical sensing and biosensing applications. This work will be divided into 2 parts. The first will be devoted to the material development and characterisation. The synthesis of photocurable sol-gel materials will be described and optical properties discussed and correlated to the material structure, with a particular emphasis on the photosensitivity of the materials [1]. The second part will deal with the photo-patterning of the developed thin film materials, employing both single and two photon polymerization (2PP) techniques (Fig. 1), for the fabrication of optical waveguides (Fig. 2) utilized in the development of our photonic LWCs and biosensor platforms [2] (Fig. 3), as well as novel microfluidic systems (Fig. 4). Performances of the developed systems will be discussed and compared with the state of the art. Original three-dimensional structures fabricated by 2PP technique [3,4] will also be presented showing the strong potential of these materials in the development of mechanically stable 3D structures (Fig. 5).

[1] M. Oubaha et al. Journal of Material Science, 46, 2, 2011, 400-408.

[2] M. Oubaha et al,. Microfluidics & Nanofluidic, In Press.

[3] M. Oubaha et al.,Applied Surface Science, 257, 7, 2011, 2995-2999.

[4] A. Ovsianikov, M. Oubaha et al, ACS Nano, 2008, 2 (11), 2257-2262.

2:50pm **PD-6 Vertical Growth of Carbon Nanotubes on Bulk Copper Substrates for Charge Storage Applications**, ***G. Atthipalli*** *(goa4@pitt.edu), R. Epur, Kumta, Y. Tang, A. Star, J.L. Gray*, University of Pittsburgh

Growth of carbon nanotubes (CNTs) on bulk copper foil substrates has been achieved by sputtering an inconel thin film on Cu substrates followed by ferrocene decomposition into iron during thermal chemical vapor deposition (CVD). The inconel film breaks up into islands acting as a catalyst and iron nanoparticles from ferrocene act as an additional vapor phase delivered catalyst. Both inconel and iron are needed for dense and uniform growth of CNTs on the copper substrates. Two hydrocarbon sources investigated were ethanol and xylene to determine the best conditions for growth of CNTs on copper. The results demonstrate the effectiveness of this simple and cost effective method of directly integrating CNTs with highly conductive copper substrates as double layer capacitors for charge storage applications. Electron microscopy, Raman spectroscopy were used to evaluate the morphology and quality of the CNTs. We report the specific capacitance and power density values of the double layer capacitors developed from the CNTs grown directly on copper substrates.

3:10pm **PD-7 Thickness Ratio Calculation of Bi-Layer TiNi Alloys to Enhance Shape Memory Behavior using Stress-Strain Properties of the Individual Thin Films**, ***M. Mohri*** *(nili@ut.ac.ir), M. Nili-Ahmadabadi*, University of Tehran, Iran

Thin film shape memory alloy (SMA) has been recognized as promising material for being used in micro-electro-mechanical-system (MEMS) for a decade. Among various SMAs, NiTi-based alloys have received wide attention due to their ability to generate large recoverable strain. In the present study Ni-Ti thin films have been deposited on NaCl substrates by dc magnetron sputtering source fitted with a 80mm diameter alloy target. In order to obtain a variety of film compositions, several discs of alloy target, prepared by vacuum arc remelting (VAR), were used. Three types of thin films have been deposited; Ti and Ni-rich thin films were separately deposited on NaCl substrate and also a composite layer of $Ni_{45}Ti_{50}Cu_5$ and Ni-rich. The as deposited Ni-Ti thin films were crystallized to change the amorphous structure to a nano-structured material to characterize shape memory and superelastic behaviors. The effect of composition on film structure, transformation temperature and mechanical behavior was studied by using X-ray diffraction (XRD), Scanning electron microscopy (SEM), electrical resistivity and nano indentation. The results of thin films behavior were used to calculate the thickness ratio of be-layer composite NiTi to obtain enhanced shape memory behavior.

3:30pm **PD-8 Novel Geometry Filtered Cathodic Arc Source**, ***P. Sathrum*** *(paul@fluxion-inc.com)*, Fluxion Inc.

A symmetrical and compact filtered cathodic arc (FCA) source that uses no magnet coils is presented. The "Radial Arc" is described and compared to other FCA, including how permanent magnets are used instead of coils. Filter properties such as ion transport efficiency and effectiveness in macroparticle removal are described. Additional features important for usefulness including cathode wear and replacement, and source maintenance are discussed. Deposition rate profiles for titanium and ta-C films are given and show an inherently uniform distribution that requires no beam scanning and a rate that is comparable to unfiltered arc.

Coatings for Use at High Temperature
Room: Town & Country - Session AP

Symposium A Poster Session

AP-1 Preparation and Annealing Study of CrTaN Coatings on WC-Co, *Y.-I. Chen (yichen@mail.ntou.edu.tw),* ***Y.-T. Lin***, National Taiwan Ocean University, Taiwan

To prevent Co diffusion from cemented carbides at high working temperatures, we fabricated CrTaN coatings by reactive direct current magnetron co-sputtering onto 6 wt.% cobalt cemented carbide substrates, to form diffusion barrier layers. The nitrogen flow ratio, $N_2/(Ar+N_2)$, during the sputtering process set at 0.4. The deposition rates of CrTaN coatings, 19 to 25 nm/min, depended on the sputter yield of targets. The CrTaN coatings crystallized into a columnar structure, without heating the substrates during the sputtering process. The CrTaN coatings were annealed at 500, 600, and 700°C for 4 hours in air. We evaluated the performance of the diffusion barrier using both Auger electron spectroscopy depth-profiles and X-ray diffraction techniques. We also investigated oxidation resistance of the CrTaN coatings annealed in air, and under a 50 ppm O_2-N_2 atmosphere, to evaluate the fabricated layers effectiveness as a protective coating for glass molding dies.

AP-2 Microstructural Evolution in NiAl-Cr-Zr Coated Superalloys During High Temperature Annealing and Oxidation, ***J.P. Alfano***, *M.L. Weaver (mweaver@eng.ua.edu)*, The University of Alabama

Nickel-based superalloy components in the hot sections of commercial gas turbine engines are often protected by aluminide coatings due to their ability to function in oxidative and corrosive environments. However, the microstructures of these coated systems are metastable and change in service due to interactions with the environment and interdiffusion with the underlying substrate. The extent of these changes depends critically upon coating microstructure, chemistry, and the environment that the coated component operates in. This paper highlights the influences of chemical composition and post-deposition annealing on the microstructures and properties of NiAl-Zr and NiAl-Cr-Zr overlay bond coatings. In particular, the results indicated that in slightly Ni-rich NiAl-based coatings, coating/substrate interdiffusion and Al-depletion within the coating could be inhibited by increasing the Zr content from 0.3 at.% to 1.0 at.%Zr. However, subsequent additions of 5 at.% Cr to coatings containing 1 at.%Zr, resulted in interdiffusion and Al-depletion levels more similar to low Zr or Zr-free coatings. This paper details the microstructural changes that occur in coated Ni-based superalloys during annealing and/or oxidation at 1050°C as functions of coating chemistry and environment. Results are discussed relative to conventional coating systems.

AP-3 Microstructural Evolution and Thermal Stability of Vertical-Cracked Thermal Barrier Coatings Through Cyclic Thermal Fatigue, ***S.-W. Myoung***, *K.-S. Song, T.-W. Kang, Z. Lu, Y.-G. Jung (jungyg@changwon.ac.kr),* Changwon National University, Korea, *U. Paik*, Hanyang University, Korea

Thermal properties and failure mechanisms of thermal barrier coatings (TBCs) are closely related to their microstructure, which is usually determined by the feedstock powder as well as the spraying condition. Recently, TriplexPro^{TM}-200 system has been launched to offer an advanced TBC performance resulting from higher particle velocity, lower particle oxidation, and higher coating density, compared with the commercial air plasma spray (APS) system using 9MB gun. Therefore, in this study, TBC samples were prepared by TriplexPro^{TM}-200 system using different commercialized powders and the microstructure of TBC was controlled by the reheating the surface of TBC without powder feeding in same equipment. The relatively porous TBC was prepared with METCO 204 C-NS and the relatively dense TBC with METCO 204 NS. The microstructure of the top coat in TBCs was just controlled, and the bond coat with about 300 mm thickness in the both top coats was prepared with AMDRY 962. The cyclic thermal exposure tests were performed at the surface temperature of 1100℃ with the temperature difference of 150℃ between the surface and bottom of sample, with a dwell time of 1 h till 24000 EOH (1143 cycles) or delamination, in a specially designed apparatus. The distance parameter is more effective in creating the vertical cracks than the gun speed, with less and shorter vertical cracks in the relative porous TBC. The hardness values on the sectional plane are gradually changed in the both vertical-cracked TBCs, indicating that those of the relatively porous TBC are changed from 6.5 (interface of the top and bond coats) to 4.2 GPa (surface of the top coat) and those of the relatively dense TBC being changed from 7.8 to 4.5 GP. After the thermal exposure tests, the vertical cracks reach down to the interface of the top coat and the TGO layer in the relatively dense TBC, and the hardness and toughness values are decreased and increased, respectively, in the both TBCs. The both vertical-cracked TBCs show a sound condition without any evidence of delamination, while the relatively dense TBC without the vertical cracks is delaminated within 8000 EOH (381 cycles) or shows an evidence of delamination at the interface of the top coat and the TGO layer after 8000 EOH. Consequently, in the both cases, the TBCs with the vertical cracks are more efficient in thermal durability than those without the vertical cracks, especially in the relatively dense TBC. The relationship between the microstructural evolution and thermomechanical characteristics of the TBCs with and without the vertical cracks is discussed.

AP-4 Effect of Pre-Nickel Plating on the Microstructure and Phase Constitution of Hot-Dipped Aluminide Coating on Mild Steel, ***W.-J. Cheng*** *(d9603505@mail.ntust.edu.tw), C.-J. Wang*, National Taiwan University of Science and Technology, Taiwan

Pre-nickel plated Mild steel was coated by hot-dipping into a molten bath containing pure Al at 670°C . The effect of pre-nickel plating layer on the microstructure and phase constitution of the aluminide layer was investigated by using a combination of scanning electron microscope (SEM), X-ray diffraction (XRD), energy dispersive X-ray spectroscopy (EDS) and electron backscatter diffraction (EBSD). The results showed that the pre-nickel plating layer of 20 µm was dissolved and reduced to 12 µm after hot-dipping for 5 seconds. Also, a continuous layer, composed of Ni_2Al_3 + $NiAl_3$ + $(Fe,Ni)_2Al_9$, formed above the nickel plating layer, while a small amount of $NiAl_3$ phase scatted in the aluminium topcoat. In the aluminide layer after hot-dipping for 60 seconds, a portion of nickel plating layer has consumed, leading to the Ni-Al phases began to transform into $FeAl_3$ and $(Fe,Ni)_2Al_9$. As the dipping time increased, the aluminide layer was composed of minor $FeAl_3$ and major Fe_2Al_5. In comparison with the hot-dipped aluminide mild steel without pre-nickel plating, the phase constitution and the thickness of the intermetallic layer with pre-nickel plating after long-term dipping time are the same as in the intermetallic layer without pre-nickel plating.

AP-5 Non Destructive Assessment by Photo-Stimulated Luminescence of EB-PVD Thermal Barrier Coatings Damaged by Laser Shock Spallation, ***G. Fabre*** *(gregory.fabre@mines-paristech.fr), V. Guipont, M. Jeandin,* Centre des Materiaux - Mines ParisTech, France, *F. Passilly, T. Maffren,* ONERA, France, *A. Pasquet, J.Y. Guedou*, SNECMA Safran Group, France

During the two last decades, plasma Spray and EBPVD TBCs have been intensively used in turbines for aircraft propulsion and power generation. However, interfacial damages due to thermal exposure and oxidation remain not totally understood. Thus, the knowledge on lifetime prediction of TBCs before spallation is still limited. In this work, the laser shock spallation has been applied to generate interfacial defects as those occurring in TBCs during thermal cycling. This method is derived from the LASAT (Laser Shock Adhesion Test) protocole to determine adhesion of ceramic coating. Depending on the laser energy and dimensions of the LASATested coatings (layers thicknesses, laser diameter mainly), it has been evidenced that the circular crack size located at the zirconia-bond coat interface can be easily varied for further non destructive assessments by photo-stimulated luminescence. Thus, different damage areas at bond coat-zirconia interface have been realized without the removal of TBC ceramic top-coat for coated samples with different aging periods of one-hour cycles at 1100°C (0 and 100 cycles). The photo-stimulated luminescence was used as a powerful Non-Destructive Assessment of the damages induced by laser shock through the measure of the released stress in the TGO and the corresponding variation in the photo-excitation of Cr3+ ions within the thermally grown oxide (TGO). The damaged areas were detected by this method and the dimensions were also measured accurately using scanned images obtained by photoluminescence piezospectroscopy. The crack damages were also investigated by visual inspection and SEM cross-sectioned observations for further comparison with actual dimensions of the interfacial defects that were deliberately induced by LASAT.

AP-6 Pore Density Control of Al Thin Films with Process Conditions of Magnetron Sputtering, ***J.-H. Yang*** *(jhyang@rist.re.kr), J.-I. Jeong, S.-H. Jang, H.-S. Park*, Research Institute of Industrial Science and Technology, Korea

Al thin films deposited with magnetron sputtering generally have a columnar structure. The columnar structure of Al films has many pores, which is origin of degradation of substrates. For the prevention of the degradation, the pore density of Al films should be decreased. In this study, the method for decrease of the pore density is suggested. Al thin films are deposited with a magnetron sputtering on cold rolled steel sheets, which the sputtering source is unbalanced magnetron source. The important factor for the decrease of the pore density is the direction and intensity of an external magnetic field by an electromagnet. Forward magnetic field is applied the sputtering source, so that the pore density of Al films increase. On the other hand, reverse magnetic field is applied which decrease the pore density of the film. In the optimum condition, the Al film shows the density of 94.7 % compared with that of bulk Al.

AP-7 Thermal Stability and Corrosion Resistance of AlTiON/CrON Multilayered Coating, ***W.-Y. Ho*** *(weiyuho@mdu.edu.tw), L.-W. Shen, Z.-S. Yang, C.-L. CHang, D.-Y. Wang*, Mingdao University, Taiwan

TiAlN/CrN coatings possess superior hardness, good thermal and chemical stability due to both multi-component constituents and a multilayer structure in nanoscale thickness. To further improve thermal stability and corrosion resistance of (Ti,Al)N/CrN multilayered coatings for aluminium die casting applications, the addition of oxygen into the (Ti,Al)N/CrN multilayered coatings by cathodic arc deposition was investigated. The studied coatings were obtained with dual $Al_{0.75}Ti_{0.25}$ and Cr targets at the O_2 and N_2 mixtured gas flows in this study. The structure of the coating was explored with B1 NaCl type structure in which AlTiN and CrN formed multilayer in the coating. The formation of oxide phases by introducing oxygen to react with Al, Cr and Ti was confirmed by X-ray photoelectron spectroscopy. The higher thermal stability of oxygen-added AlTiN/CrN coating was obtained compared to that of AlTiN/CrN coating. The imersion tests were evaluated in aluminium melt. Compared to AlTiN/CrN, the addition of oxygen into AlTiN/CrN multilayered coatings improved the corrosion resistance. The performance of corrosion resistance is dramatically enhanced as a result of oxygen content in the AlTiN/CrN multilayered coatings.

AP-9 Nano Modified NiCrAlY Coatings for High Temperature Applications, ***S. Sahu***, *A.S. Khanna (khanna@iitb.ac.in)*, Indian Institute of Technology, India

Oxidation behaviour of NiCrAlY powder, blended with nano and micro sized Al_2O_3 and Y_2O_3 was studied to understand the effect of nano oxide powder dispersion. The blended powders were applied on the IN 718 by HVOF technique. The present work compares the oxidation behavior of NiCrAlY dispersed with nano and micro Y_2O_3, Al_2O_3 oxide. Coated samples were characterised by XRD, SEM/EDAX in terms of surface composition, scale cross section and the identification of different phases.The oxidation tests were carried out at 1223K, 1323K, 1423K in air. Oxidation kinetcs were determined from these tests which infer that nano and micro size Al_2O_3 and Y_2O_3 was effective in lowering oxide growth.

AP-11 Thermal Properties Characterization of Gradient $RE_2Zr_2O_7$/YSZ Bilayer Thermal Barrier Coatings Obtained by the APS Method, *G. Moskal,* ***A. Rozmyslowska-Grund*** *(arozmyslowska@gmail.com)*, Silesian University of Technology, Poland

Presented investigations will concern characteristics of the gradient TBC double-layer type $Gd_2Zr_2O_7$ - $ZrO_2Y_2O_3$ (YSZ). The layers were placed on a nickel superalloys type AMS5599 with an bond-coat type NiCrAlY, obtained by the VPS (vacuum plasma spraying) method. Ceramic layers were applied in a result of plasma spraying by the APS method with powders of a general formula $Gd_2Zr_2O_7$ and $ZrO_2Y_2O_3$ obtained by a spray drying method. Four types of samples were prepared. They varied according to volumetric fraction of ceramic powders situated in loaders during APS process ($Gd_2Zr_2O_7$ and $ZrO_2Y_2O_3$ powders volumetric fractions, respectively: 25% - 75%; 50% - 50%; 75% - 25%; 100% -100%).

The last sample with 100% - 100% volumetric fraction - bilayer coating was obteined in different way than others: $ZrO_2Y_2O_3$ layer was applied firstly and than $Gd_2Zr_2O_7$ layer was sprayed on it.

A range of investigations, presented in the paper will comprise:

· evaluation of microstructure of a ceramic layer from a point of view of thickness, quality of a layer and quantity characteristics of cracks and pores architecture;

· evaluation of thermal diffusivity of a ceramic layer within a range of temperature 25-1100°C;

· determination of thermal conductivity of the TBC louble-layer type $Gd_2Zr_2O_7$ - $ZrO_2Y_2O_3$.

Results, presented in the paper, are effects of long-running investigations, carried out by the Department of Materials Science in the Silesian University of Technology, and these investigations concerned heat-resisting coatings and layers type TBC.

Financial support of Structural Funds in the Operational Programme – Innovative Economy (IE OP) financed from the European Regional Development Fund -Project No POIG.01.01.02-00-015/09 is gratefully acknowledged.

AP-12 Characteristics of Microstructural Phenomena in TGO Zone of TBC Layer of $Re_2Zr_2O_7$ Type, *G. Moskal,* ***R. Swadźba*** *(rswadzba@gmail.com)*, Silesian University of Technology, Poland

The scope of this study covers characterization of the microstructure and chemical composition of the TGO zone in the TBC layers isothermally annealed at 1100°C in air or argon. Conventional layers based on 8YSZ powders and a new type of layer based on a zirconate powder $Gd_2Zr_2O_7$ with a pyrochlore structure were studied. Annealing proceeded over 2 or 10 h in argon, and over 10 h in air. The samples were microstructurally analyzed using scanning microscopy and an assessment of the chemical composition of the micro-areas was conducted. The thickness and structure of the oxide zone was determined for the different annealing atmospheres and annealing times. TBC coatings were obtained by the APS method, in which the standard parameters for the spraying process were applied. Analysis showed that the TGO zone thickness of the new type of layer was approx. 50% smaller in comparison with the thickness of the conventional TBC (YSZ). In both cases, the main ingredient of this zone was aluminum oxide. The thickness of the argon-annealed oxide layer was larger than the thickness of the air-annealed layer, and complex oxides formed with nickel and chromium on the outer parts of the TGO in the second case.

Financial support of Structural Funds in the Operational Programme – Innovative Economy (IE OP) financed from the European Regional Development Fund -Project No POIG.01.01.02-00-015/09 is gratefully acknowledged.

AP-13 Comparison of Surface Quality, Machining Time in P-20 Steel and Alumold in the Manufacture of Thermoplastic Injection Mold, ***W. Mattes*** *(mattes@unerj.br)*, SENAI-SC, Brazil

Analysis of surface quality, strength and time in machining using alumold and steel P – 20 (WNr 1.2312) in the manufacture of thermoplastic injection mold where the two materials were compared and the same techniques using the HSM. Alumold Forged is a high quality, high strength aluminum alloy intended for the plastic forming industry and for other tooling applications. With its high strength and surface hardness it is suitable for polishing and texturing and is wieldable. It is supplied in the forged, heat treated, quenched, cold compressed and aged condition. Alumold Forged possesses better than normal mechanical properties in all sizes, excellent thermal conductivity and very good machinability together with good stability. Within a project a test stand for the direct measurement of dynamic cutting force coefficients was designed and implemented. Test results the need for more complex dynamic cutting force coefficients was designed and implemented. Test results show the need for a more complex dynamic cutting force model in order to reach an acceptable level of accuracy in stability simulation for HSC machining operations.

AP-14 Phase Transformation of MoS2-Nb Composite Coated Films at the High Temperatures, ***I. Efeoglu*** *(iefeoglu@atauni.edu.tr),* Atatürk University, Turkey*, -. Altintas,* Bogazici University, Turkey*, E. Arslan,* Atatürk University, Turkey*, O. Baran,* Erzincan University, Turkey*, D. Ugur*, Bogazici University, Turkey

The crystalline transformation of MoS2-Nb composite films prepared by magnetron sputtering as a function of high temperature vacuum environment has been studied using X-ray diffraction. Crystallization heat treatments were carried out in situ heat treatment. Variations in the transformation as function of the temperature for each sample were attributed to differences in the elemental concentration in the composite structured films.

AP-15 Cyclic Oxidation Behavior of HVOF Bond Coatings Deposited on La- and Y-doped Superalloys, ***M.A. Bestor*** *(bestorma@ornl.gov), J.A. Haynes, B.A. Pint*, Oak Ridge National Laboratory

One suggested strategy for improving the performance of thermal barrier coating (TBC) systems used to protect hot section components in gas turbines is the addition of low levels of dopants to the Ni-base superalloy substrate. For the more aggressive environment expected for coal-derived, synthesis gas-fired turbines, this strategy may be effective in retaining TBC durability. To quantify the benefit of these dopants, coupons of three commercial alloys with different Y and La contents were coated with a NiCoCrAlYHfSi bond coating by high velocity oxygen flame spraying. Coupons were oxidized in cyclic exposures at 1050°, 1100° and 1150°C; and the oxidation rate and alumina scale adhesion were compared in an effort to better understand the benefit of superalloy dopants. In addition, some of these substrates will be spray coated with yttria-stabilized zirconia to determine the effect of dopants on coating lifetime.

This research was sponsored by the U.S. Department of Energy, Office of Coal and Power R&D, Office of Fossil Energy, (R. Dennis program manager).

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

Symposium B Poster Session

BP-2 Oxygen Impurities in Ti-Si-N System are Hindering the Phase Segregation, Formation of Stable Nanostructure and Degrading the Cutting Performance of Tools Coated with the Nanocomposites, ***S. Veprek*** *(stan.veprek@lrz.tum.de), M. Veprek-Heijman,* Technical University Munich, Germany*, M. Jilek,* SHM Ltd., Czech Republic*, M. Piska,* Brno Technical University, Czech Republic*, X. Zeng,* Singapore Inst. of Manufacturing Technology, Singapore*, A. Bergmaier,* Universität der Bundeswehr, Germany*, Q.F. Fang*, Chinese Academy of Sciences, China

We have shown earlier, that oxygen impurities of >3000 atomic ppm strongly degrade the hardness of the nc-TiN/a-Si_3N_4 nanocomposites. Here we show that such impurities also hinder the phase segregation and formation of stable and strong nanostructure consisting of 3-4 nm size TiN nanocrystals "glued" together by about 1 monolayer thick interfacial Si_3N_4 -like layer, thus apparently stabilizing the solid solution at high temperature of ≥900°C, which has been reported by other researchers. At the impurity content of only few hundred at. Ppm, the segregation is completed, and stable nanostructure formed at temperature of ≤550°C, whereas with increasing oxygen impurity content the temperature needed for the segregation strongly increases. By decreasing the impurity content from 2000-3000 ppm down to about 700-1000 ppm in an industrial PVD coating unit, the life time of cutting tools has been increased by about a factor of ≥2. The results to be presented will underline the need for the improvement of the purity of the nanocomposite coatings applied in the industry, as well as those used for fundamental studies in academia.

BP-3 Structural and Mechanical Properties of Multilayered ZrN/CrAlN Coatings Synthesized by a Cathodic-Arc Deposition Process, ***T.-H. Yang****, Y.-Y. Chang (yinyu@mail2000.com.tw), C.-Y. Hsiao*, Mingdao University, Taiwan

Multilayered ZrN/CrAlN coatings with superlattice structure were deposited by using cathodic-arc evaporation with plasma enhanced duct equipment. Zirconium and $Cr_{0.3}Al_{0.7}$ alloy (30/70 at.% ratio) cathodes were used for the deposition of ZrN/CrAlN coatings. During the coating process of multilayered ZrN/CrAlN, ZrN was deposited as an interlayer. The total cathode current of both Zr and CrAl targets was controlled at 140 A. With different cathode current ratios ($I_{[CrAl]}/I_{[Zr]}$) of 0.75, 1.0, and 1.33, the deposited multilayered ZrN/CrAlN coatings possessed different chemical contents and periodic thicknesses. The effect of alloy content (Al, Cr, and Zr) and layer thickness ratio of CrAlN/ZrN on the mechanical properties of ZrN/CrAlN coatings were investigated. From the X-ray diffraction (XRD) and high resolution transmission electron microscopy (HRTEM) analyses, the crystal structure of CrAlN layer in the ZrN/CrAlN multilayers has a metastable cubic lattice structure, matching coherently with the ZrN layer. The periodic thickness and layer thickness ratio of CrAlN/ZrN increased with I[CrAl]/I[Zr] cathode current ratio. Hardness and Young's modulus of the deposited coatings were determined by nano-indentation. The multilayered ZrN/CrAlN coating with layer thickness ratio of CrAlN/ZrN=1.4 exhibited the highest H^3/E^{*2} ratio value of 0.338 GPa, indicating the best resistance to plastic deformation, among the studied ZrN, CrAlN and multilayered ZrN/CrAlN coatings.

BP-4 Evaluation of Depth Profile of Residual Stress in a TiN Thin Film, ***C.-J. Lan****, J.-H. Huang (jhhuang@mx.nthu.edu.tw), G.-P. Yu*, National Tsing Hua University, Taiwan

Residual stress plays an important role on structure and properties of thin films. Most measurement methods determine the average residual stress in thin film, but not the depth profile of stress along thickness. In this study, the depth profile of residual stress of a titanium nitride (TiN) thin film was established using grazing incident X-ray diffraction (XRD) accompanied with calculation using layer-by-layer method. TiN films were deposited by unbalanced magnetron sputtering (UBMS). Laser curvature technique was used to measure the residual stress and conventional sin2ψ XRD method was employed to determine the strain components in the thin films. By combining these two techniques, the X-ray elastic constants (XECs), Young's modulus and Poisson's ratio, of the thin films can be obtained. A modified sin2ψ method, cos2αsin2ψ method, with asymmetric Bragg–Brentano (B-B) geometry using grazing incident X-ray was adopted to measure the residual stress at different depth. The cos2αsin2ψ method has the advantages of increasing diffraction volume and reducing anisotropic effect of thin film specimens. The XECs determined by the X-ray and laser curvature combining technique can be applied in the cos2αsin2ψ method to obtain the residual stress at different depth by appropriately changing the grazing angles γ (α = θo-γ, where θo is the diffraction angle of the chosen diffraction plane.). Then simplified layer-by-layer method was used to establish the depth profile of residual stress in the TiN thin film. The stress gradient in the thin film was compared with that modeled by Finite element method.

BP-5 Measurement of Fracture Toughness on TiN Thin Films*, **A.-N. Wang**, G.-P. Yu, J.-H. Huang (jhhuang@mx.nthu.edu.tw)*, National Tsing Hua University, Taiwan

This research was in an attempt to develop a new method without applying external stress for measuring fracture toughness of transition metal-nitride (TMN) thin films. TMN thin film was selected to be the model material, owing to its well-characterized mechanical properties and appropriate elastic isotropy. At present, there has been no standard methodology or test procedure for assessing the fracture toughness of hard coatings. Previous literatures have proposed various approaches on the measurement of fracture toughness, which can be divided into two categories: stress based or energy based. However, those methods need to design special specimen geometry because of the requirement in producing valid pre-cracks, and thus the substrate effect cannot be eliminated. In addition, special stages are often needed to externally apply stress, which increases the difficulty of the test methods. TiN thin films deposited by PVD methods normally have high residual stress which can be controlled by adjusting deposition parameters and measured nondestructively. Instead of externally applying stress, the residual stress was utilized in the assessment of fracture toughness. From Griffith 's criterion, energy stored in the film due to elastic mismatch strain can be released by the formation of cracks. The difference in stress states before and after crack initiated was used to evaluate the average energy release rate, from which fracture toughness can be calculated by fracture mechanics. This method involved residual stress measurement by laser curvature technique and elastic modulus measurement by nanoindentation according to ISO 14577-4:2007. The Poisson's ratio of single-crystal TiN was used. The results were compared with those obtained from other techniques and the strong and weak points of this method were discussed.

BP-6 Nanocomposite PVD Coatings for Milling of Hardened Steels and Cast Ion, ***P. Immich*** *(PImmich@lmt-fette.com), U. Schunk, U. Kretzschmann*, LMT Fette, Germany

The ever increasing demand for higher productivity in manufacturing requires advanced PVD hard coatings. The coatings can be tailored to exhibit for example higher hardness and / or enhanced oxidation resistance and good adhesion. One such way to influence coating properties is addition of silicon to a conventional TiAlN coating made by arc PVD. As silicon cannot be easily incorporated into the cubic lattice a so-called nanocomposite coating with special properties is formed. The silicon content of coating can be varied in a wide range resulting in different mechanical properties and coating structure. The properties of the deposited films were analyzed by common thin film techniques revealing hardness, Young´s modulus and coating adhesion. As a result from theses investigations a nanocomposite coating with excellent coating properties like a high hardness and a good adhesion was developed and deposited onto special carbide shank tools. These tools are tested in cutting experiments in, hardened steel (> 54 HRC) and cast iron, comparing conventional state of the art coatings and the developed nanocomposite coating. The developed coating shows an increase of tool with a significant reduction in the tool wear during the milling operation.

BP-7 An Experimental Trial of Prediction and Control Technology of Film Properties by a Numerical Model in Vacuum Vapor Deposition*, J.-I. Jeong (jijeong@rist.re.kr), J.-H. Yang,* ***H.-S. Park****, S.-H. Jang*, Research Institute of Industrial Science and Technology, Korea

In vacuum vapor deposition techniques such as physical vapor deposition (PVD) and chemical vapor deposition (CVD), the film properties are strongly depending on the process conditions. It is customary and is considered to be reasonable that the deposition system be controlled by the ordered sequence with pre-determined parameters. The process conditions were fixed by the operator and the values are determined prior to deposition. After the coating, the film properties are evaluated and then the process conditions are changed to obtain optimum film properties. Generally, this optimization process is troublesome and it takes much time to have optimum process conditions, especially for complex films having multilayer or multistep structures with so many parameter values.

In this study, it has been tried to predict and obtain best coating quality by a numerical model. The model was based on the data obtained from the experimental values and interpolation and/or extrapolation method was employed. The synchronization of the system, i.e., the unification of the difference between one system and the other was fulfilled on a trial basis by diagnostic equipments such as Langmuir probe and/or Optical Emission Spectroscopy (OES).

The first preliminary trial was manifested with TiN coating on the stainless steel plate. The brightness was measured with two variables of nitrogen flow rate and substrate temperature. The numerical equation was derived from the measured data according to the variation of the two variables. The interpolation method was used to obtain the best curve fitted to derive the numerical equation. With this equation the system was operated by inputting the user-defined brightness value. The hit rate which signifies the accuracy of brightness prediction turned out to be more than 70%.

BP-8 The Effect of Laser Annealing on the Crystal Structure of Magnetron Sputtered Alumina Thin Films, ***H. Abu-Safe*** *(husam.abusafe@lau.edu.lb),* Lebanese American University, Lebanon*, F. Rawwagh,* Yarmouk University, Lebanon*, M. Tabbal,* American University of Beirut, Lebanon*, M. Roumie*, the National Council for Research, Lebanon

The effect of laser annealing on the crystal structure of alumina thin films has been investigated. The crystal structure of the films is basically determined by the deposition conditions during the process. Gibbs free energy stored in the various films is changed with an external thermal deposition. The thermal deposition is established using a cw Ar ion laser system. Within certain thermal limits, an exothermic process in the crystal planes is activated leading to partial release of the internal energy in the fabricated films. The crystal structure of the processed films is "*healed*" to the minimum energy status which will lead to the alpha phase. Three sets of alumina thin films have been prepared for this study using an inverted cylindrical magnetron sputtering system with an unbalanced magnetic field. All sets were laser annealed at different energy densities and annealing times. The crystal structure before and after annealing is investigated and the stoichiometry of the fabricated films are reported.

BP-9 Wear and Corrosion Properties of TiSiN and TiSiN/CrN Coatings by Cathodic Arc Deposition, *W.-Y. Ho (weiyuho@mdu.edu.tw),* ***C.-H. Hsieh****, Y.-Y. Chang, C.-L. CHang, C.-J. Wu*, MingDao University, Taiwan

In a thermodynamically favored process, TiSiN ternary system segregates into the two binary compounds which are usually formed by nanocrystalline TiN embedded in a matrix of amorphous SiN_x. The influence of the Si content in the coatings on the

mechanical properties and tribological behaviors of the TiSiN coatings were systematically studied by several researches. Nanoindentation result shows that the hardness and Young's modulus of the TiSiN coatings increase with increasing Si content in the coatings. TiSiN coatings exhibit an increase in the friction coefficient with an increasing Si content in the coatings.

The advantage of TiSiN coating is feasible for machining applications owing to its dense, highly adhesive, high hardness properties. However, TiSiN coating, in general, shows poorer performance than TiN in the case of low sliding speed or interrupted cutting process due to its brittleness and high friction coefficient. Previous study shows that TiSiN/TiAlN were dependent on lamellae thicknesses in film structure, resulting in improved mechanical, wear and corrosion properties. The similar study presented that the mechanical and tribological property can be improved by the design of multilayered TiSiN/CrN coating. It showed the multilayered TiSiN/CrN coating possessed excellent resistance to plastic deformation as compared with the monolayered TiSiN. However, the effect of the deposition parameters on the properties of TiSiN/CrN coating was not studied in combination of bias voltage and multilayer structure.

In this study, a monolayered TiSiN and a multilayered TiSiN/CrN coatings deposited with different bias voltages were synthesized by a cathodic arc deposition process. TiSi (80/20 at.%) and chromium targets were used for the deposition of TiSiN and multilayered TiSiN/CrN coatings. The performance of the coating was evaluated by microstructure, ball-on-disc wear test and corrosion test.

BP-10 Properties of Carbon-Based Coatings on Injection Mold Steel Prepared by Nitriding and PCVD Hybrid Process, ***K.H. Lee*** *(k-hwanglee@rist.re.kr), J.W. Park, K.S. Park, D.W. Kim*, Research Institute of Industrial Science and Technology, Korea

Industrial application of carbon-based coatings has been paid attention owing to their excellent mechanical properties, such as high hardness, elastic module and low friction coefficient. In recent, exciting ongoing researches try to deposit carbon-based protective film on automobile engine parts, tools and molds taking into account not only high hardness, but also solid lubricating properties. On the other hand, it is well known that carbon-based coatings have a low adhesion to metal surface due to their high internal stress. It is a big problem to apply on automobile, tool and mold industrials. It is also difficult to increase a film thickness.

In this study, carbon-based coatings were prepared on injection mold steel and silicon wafer by plasma chemical vapor deposition after plasma nitriding in the same chamber as continues process. Plasma nitriding process was performed under 0.1 torr of pressure using N_2 and H_2 gases with a pulsed DC bias voltage of -400V at 400°C for 3 hours. Carbon-based coatings were fabricated under pressure of 0.05 and 0.1 torr with CH_4 gas, temperature of room temperature, 100°C and 150°C, and bias voltage of -400V, -500V and -700V, respectively. In case of nitriding and PCVD hybrid process, the temperature of chamber was controlled to test condition after plasma nitriding process. Hardness was evaluated by nanoindentation and low load vickers hardness tests. Friction coefficients against a SUJ2 (JIS) steel ball were measured by tribometer (ball-on-disk) with load of 5 N under humidity of 56 to 76%. Chemical bonding states were investigated by X-ray photoelectron spectroscopy and Raman spectrometry. Surface morphology was observed by atomic force microscopy.

Several types of samples were prepared. The sample (#1) of plasma nitriding without carbon coating is showed above two times higher hardness than the sample without substrate (KP4). Hardness for the sample(#2) prepared by PCVD carbon coating shows 1224 Hv. The sample(#3) prepared by nitriding and PCVD hybrid process with carbon coating shows lower hardness than that of #2. It is considered that hardness is affected the nitrided substrate owing to overly thin film thickness. Friction coefficient of samples showed about 0.4 for sample #1, 0.3 for sample #2, 0.15 for sample #3. Friction coefficient for sample #2 shows the lowest in initial stage, but it is gradually increased to 0.3, and then stabilized to the end of the test. It is considered that coating delamination occured from substrate. This study will be discussed on the properties of carbon-based coatings injection mold steel prepared by hybrid process, and designing layers and complex materials.

This work was financially supported by the grant from the Industrial Strategic Technology Development Program, Republic of Korea.

BP-13 Tetrahedral Amorphous Carbon Tetrahedral Amorphous Carbon Deposited by Filtered Cathodic Vacuum Arc Bombarded by Argon Ions, ***E.F. Motta*** *(edimotta@if.unicamp.br), G.A. Viana, D.S. Silva, A.D.S. Cortês, F.C. Marques*, Universidade Estadual de Campinas, Brazil

The effect of argon bombardment in tetrahedral amorphous carbon (ta-C) deposited by the filtered cathodic vacuum arc (FCVA) technique is investigated. The films were prepared with 5 ms current pulses of 190 A at a frequency of 3 Hz. The deposition substrate was polarized in the 0 to -500 V bias voltage range. The density of the films, also determined by RBS, was in the 2.5 to 3.0 g/cm^3 range, depending on the substrate bias voltage. The stress of the films (up to about 10 GPa) was determined by the bending beam technique. Nanohardness measurements were performed indicating that the films prepared in the 100-200 bias voltage is about 50 GPa. Argon gas was incorporated in a series of films using an ion gun source to simultaneously bombard the films with a beam of argon ion with energy in the 0-180 eV range. Argon concentration in the films was determined by RBS measurements. A study of argon effusion, realized from room temperature up to 1000 ºC, shows that the structure of the films depends on the bombardment energy of the argon ions. It was observed that the stress reduces significantly as a function of the effusion temperature. Raman measurements were used to investigate the structure of the films as a function of the bias voltage and annealing temperature.

BP-14 Thermal Stability of V-Al-C Thin Films Grown by DC Magnetron Sputtering Using a Multi-component Target, ***Y. Jiang*** *(yan.jiang@mch.rwth-aachen.de), R. Iskandar, T. Takahashi, J. Zhang, M. to Baben, M. Joachim, J.M. Schneider*, RWTH Aachen University, Germany

V-Al-C thin films were deposited on Al_2O_3 (11-20) substrate at 500°C by DC magnetron sputtering using a hot-sintered multi-component target with 2:1:1 MAX phase-like composition. TEM and XRD data suggest that hexagonal Al-containing vanadium carbide solid solution was formed. The films exhibited a strong basal plane texture. The lattice parameter of the hexagonal solid solution was dependent on annealing time and temperature: the c lattice parameter of $V_2(Al)C$ decreased by 3.5 % after annealing for 1 hour at 750°C as compared to the as deposited film. Meanwhile, the formation of V_2AlC MAX phase was observed at 650°C and a phase-pure V_2AlC thin film was obtained at 850°C. Previously, the formation of phase-pure V_2AlC thin films was reported at 750°C, suggesting that surface diffusion is affecting the structure evolution of V_2AlC thin films at low substrate temperatures.

BP-15 The Effect of Composition on the Structure, Mechanical Properties, and Thermal Stability of Sputter Coated Ternary Chromium-Molybdenum-Nitride Coatings, ***Y. Zou*** *(yujiaoz@uab.edu)*, University of Alabama, Birmingham

Hard nitride coatings of the group VIB transition metals are increasingly used in a wide range of tribological applications to improve performance and to extend the life of metal cutting, drilling, and forming tools, as well as bearings and various machine parts. Among the nitrides of group VIB elements, binary CrN and MoN have been well studied. CrN has excellent corrosion resistance under severe environment conditions, superior oxidation resistance, and good wear resistance; MoN has been found to have many unique physical and mechanical properties such as high hardness, low solubility in non-ferrous alloys and low friction, etc. As a result, ternary Cr-Mo-N coatings could have superior properties tailored through appropriate combinations of CrN and MoN.

We have prepared ternary Cr-Mo-N coatings with different compositions on Si wafers by using a dual rf-magnetron sputtering system with Cr and Mo targets and nitrogen as reactive gas. The metal target bias voltages were varied from -500 V to -900 V which allowed to preparing the ternary layers with Cr/Mo ratios in the range from 1/3 to 3/1. Binary CrN and MoN coatings were also prepared under similar conditions for comparison. The resulting coatings had up to 1.8 micron thickness and were well adherent to the substrate. The hardness, surface morphology, microstructure, and composition were studied by nanoindentation, SEM, AFM, XRD, and XPS, respectively. All coatings were smooth and nanocrystalline with mean grain size 15-20 nm and showed single XRD-observable phase with the characteristic XRD peaks varying between those of CrN and MoN depending on the composition. The hardness and Young's modulus were found in the range of 9.0 - 16 GPa and 120 - 215 GPa, respectively, with larger values observed for Mo-richer layers. To investigate the effect of thermal treatment on the microstructure and mechanical properties, the samples were annealed in air at temperatures up to 700 °C for 1 hour. The thermal stability of the coatings was found to increase with a larger amount of Cr in the ternary system. The MoN coating was completely oxidized after annealing in air at 600 °C for one hour, whereas the ternary Cr-Mo-N coatings with Cr content more than 75 at.% survived under up to 700 °C without cracking or delamination. The final result of the annealing was Cr_2O_3 as main crystalline phase. However, the hardness was increased at intermediate annealing temperatures while the coatings maintained their initial structure.

This work has been supported by the U.S. National Science Foundation Grant #DMR-0806521 and the Regional Council of Burgundy, France.

BP-16 Oxidation Resistance and Microhardness of (Ti,Al,Si)N/(Cr,Al,Y)N Nano-Multilayered Film, ***T. Mori*** *(ssznogg9@yahoo.co.jp), K. Yoshiwara, M. Takahashi,* Keio University, Japan, *T. Watanabe,* Kanagawa Industrial Technology Center, Japan, *T. Suzuki*, Keio University, Japan

In the field of hard coatings, oxidation resistance and high hardness of the coatings are among the main concerns. Incorporation of yttrium into ceramics has become an attractive method to impart improved mechanical and chemical properties to the ceramics. Multilayered structure of the coatings has also attracted much attention as an effective approach to obtaining improved properties. We have reported superior oxidation resistance of (Cr,Al,Y)N compared to (Cr,Al)N and improved mechanical and chemical properties of (Ti,Al,Si)N/(Cr,Al)N multilayered films.

In this study, we synthesized nano-multilayered (Ti,Al,Si)N/(Cr,Al,Y)N films and investigated their oxidation resistance and microhardness. The films were deposited on Si or WC-Co substrates by cathodic arc ion plating (AIP) method using TiAlSi and CrAlY alloy targets. The two nitrides, (Ti,Al,Si)N and (Cr,Al,Y)N, were deposited alternately on the substrates and the multilayer period was controlled by varying the rotation speed of the substrates from 2.5 to 5.0 rpm. Microstructure of the films was investigated under scanning electron microscope (SEM) and transmission electron microscope (TEM). The microhardness was measured using a conventional micro-Vickers hardness tester. For the evaluation of the oxidation resistance, X-ray diffraction (XRD) and glow discharge optical emission spectrometry (GDOES) were performed to identify oxide layers of the films before and after annealing at 900ºC and 1000ºC for 1 hour.

The microhardness of (Ti,Al,Si)N/(Cr,Al,Y)N film was about 33 GPa, which was higher than the value calculated based on the rule of mixtures. Some metal oxide peaks were observed for (Ti,Al,Si)N or (Cr,Al,Y)N films annealed at 900ºC and 1000ºC, while no peaks indicating metal oxide were observed for the (Ti,Al,Si)N/(Cr,Al,Y)N films. These results demonstrate that the (Ti,Al,Si)N/(Cr,Al,Y)N multilayered films possess highly improved oxidation resistance with higher hardness compared to monolayer films, which indicates that the multilayered films presented here could be a suitable candidate for cutting tools.

BP-17 Evaluation of Ti_3SiC_2 Coatings Deposited by HTCVD from Methyltrichlorosilane and Titanium Tetrachloride, *A. Claudel (aclaudel@acerde.com), S. Luca, R. Martin, P-O. Robert, D. Pique,* ACERDE, France, *M. Morais, E. BLANQUET,* ***M. Pons***, SIMAP, France

MAX phases received great interest the last years due to a combination of metallic and ceramic properties: they are very good thermal and electrical conductors and are easily machinable. They exhibit a great interest for electrical contacts and also for machining tools.

Compared to PVD techniques (such as magneton sputtering or PLD) which are largely adopted for MAX phases thin films deposition, it seems to be more difficult to obtain single –phase Ti_3SiC_2 by CVD techniques. Few studies on the direct deposition of Ti_3SiC_2 coating by CVD using $TiCl_4$ – $SiCl_4$-CCl_4 (or CH_4)-H_2 system are reported. Ti_3SiC_2/SiC multi layer coatings were fabricated by reactive CVD (RVCD) using the reaction between a gas mixture ($TiCl_4$/H_2) and solid SiC.

In this paper we present the first study on the fabrication of the Ti_3SiC_2 MAX phase coatings by High Temperature Chemical Vapor Deposition (HTCVD). Experiments have been conducted (using Methylchlorosilane (MTCS) and Titanium Tetrachloride ($TiCl_4$) as reactants (with hydrogen as carrier gas) from 1200°C to 1350°C, with different values of $TiCl_4$ to MTCS ratio and of the dilution coefficient $\alpha = Q(H_2)/(Q(MTCS) + Q(TiCl_4)$

Thermodynamic calculations performed on this system in the temperature range are compared to the experimental results.

The composition of the deposited films was analysed using X-ray diffraction technique and WDS (Castaing microprobe). SEM (Scanning Electron Microscopy) and TEM (Transmission Electron Microscopy) were used to observe the coatings microstructure. It was found that nearly pure Ti_3SiC_2 was deposited at 1300°C with a high dilution coefficient of the reactants in hydrogen.

BP-18 Annealing Effect on Microstructure and Mechanical Properties of Titanium Nitride Thin Film, *S.-C. Her (mesch@saturn.yzu.edu.tw),* ***W. N. Lin****, C.-L. Wu*, Yuan Ze University, Taiwan

Titanium Nitride (TiN) coatings with high surface hardness, good wear and corrosion resistance, low friction coefficient have been widely used in many applications such as a hard coating of cutting tool, a diffusion barrier layer. In this work, TiN thin films were deposited by D.C. magnetron sputtering process on SUS 304 steel substrate. The effects of postdeposition annealing on the microstructure and mechanical properties of TiN thin films were studied in details using atomic force microscopy, potentiostat and nanoindentation test. The TiN films were annealed at temperatures ranging from 100ºC to 300ºC in steps of 100ºC by using thermal annealing equipment in air for 80 minutes. The thicknesses of the films measured by surface profiler were decreased from 181nm to 137nm as the annealing temperatures increasing from 100ºC to 300ºC. The surface roughnesses of the films observed by atomic force microscopy were decreased from 3.83nm to 2.43nm as the annealing temperatures increasing from 100ºC to 300ºC. The corrosion rates of the films measured by a potentionstat in 0.5 molar H_2SO_4 solution were decreased from $8.57x10^{-2}$ mmPY to $4.59x10^{-2}$ mmPY as the annealing temperatures increasing from 100ºC to 300ºC. The increase in the corrosion resistance is attributed to the increase in hardness and modulus of the film with the annealing temperature. Atomic force microscopy image of the film revealed fine-grained morphology for the TiN annealed at higher temperature. Experimental results showed that the mechanical properties of TiN films could be significantly improved by the annealing process. The control of annealing process is proved to be critical for the improvement of the TiN film performance.

BP-19 Texture and Magnetic Properties of Electrodeposited FePd Films, ***H.-P. Lin****, J.-C. Kuo (jckuo@mail.ncku.edu.tw)*, National Cheng Kung University Taiwan

The preferred orientation (texture) and magnetic properties of electrodeposited FePd films were investigated using electron back-scatter diffraction (EBSD) and vibrating sample magnetometer (VSM). Fe-Pd films were electrodeposited on brass and Cu (001) substrates using an alkaline electrolyte which was composed of Fe sulfate, Pd chloride and 5-sulfosalicylic acid and ammonium sulfate. The potential for the electrodeposition process was varied from -0.9V to -1.1V. The chemical compositions of the deposited films were analyzed using EDS, and the crystallographic structures of deposited films were characterized using XRD, TEM and EBSD.

BP-20 Effect of Oxygen in Aerosol Assisted Chemical Vapor Deposition of TiO_2 Using Titanium tetra-*iso*-propoxide/acetylacetone Solutions., ***F. Maury*** *(francis.maury@ensiacet.fr), D. Duminica*, CIRIMAT CNRS-INPT-UPS ENSIACET, France

Functional titania thin films have been deposited on various substrates under atmospheric pressure to produce self-cleaning surfaces by aerosol assisted chemical vapor deposition (AACVD). Titanium tetra-*iso*-propoxide (TTIP) was used as titanium source in solution with acetylacetone (acac). The influence of an oxygen partial pressure has been investigated in the temperature range 723-923 K. The growth rate increases by 10-40 % in presence of O_2 using a 1.5 M TTIP/acac solution. The films grown at 773 K on Si and glass substrates in presence of O_2 using pure TTIP are single phased (anatase structure) while those synthesized without O_2 exhibit a low proportion of rutile. By contrast, always at 773 K, the presence of O_2 favors the formation of rutile for the films grown on steel. Without addition of O_2 the C content of the films is high and it was found to increase with the deposition temperature. It essentially originates from the acac solvent. The C contamination decreases in presence of O_2. The by-products of the growth process were analyzed by IR and NMR to elucidate the role of O_2 in the mechanism. When oxygen partial pressure is used the formation of CO_2 at the expense of propene gives evidence for a mechanism of combustion in addition to pyrolysis. The hydrophilicity of the layers increases with the O_2 partial pressure. The wettability is not improved by UV irradiation when acac solvent is used in the AACVD process likely because the photocatalytic behavior of these layers is not efficient.

BP-21 Cylindrical Magnetrons Sputter Deposition of Ta on Carbon Steels using DC Magnetron Sputtering, HIPIMS and MPPMS, *R. Wei (rwei@swri.org)*, Southwest Research Institute, ***S. Lee***, *M. Riley*, US Army ARDEC Benet Labs

In this paper, we present the results from a study in which Ta was sputter deposited on the inner surface of tubes of carbon steels using various cylindrical magnetron sputtering processes. The inner surface of cylinders often requires protection from erosion and corrosion from high temperature chemicals. Currently electroplated Cr is applied for protection. To reduce and eventually eliminate electroplating for this application, cylindrical magnetron sputtering (CMS) driven by a DC power supply has been pursued for a number of years. Pulsed DC power supplies that promise to deliver extremely high peak power have been used in conventional planar magnetron sputtering, and the resultant films are proven to be significantly better in microstructural characteristics and tribological performance than those produced using standard DC power supply. In the current study, three sputtering methods were used to deposit Ta on the inner surface of cylinders (100 mm in diameter by 300 mm long) made of carbon steels 1018 and A723. These three sputtering methods include DC magnetron sputtering (DCMS), high power impulse magnetron sputtering (HIPIMS) and modulated pulsed power magnetrons sputtering (MPPMS). Carbon steel 1018 was used for the initial study; then thick Ta coatings were deposited on A723 steel. After the deposition, SEM, XRD, AFM, microhardness, Rc indentation, and scratch test were performed to understand the coating microstructure including the phase formation and transformation, and mechanical properties including the coating adhesion and internal stress. It has been observed that all coatings produced by these three techniques are dense with fairly good adhesion. The coating internal stress is similar for both DCMS and HIPIMS and increases with the coating thickness. Under the same average power, the HIPIMS process resulted in a similar deposition rate as the DCMS, in contradiction with the results obtained in the planar magnetron sputtering. This paper will present the detailed microstructural and mechanical characterization results.

BP-22 Effects of Nitrogen Ratio on Resistive Switching Characteristics of Titanium Oxynitride Thin Films by DC Reactive Magnetron Sputtering, *L.-C. Chang (lcchang@mail.mcut.edu.tw), K.-H. Chang,* Ming Chi University of Technology, Taiwan, ***K.-H. Liu***, Chang Gung University, Taiwan, *H.-J. Tsai, W.-Z. Wang*, Ming Chi University of Technology, Taiwan

$Ru/TiN_xO_y/Ru$ structures were prepared by dc magnetron sputtering. The resistive switching characteristics of $Ru/TiN_xO_y/Ru$ structures were investigated as a function of nitrogen partial pressure during TiN_xO_y deposition. Reproducible resistive switching characteristics were observed in TiN_xO_y thin films deposited at N_2/O_2 ratios of 2.0, 2.5, and 3.0. The conduction mechanisms in high and low resistance states are dominated by space-charge-limited conduction and ohmic behavior respectively, which suggests that resistive switching behaviors in such structures are related to filament formation and rupture. It is also found that the reset current decreased as nitrogen partial pressure increased, due to the variation of oxygen vacancy concentration in the TiN_xO_y thin films.

BP-23 Plasma Diagnostics for Pulsed-dc Plasma-Polymerizing Para-Xylene using QMS and OES, *C-.M. Chou,* Feng Chia University & Taichung Veterans General Hospital, Taiwan, *C.-C. Chuang, C.-H. Lin,* Feng Chai University, Taiwan, ***C.-J. Chung*** *(cjchung@seed.net.tw),* Central Taiwan University of Science and Technology & Taipei Medical University, Taiwan, *J.-L. He*, Feng Chai University, Taiwan

Following the successful demonstration of our work on plasma-polymerized para-xylene (C_8H_{10}, C_8H_9, C_7H_7, C_6H_5, CH_3, $H_2(H_3C$ -C_6H_4-CH_3, PPX) thin films for biomedical applications in our previous study, we used quadrupole mass spectrometry (QMS) and optical emission spectrometry (OES) to identify active species in plasma space in this study, so as to link process parameters (para-xylene monomer flow rate, f_p, and pulse frequency of the power supply, ω_p, in particular) with film microstructure and properties. In QMS analysis, C_8H_{10}, C_8H_9, C_7H_7, C_6H_5, CH_3, H_2 and H were found (with their concentration increased as a function of f_p) in plasma space, while the molecules C_xH_y ($2 \leqq x \leqq 5$), bond-broken from the benzene ring, were not detected due to their prompt condensation into solid film. By increasing ω_p (equivalent to the increased power density), significant fragmentation occurred to the larger molecular species (C_8H_{10}, C_8H_9, C_7H_7, C_6H_5). This accounted for the films that were obtained at low f_p and high ω_p, which exhibited a long-chain alkene inorganic feature, and consequently less water repelling. Moreover, the increased H_α and H_2 at an increased ω_p detected by OES in plasma space indicated that the recombination of active species (in plasma) and dehydrogenation reaction (with the condensed film) prevailed. The dehydrogenation effect explains the decreased film growth rate as well as the decreased surface roughness of the films deposited at an increased ω_p.

BP-24 Corrosion Evaluation of Ductile Iron Duplex-Treated by Electroless Ni-P and TiAlZrN Coating, *C.-H. Hsu,* Tatung University, Taiwan, *C-.K. Lin (cklin@fcu.edu.tw),* Feng Chia University, Taiwan, ***K.-L. Chen***, *Y-.H. Chang,* Tatung University, Taiwan, *C.-Y. Su*, National Taipei University of Technology, Taiwan

This study utilized two surface techniques consisting of electroless nickel (EN) and arc ion plating (AIP) to treat the ductile iron substrates. That is, EN was first used as an interlayer, and then TiAlZrN film was coated on superficial by using the AIP method. Coating morphology, structure, and adhesion were analyzed, as well as polarization and immersion tests were also performed for understanding the effect of the duplex coatings on corrosion behavior of ductile iron. The results showed that EN is an amorphous structure, while the TiAlZrN film is a multilayer type. Ductile iron after the monolithic EN or TiAlZrN coating has better corrosion resistance as compared with uncoated one. In particular, a combination of EN/TiAlZrN duplex coatings not only increases the adhesion, but also evidently improves the corrosion resistance of ductile iron in 3.5 wt% NaCl and 10 vol.% H_2SO_4, respectively.

BP-26 Microstructures and Mechanical Properties of Nano-Structured TiAlCN/Amorphous Carbon Films, *W.-H. Wu, Y.-Y. Chang (yinyu@mail2000.com.tw),* ***H-.Y. Kao***, Mingdao University, Taiwan

Ternary TiAlN and TiAlCN/amorphous carbon(a-C) coatings with different carbon contents were synthesized by a cathodic arc evaporation process, equipped with a plasma enhanced duct, using AlTi (25/75 and 50/50 at. % ratio) alloy targets. Reactive gas (N_2) and CH_4 activated by the AlTi alloy plasma in the evaporation process was used to deposit the TiAlCN/a-C coatings. At a total gas pressure of 2.0 Pa, a mixture of reactive N_2 and CH_4 with different CH_4 flow rate from 0 sccm to 25 sccm was introduced into the chamber to form the TiAlCN/a-C coating with different carbon contents. The crystallographic texture of the deposited coatings was characterized using glancing incidence X-ray diffraction (GIXRD), while the structure was studied using field emission scanning electron microscopy (FESEM) and cross-sectional transmission electron microscopy (TEM). The characteristics of composition and chemical binding of the deposited films were identified by X-ray photoelectron spectrometry (XPS). It showed the nano-grain structure transformation by the addition of carbon to TiAlN films. A nanocomposite structure of coexisting metastable hard TiAlCN crystallites and amorphous carbon phases was found in the coatings, those possessed smaller crystallite sizes than the ternary TiAlN film. Scratch tests and Rockwell indentation were performed to determine the interfacial adhesion between substrate and TiAlCN/a-C films. Mechanical properties, such as hardness and elastic modulus, were measured by a nano-indentation test. Tribological investigations were performed by using a ball-on-disk test. The effects of carbon concentration on the microstructure and mechanical properties of TiAlCN/a-C coatings were studied.

BP-27 The Effect of Bias on The Structure and Property of (Ti,Zr)N Thin Film Deposited by Radio Frequency Magnetron Sputtering, ***Y.-W. Lin***, Instrument Technology Research Center, Taiwan, *J.-H. Huang,* National Tsing Hua University, Taiwan, *G.-P. Yu (gpyu@ess.nthu.edu.tw)*, National Tsing Hua University, Taiwan, Republic of China

Nanocrystalline thin films of (Ti Zr)N were deposited by radio frequency magnetron sputtering based on our previous optimum coating conditions for TiN and ZrN. The effect of bias on the microstructure and properties of (Ti Zr)N film was investigated . The negative bias voltage ranging from –20 V to –120 V was applied to the substrate. The film thickness measured by SEM ranges from 588 to 1827 nm. The grain size of (Ti Zr)N thin films can be obtained from the FWHM of (111) or (200) peaks using Scherrer equation, the grain sizes of the nanocrystalline (Ti Zr)N are about 10~18 nm. The packing factors and N/(Ti,Zr) ratios of the (Ti Zr)N films were obtained byRutherford backscattering spectroscopy (RBS). The packing factor of (Ti,Zr)N films relate with the substrate bias, the increase of the packing factor was from 0.83 to 1 with low substrate bias ranging from –20V to –60V. Hardness of the (Ti,Zr)N films was measured with the nanoindenter. Hardness of (Ti,Zr)N films was ranged from 30.2 ~ 37.8 GPa, increasing with increasing packing factor. Electrical resistivity decreased with the negative bias from 20 V to 60 V and then increased with the negative bias from 60 V to 120 V. Proper substrate bias may enhance the mobility of the adatoms to stable site on the substrate surface, it will decrease the resistivity and increase the crystalline quality. However, a high substrate bias may induce radiation damage to the growing film and produce lattice defects.

BP-28 Microstructures and Mechanical Properties of Cr-Si-B-N Films Synthesized by Unbalanced Magnetron Sputtering, *C.-L. CHang (clchang@mdu.edu.tw),* ***C.-Y. Hung***, Mingdao University, Taiwan, *J.-Y. Jao*, National Chung Hsing University, Taiwan,

Nano-composite Cr-Si-B-N films have been deposited on Si wafer and cemented carbide substrates using Si and Cr0.88B0.12 alloy targets by a dual reactive unbalanced magnetron sputtering system. The influences of target power on the microstructure and mechanical properties of the Cr-Si-B-N films were investigated by utilizing a field-emission scanning/transmission electron microscope, atomic force microscope, glancing-angle X-ray diffraction, X-ray photoelectron spectroscopy, nanoindenter and tribometer. Results indicate that the Cr-Si-B-N coatings present a nanocomposite structure consisting of nano-crystalline CrN, and amorphous Si_3N_4 and BN in the film, similar to the Cr-B-N or Cr-Si-N structure. Both the hardness and residual stress of the films increased up to 36 Gpa and -6.5 Gpa, respectively because of the effect of both the stoichiometric and phase volume fraction of the nanocrystalline structure formed. Wear test results show that the Cr-Si-B-N film has a variable coefficient of friction with a values between 0.2 and 0.4, which strongly depends on the amorphous volume fraction. Moreover, a decrease in the surface roughness results in an increase in the contact angle, because of an increasing in the volume fraction of Si_3N_4 and BN amorphous matrix in Cr-Al-B-N films.

BP-29 Multi Pulse Modulated Pulse Power (MPMPP) Magnetron Sputtering of the Structural Modulated Hard Tribological Coatings, ***J. Lin*** *(jlin@mines.edu), J.J. Moore,* Colorado School of Mines, *W.D. Sproul,* Reactive Sputtering, Inc., *S. Lee*, US Army ARDEC Benet Labs

The multi pulse modulated pulse power (MPMPP) magnetron sputtering is a new form of the modulated pulse power (MPP) magnetron sputtering technique. In the MPMPP technique, two different high power pulses, which generate different peak target powers and currents on the same target, are fast switched alternately by the MPP generator for different durations. With this approach, thin films with periodical structure modulation in the nanometer range can be obtained. In this study, CrN coatings have been deposited by sputtering of a metal Cr target in an Ar and N_2 gas mixture in a closed field unbalanced magnetron sputtering system using the MPMPP technique as the technical example. The films deposited by direct current magnetron sputtering (DCMS) and single pulse MPP techniques were used as the baseline. The microstructure and properties of the films were characterized using x-ray diffraction, transmission electron microscopy, nanoindentation, and ball-on-disk wear tests. The MPMPP CrN films exhibited decreased grain size and increased density as compared to the DCMS and single pulse MPP CrN films . The Structure and properties of the MPMPP CrN films depended on the durations of different pulse shapes, which determine the modulation period of the nanolayered structure. The MPMPP CrN films exhibited high hardness (27-30 GPa), significantly improved H/E ratio (>0.9) and wear resistance (low coefficient of friction of 0.23) as compared to the DCMS and single pulse MPP CrN coatings.

BP-31 Multilayer Diamond Coatings for the Machining of Aircraft Materials, *C. Bareiss (christian.bareiss@cemecon.de), W. Koelker, M. Weigand,* ***Ch. Schiffers***, *O. Lemmer*, CemeCon AG, Germany

Since several years CFRPs are getting more and more important as construction material in the aircraft industry. Their unique combination of light weight and high performance predestine these materials for airplanes of the newest generation and open up new perspectives in various other applications. One of the dominating problems in all these applications is the machining of the extreme abrasive CFRP materials, where diamond coatings demonstrated already their suitability for an economic and reliable production process. For mastering the future machining of the ongoing material improvement, the CemeCon AG developed new multilayer diamond coatings on cemented carbide tools, which combine the excellent performance and fracture toughness of micro-crystalline diamond films and the smooth component part surface, achieved by nano-crystalline, smooth diamond films. On the one hand these multilayer diamond films already proofed their excellent performance in the machining of CFRPs and are commonly used in the run production process. On the other hand they are under continuous further development for future challenges in working with CFRPs. Various results of the multilayer diamond films in the development and in the run production will be presented and compared to other coatings and uncoated tools.

BP-32 Characterization of NiAl / TiAlSiN Thin Films Deposited by Unbalanced Magnetron Sputtering for Glass Modeling Dies Application, *D.-Y. Wang (jackaljr@mdu.edu.tw),* ***W.-C. Chen***, *T.-A. Li*, Mingdao University, Taiwan

On the advent of the high demand for high quality and high productivity of non-spherical glass lenses in cell phone, compact camera and car electronics industries, glass modeling becomes the fabrication technique of choice for producing high precision glass lenses at low cost. In this study, the NiAl surface releasing films co-deposited on top of a supportive TiAlSiN thin film was examined as a protection mechanism for glass modeling dies. NiAl /TiAlSiN nano-layered thin films were deposited from Ni, Al and $Ti_{80}Si_{20}$ compound alloy targets by using pulsed magnetron sputtering technique. The results indicated that the nano-layered NiAl /TiAlSiN films showed higher hardness (28-32 Gpa), higher residual stress (-5GPa), lower surface roughness(Ra<10nm) and better adhesion strength than the conventional mono-layered coatings. The films were characterized by using scanning electron microscopy (SEM), X-ray diffractomery (XRD), X-ray photoelectron spectroscopy (XPS), Nano-indentation, Atomic Force Microscope (AFM) and thermal gravimetric analysis (TGA)/differential scanning calorimetry (DSC) and contact angle measurement.

BP-33 Evaluation of Ca Doped $Ce_{0.8}$ $Gd_{0.2}O_{1.9}$ Electrolyte by Various Deposition Method, ***S.H. Yang***, *K.H. Kim, H.W. Choi (chw@kyungwon.ac.kr)*, Kyungwon University, Korea

SOFCs (Solid oxide fuel cells) based on doped ceria electrolytes offer operating low temperatures. Recently much attention was aimed at successful powder preparation with high sinter activity and conductivity. The properties of ceria electrolyte are very sensitive to impurities introduced during powder and electrolyte fabrication. So, electrolyte powder made of 2% Ca dope $Ce_{0.8}$ $Gd_{0.2}O_{1.9}$ (GDC) by glycine-nitrate process and supported by Ni-GDC cermet anode pellets. GDC electrolyte was vapor deposited by screen printing method, RF-magnetic sputtering and E-beam evaporating on the Ni-GDC cermet anode pellets surface. The formation of single-phase monoclinic structure was confirmed by X-ray diffraction (XRD) for the doped 2% Ca $Ce_{0.8}$ $Gd_{0.2}O_{1.9}$ (GDC) electrolyte and Ni-GDC anode. The crystal structure and morphology were measured by scanning electron microscopy (SEM) for the sintered samples were performed. The as complex impedance were measured in the temperature of ~60°C (Computer Impedance Grain-Phase Analyzer).

BP-34 Large Scale Deposition of TiC/a-C Nanocomposite Coatings by Magnetron Sputtering using Novel Ceramic Compound Targets, ***M. Stueber*** *(michael.stueber@kit.edu), S. Ulrich, H. Leiste,* Karlsruhe Institute of Technology, Germany, *P. Polcik, M. O`Sullivan*, PLANSEE Composite Materials GmbH, Germany

Carbon-based nanostructured composite thin film materials such as TiC/a-C have attracted large scientific and technical attention with regard of their interesting properties, addressing not only excellent tribological applications (by high wear resistance and simultaneously low friction coefficients) but also electrical, optical and other applications. In the past few years the knowledge on the correlation between synthesis conditions, growth, microstructure and properties of these kind of materials has enormously increased. On the other hand, industrial applications have so far mainly been established for WC/a-C coatings in tool applications. This situation is partially related to the lack of appropriate processes for large scale deposition of such materials over a wide range of coating compositions and on complex shaped component geometry. In this article the large scale deposition of TiC/a-C nanocomposite coatings by means of non-reactive d.c. magnetron sputtering is reported. A novel process route on production level using innovative, newly developed hot-pressed ceramic compound targets of individual TiC:C compositions is presented. The sputtering experiments were carried out with a Hauzer HTC 625 system in the unbalanced magnetron mode. TiC/a-C nanocomposite coatings were deposited under systematic variation of the cathode coil current, substrate temperature, and substrate bias, while the sputtering power density and the gas pressure were kept constant. Coatings of 3-4 microns thickness, well adherent to cemented carbide substrates, are thoroughly characterized by electron microprobe analysis (EPMA), X-Ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), Vickers micro hardness measurements, stress measurements and scratch tests. It is clearly shown, that TiC/a-C coatings of identical constitution, microstructure and properties as reported earlier on laboratory scale magnetron sputter deposition from similar hot-pressed ceramic compound targets can be synthesized by this new method. The coatings exhibited

Vickers micro hardness values up to 1750 HV0.05, moderate compressive stress up to – 1 GPa and critical load of failures L_{c1} of up to 40 N. Applying the new ceramic compound targets very stable, reproducible and easily to control and monitor deposition processes on large scale are available. The results will be discussed both from a materials science perspective and as well with regard to future improving and utilization of the new process and target technology for advanced nanocomposite coating development.

BP-36 Enhanced Efficiency in Dye-Sensitized Solar Cells Based on TiO_2 Nanotube/Nanoparticle Composition Powder, ***C.-H. Lee***, *K.H. Kim, H.W. Choi (chw@kyungwon.ac.kr)*, Kyungwon University, Korea

Enhancing efficiency of dye-sensitized solar cells by combining use of TiO_2 nanotube and nanoparticle. TiO_2 nanotube is prepared by hydrothermal growth method. TiO_2 nanotube and nanoparticle was coated on FTO glass by screen printing method. The dye-sensitized solar cells were fabricated using dye of ruthenium(II)(N719) and electrolyte (I_3/I_3^-). The crystalline structure and morphology were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM). The absorption spectra was measured by UV-vis spectrometer. The conversion efficiency was measured by solar simulator (100mW/cm^2). The size and structure of TiO_2 nanotubes were adjusted by hydrothermal temperatures. It was found that the conversion efficiency of dye-sensitized solar cells was highly affected by the properties of TiO_2 nanotubes. The dye-sensitized solar cell based on TiO_2 nanotube/nanoparticle hybrids showed a better photovoltaic performance than the cell purely made of TiO_2 nanoparticles.

BP-39 Theoretical Investigation of the Dynamical and Thermodynamic Stability of One Monolayer SiN_x Interfaced with TiN, *T. Marten, E.I. Isaev,* ***B. Alling*** *(bjoal@ifm.liu.se), L. Hultman, I. Abrikosov*, Linköping University, Sweden

The Ti-Si-N system is attractive for its superhardening, for use as e.g. coatings on cutting tools. The increased hardness upon Si addition to TiN has qualitatively been ascribed to the nanometer dimension of the TiN grains together with the prevention of grain boundary sliding by the so called SiN_x tissue phase. However, a quantitative understanding of the hardness enhancement is still not present. The structure of the tissue phase is an important issue and is discussed in the literature.

We study the dynamical and thermodynamic stability of a single monolayer of SiN_x embedded isostructurally between B1TiN (001) and (111) oriented slabs. Phonon calculations show that upon distortion of the SiN bond the (001) interface is almost stabilized dynamically while the (111) interface is dynamically stable. Moreover, the stoichiometric degree of freedom was relaxed by allowing for Si vacancies in the lattice. Calculations show that the ideal 1:1 SiN stoichiometry in both interfaces are thermodynamically unstable with respect to Si vacancy formation. Thus, the real structure of TiN/SiN_x should have another stoichiometry than the ideal B1 interfaces.

BP-41 Magnetron Sputtered ZrN/SiN_x Nanocomposite Thin Films: Relationship Between Chemical Composition, Film Morphology and Electrical Properties, *D. Oezer (david.oezer@epfl.ch), S.C. Sandu,* ***R. Sanjinés***, EPFL, Switzerland

ZrN/SiN_x nanocomposite thin films have been deposited by reactive magnetron co-sputtering using a negative bias voltage of -150V applied to the substrate. X-ray diffraction measurements and TEM investigations suggest a picture of film morphology consisting of ZrN crystallites surrounded by a SiN_x layer, where both the size of the ZrN crystallites and the composition of the grain boundaries depend on the deposition parameters. Besides the dependence of the film properties on the substrate temperature and the Si content, the nitrogen flow during the deposition process strongly influences the film structure. Whereas slightly sub-stoichiometric coatings ZrN_y/SiN_x films (with $0.9 < y < 1$) are polycrystalline without preferential orientation, nearly stoichiometric films develop a slight (200) texture in growth direction. Furthermore sub-stoichiometric films show relatively moderate room temperature resistivity values of about 40μΩcm to 100μΩcm depending on the Si concentration, whereas nearly stoichiometric coatings exhibit values that are more than one order of magnitude higher for comparable Si concentrations. The enhancement of the resistivity can be understood by means of higher grain boundary scattering rates due to higher Si incorporation in the grain boundary regions and higher degree of nitridation at the grain boundaries.

BP-42 The Effect of H_2S Addition on the Crystal Quality of the Nanocrystalline Diamond Films Grown by the Down-Flow Microwave Plasma-Assisted Chemical Vapor Deposition, *H. Gamo (mngamo@toyo.jp)*, Toppan Printing Co., Ltd., Japan, *M. Kikuchi, K. Shimada*, Toyo University, Japan, *T. Ando*, Northeastern University, Japan, ***M.N. Gamo***, Toyo University, Japan

Nanocrystalline diamond growth has been extensively studied because its optical, mechanical, and electrical properties are expected to be attractive for both of future applications and scientific interests. In order to grow diamond nanocrystallites, many studies have been performed to introduce defects into diamond structure. For introducing defects, high-energy ions are used to impact the growth surface by applying DC bias voltage to the surface in the plasma. Contrary to this, our growth method in this study focused to realize a damage-free growth process suitable for a high-quality crystal growth.

We used tubular type microwave plasma chemical vapor deposition (MPCVD) reactor for the growth experiments. In our system, the substrate position was apart from the plasma-ball during the growth in the MPCVD quartz reactor. The down stream position is expected to prevent the growth surface from being damaged by ion bombardments and electron irradiation from the plasma. The flow ratio of CH_4 to H_2 was 10%, and that of H_2S to H_2 was varied in the range of 0-5.0%. From the analogy of the effect of H_2S both on the diamond MPCVD growth and the carbon nanotube MPCVD growth, the added H_2S is expected to enhance the sp^3 formation and assist the diamond crystal growth.

The film grown with 0.1% H_2S in the gas phase was consisted with diamond nanocrystallites approximately 1-2 nm in size from a TEM observation. Negligible amorphous phases and defects were observed in the grain boundaries. The crystal quality was high. The electron diffraction pattern of the film revealed that the nanostructure was diamond.

BP-44 Characterization of Cu-Ag Alloy Thin Films, *J.-H. Hsieh (jhhsieh@mail.mcutedu.tw),* ***S.-Y. Hung***, Ming Chi University of Technology, Taiwan

Cu-Ag thin films are known to have better mechanical and electrical properties than Cu or Ag alone. In this study, Cu-Ag thin films with various compositions were prepared using co-sputtering technique followed by rapid thermal annealing at various temperatures. The films' mechanical and electrical properties were then characterized using XRD, AFM, FESEM, and TEM, as functions of compositions and annealing conditions. The results show that the as-deposited films would transform from one-phase structures to two-phase ones without annealing. The hardness would reach the maximum and 50/50 alloy compositions, and the resistivity would follow Nordheim's rule prior to the formation of separated phases. After being annealed, the films' resistivity would follow the mixture rule roughly, mainly due to the formation of Ag-rich and Cu-rich phases. The surface morphology and structure would vary as a function of annealing temperature. From the results, it is found that grain growth varied depending on Ag-Cu compositions.

BP-46 A Comparative Research on Magnetron Sputtering and Arc Evaporation Deposition of Ti-Al-N Coatings, ***L. Chen*** *(chenli_927@126.com), S. Wang*, ZhuZhou Cemented Carbide Cutting Tools Co., LTD, China

Ti-Al-N coating has been proven to be an effective protective coating for machining applications. Here, the differences of cubic Ti-Al-N coatings with a similar Ti/Al atomic ratio of 1 deposited by magnetron sputtering and cathodic arc evaporation have been studied in detail. Main emphasis was laid on the characterization of the thermal stability and cutting performance. Both coatings during annealing exhibit a structural transformation into stable phases c-TiN and h-AlN via an intermediate step of spiondal decomposition with the precipitation of c-AlN, however, a difference in decomposition process. Compared to sputtered coating inserts, an increase of tool life-time by 42% is obtained by evaporated coating inserts at the higher speed of 200 m/min, whereas the similar cutting life is observed at the speed of 160 m/min. It is attributed to the better stability of evaporated coating due to its later structural transformation at elevated temperature. A post-deposition vacuum annealing of both coated inserts in their corresponding temperature range of spiondal decomposition improves their cutting performance due to an increase in hardness arising from the precipitation of coherent cubic-phase nanometer-size c-AlN domains. Additionally, the sputtered coating behaves worse oxidation resistance due to its more open structure. These behaviors can be understood considering the difference in microstructure and morphology of as-deposited coatings originating from adatom mobility of deposited particles, where arc evaporation technique with higher ion to neutral ratio shows higher adatom mobility.

BP-48 Evaluation of Microstructures and Mechanical Properties of Niobium and Vanadium Carbide Coated H11 Tool Steels, ***J.-W. Lee*** *(jefflee@mail.mcut.edu.tw)*, Mingchi University of Technology, Taiwan, *C.-T. Lin*, Unilift Corp., Taiwan, *M.-K. Wu, J.-C. Huang*, Tungnan University, Taiwan

Niobium and vanadium carbide coatings provide a surface modification layer on steel surface with high hardness and adequate wear resistance. In this study, AISI H11 tool steel was immersed in a molten bath consisting of borax, boric acid, and ferro-niobium and ferro-vanadium to form a carbide coating mixture on the surface.

Surface and cross-sectional morphologies of carbide layers were studied with a scanning electron microscope (SEM) and Energy dispersive spectrometer (EDS). The hardness and elastic modulus of carbide layer was evaluated by nanoindentation. The wear resistance of steels was investigated by pin-on-disk wear tests. Daimler-Benz Rockwell-C adhesion and scratch tests were further conducted to explore the adhesion properties of carbide layers. Carbide layer around 10 um thick with an outer V_8C_7 and inner $(Nb)_6C_5$ phases were observed. The adhesion strength quality of carbide layers was related to HF1 indicating good adhesion properties. It is concluded that the hardness and tribological properties of AISI H11 tool steel were improved effectively by the vanadium and niobium carbide coating.

BP-50 Effect of Nitrogen Content in SiC_xN_y Thin Films Deposited by Magnetron Co-Sputtering Technique, *R.S. Pessoa (rspessoa@ita.br),* ***H.S. Medeiros****, L.V. Santos, H.S. Maciel, A. S. da Silva Sobrinho, M. Massi*, Technological Institute of Aeronautics, Brazil

The industries of microelectronic devices have been searching for materials capable to operate at aggressive environment. For this, the SiC thin films is a great candidate for this application due some properties as, for example, high operate temperature, good thermal conductivity and high breakdown electric field. However, to improve the electric conductivity is necessary to add nitrogen to the film.

Studies about the effect of nitrogen content in SiC_xN_y thin films deposited by magnetron co-sputtering technique without substrate heating are presented. This consists of two magnetrons targets arranged in parallel and angled at approximately 20º of the central axis. The magnetron targets are made of 100 mm diameter and 90 W, respectively. The working pressure was fixed at 5 mTorr and the N_2/Ar flow ratio was adjusted by varying the N_2 flow rate and maintaining the Ar flow rate at 10 sccm. Moreover, SiC_xN_y films were deposited on p-type (100) silicon substrate that was placed at a substrate-to-target distance of 160 mm. Fourier Transformed Infra Red (FTIR), Composition, chemical bonds and thickness of as-deposited Si_xC_y films were investigated by Rutherford Back Scattering (RBS), Raman spectroscopy and profilometry, respectively. The RBS results indicate that the condition of applied power in magnetron targets allows obtaining approximately stoichiometric SiC films at pure Ar plasma. With the addition of N_2 in plasma, the carbon concentration increases for N_2 flow > 5 sccm due to the effect of chemical sputtering of carbon target by N_2 gas. Raman spectra clearly reveal that the deposited SiC_xN_y films are amorphous and exhibited C-C bonds corresponding to D and G bands.

BP-52 Enhancement of Thermal Stability on DLC Nanofilm by Using Addition of Silicon Top-Layer, *C.-K. Chung (ckchung@mail.ncku.edu.tw), T.-Y. Chen, C-W. Lai,* ***M.-W. Liao***, National Cheng Kung University, Taiwan

The effect of added silicon top-layer on thermal stability of diamond-like carbon (DLC) film annealed at 750°C and 900°C has been investigated. Single carbon film and two-layer Si/C film with thickness of 100 nm and 50/100 nm were used to realize the influence of Si top-layer on the hardness and thermal stability of carbon nanofilm under rapid thermal annealing (RTA). The evolution of surface morphology, microstructure and reaction between C and Si was examined by high resolution field emission scanning electron microscope, Raman and FTIR spectroscopy. The hardness of films was investigated using G-200 Nano Indenter® with Nano CSM-DCM technique. After 750 -900°C annealing, the hardness of single carbon layer decreased seriously at 750°C and then slightly increased at 900 °C due to the formation of SiC at the interface between carbon film and silicon substrate. On the other hand, no significant variation occurred on the hardness of two-layer Si/C film under RTA at 750 -900°C . Although the higher annealing temperature resulted in higher sp^2/sp^3 bonding ratio as well as more sp^2 bonding formation in the carbon layer to soften the structure, the added Si top-layer can sustain the hardness of the composite film because of the SiC film formed on the surface and/or the residual compressive stress of two-layer Si/C films.

BP-53 Formation and Characteristics of ZnNO Thin Film From n-Type to p-Type Conductivity by Thermal Annealing, ***Y.-J. Chen****, T.-F. Young (youngtf@mail.nsysu.edu.tw), T.-C. Chan, T.-M. Tsai, K.-C. Chang, C.-H. Li*, National Sun Yat-Sen University, Taiwan

In this work, the p-type zinc oxinitride films were fabricated by thermal annealing in air ambience. The Zinc nitride films were deposited onto glass substrate in N_2–Ar mixtures by reactive RF magnetron sputtering. The as-grown zinc nitride thin film is a n-type material. It is found that the film treated at 300°C for 3 hours can be changed to a p-type material. The zinc oxinitride films reveal a very low resistance (2.2×10^{-2} Ω-cm) and high carrier concentration (3.88×10^{19} cm^{-3}) after the heat treatment. The optical band gap of zinc nitride was determined as a direct band gap varying from 1.1 eV to 1.6 eV according to the temperature of heat treatment. The zinc oxinitride can be prepared with various electrical characteristics and the band gaps modulation by controlling the temperature of heat treatment.

BP-54 Microstructure and Properties of Arc Sprayed Coatings Prepared by Conventional and Nanocomposite Cored Wires, *M. Tuiprae,* ***S. Wirojanupatump*** *(wish-2000@hotmail.com), S. Jiansirisomboon*, ChiangMai University, Thailand

Ni-base and Fe-base cored wires including WC-Cr-Ni, WC-Cr-Fe, and W-Cr-Fe nano-composite were arc sprayed. The starting cored wires and coatings obtained were characterized by optical microscope (OM), scanning electron microscopy (SEM), X-ray diffraction (XRD), Vicker microhardness tester and dry sand rubber wheel abrasion tester. The results showed that WC-Cr-Fe nanocomposite coating had superior coating microstructure and properties; smoother surface, lower porosity and highest hardness compared to that of conventional cored wire (WC-Cr-Fe and WC-Cr-Ni coating). WC-Cr-Ni coating having high carbide content resulted in high coating hardness; however, this coating exhibited a less dense structure. The WC-Cr-Fe nanocomposite coating exhibited higher abrasive wear resistance than others. Correlation between coating properties and cored wire characeristics will be presented.

BP-56 Study of the Structural and Mechanical Properties of Tungsten Zirconium Nitride Nanostructured Coatings Deposited by by Physical Vapor Deposition, *P. Dubey,* ***R. Chandra*** *(ramesfic@iitr.ernet.in)*, Indian Institute of Technology Roorkee, India

We hereby report the synthesis of Nano-ceramic thin films of Tungsten zirconium nitride on Silicon and 13-4 Cr-Ni steel substrate through DC/RF reactive magnetron sputtering. We have studied the effects of the deposition parameters on the structural and mechanical properties. XRD analysis of the nano-structured samples shows that at low nitrogen pressure the samples are polycrystalline while at high nitrogen pressure it becomes single crystalline. XRD analysis also reveals that there is reduction in grains size with increase in the nitrogen pressure. Microstructural analysis using FE-SEM reveals that the thickness of the film decreases with increase in nitrogen percentage in mixture. AFM study shows, that the roughness of the samples decreases with increase in the percentage of N_2 in the ambient gas.

As par survey, we have not found any literature reporting on tungsten zirconium nitride (W-Zr-N) nano-ceramic coating so far. Thus W-Zr-N coating represent a new class of materials which exhibit improved mechanical properties including high hardness and high fracture toughness.

BP-58 Coating of Superalloy with Laser Surface Alloying, ***M.H. Rhee*** *(mhrhee@katech.re.kr),* Korea Automotive Technology Institute, Korea*, W. Y. Jeung,* Korea Institute of Science and Technology, Korea*, J.W. Min, W.Y. Chung*, Korea Automotive Technology Institute, Korea

Superalloys based on Cr-Ni-V-Mo-Fe composition were synthesized by Laser Surface Alloying. The surface treatment temperature of coatings was accurately controlled using continuous wave Nd:YAG laser combined with an infrared sensor in compressed nitrogen atmosphere. For the coatings, multilayer or mixed compounds for the listed Cr-Ni-V-Mo-Fe composition was jointly deposited by RF sputtering and Laser coating at various temperature in nitrogen atmosphere and then synthesized into superalloys through laser surface alloying. Experimental results depending on laser power of depositing and surface alloying, surface temperature of depositing and alloying, and alloying time will be presented. In addition, test data SEM morphology and the evaluated friction resistance of superalloys will be posted. This coating showed a good high temperature resistance behavior and comparatively high were resistance.

BP-60 Heat Treatment of Nanocrystaline TiZrN Film Deposited by Unbalanced Magnetron Sputtering, ***Q.-Y. Chen****, J.-H. Huang, G.-P. Yu (gpyu@ess.nthu.edu.tw),* National Tsing Hua University, Taiwan*, Y.-W. Lin*, Instrument Technology Research Center, Taiwan

Metal nitride films have been commonly used in industry as protective coatings and metallization layer in industry due to its excellent properties. Moreover, improvements in the properties of thin films were obtained by the deposition of binary, ternary or even higher component systems.

In this study, the nanocrystalline TiZrN thin films were deposited on Si(100) wafer and AISI 304 stainless steel substrate respectively using unbalanced magnetron sputtering. Specimens were later annealed in flowing nitrogen at different temperature ranging from 500°C to 1100°C for two hours. The process of heat treatment affected its microstructure and properties. The texture of the TiZrN films was characterized by X-ray diffraction (XRD); grain sizes were both calculated according to the result of θ/2θ scans. The FWHMs of specimens are decreased with increased temperature. The thickness of the TiZrN thin films was further observed and measured using field-emission gun scanning electron microscope (FE-

SEM), measuring about 500 nm. The composition and packing factor of the TiZrN thin films were determined by the Rutherford Backscattering Spectroscopy (RBS). The hardness of the TiZrN films was measured using nanoindenter, which was then observed obviously varying with annealing temperature. The compositional depth profiles were characterized using Auger electron spectroscopy (AES). 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 5%NaCl and 1M H2SO4 + 0.05M KSCN solutions respectively.

BP-61 Morphology and Growth Mechanism of SiC Films Synthesized by Liquid Phase Epitaxy Assisted Chemical Vapor Deposition, ***P.-T. Lee***, National Cheng Kung University, Taiwan, *S.-C. Wang*, Southern Taiwan University, Taiwan, *P.-K. Nayak*, National Cheng Kung University, Taiwan, *J.-C. Sung*, KINIK Company, Taiwan, *J.-L. Huang (jlh888@mail.ncku.edu.tw)*, National Cheng Kung University, Taiwan

Silicon carbide layers were grown on a Si substrate by liquid phase epitaxy assisted chemical vapor deposition (LPECVD) at a temperature below 1100^{o}C and pressure of 1 atmosphere without SiC seeding. The liquid phase epitaxy assisted chemical vapor deposition was carried out in a tube furnace through cyclic heating process using methane as a carbon source and Sm-Co mixed powder as a solvent for carbon and silicon. The growth of SiC from rare earth Sm-based solvent is an innovative approach, and Co can promote the formation of solvent during the process. X-ray diffraction (XRD), micro-Raman spectroscopy, Electron probe micro-analyzer (EPMA), Scanning electron microscopy (SEM) and Transmission electron microscopy (TEM) were used to characterize the properties of SiC. The growth mechanism of SiC deposited by LPECVD was also discussed in this study. Results indicated that β-SiC was successfully fabricated on (111) Si substrate without SiC seeding by LPECVD. The heterogeneous nucleation of β-SiC was found to be observed initially at the edge of triangle-shaped sites on (111) Si surface, which was formed due to the existence of Co, and then grew and expanded to form β-SiC film.

BP-62 Synthesis of CrN and CrAlN Coatings for High Temperature Wear Applications, ***H. ALAGÖZ*** *(alagoz@bilkent.edu.tr)*, *M.F. Genisel*, Bilkent University, Turkey, *M. UĞRAŞ*, Atılım University, Turkey, *E. BENGÜ*, Bilkent University, Turkey

Transition metal nitrides as protective coatings have been studied by scientists and engineers, since they were shown to have good wear, erosion and corrosion resistance. In this study, two of the most promising nitride based-coatings, namely CrN and CrAlN, were synthesized by reactive magnetron sputtering technique on Si(100) and steel (100Cr6) substrates using different gas ratios, substrate bias and target power levels. We investigated the change in the phase make-up, hardness, high-temperature wear properties and surface roughness of these coatings. Scanning electron microscopy (SEM) was used to understand the effect of process parameters on surface roughness and microstructure of the films. We utilized atomic force microscopy to quantify the roughness of the films. Also, during SEM investigation, we used energy dispersive spectroscopy (EDS) to obtain the Cr/Al ratios of the films. The hardness values of the films were measured using the nano-indentation technique and, we used a high-temperature tribometer (up to 800°C) to investigate the high-temperature wear-rates of the coatings. X-ray photo-electron spectroscopy (XPS) has been employed to understand the bonding states of Cr and Al to nitrogen and oxygen on the as-deposited surfaces and on wear tracks. Our findings revealed that the surface roughness of the films improved with decreasing the Ar/N_2 ratio, while measured hardness values for the films increased. Increasing the Al content of the films caused an improved high-temperature behavior, as well. Furthermore, our investigations at the wear tracks showed presence of higher ratio of Al-O species which we believe to have contributed to the lower wear rates of the CrAlN coatings with higher Al content.

BP-64 Hot Filament CVD Grown Diamond Films at Various Total Mass Flow Rates under Constant Residence Time, *M.A. Ali*, ***M. Urgen*** *(urgen@itu.edu.tr)*, Istanbul Technical University, Turkey

In the present study, a self-biased Hot-Filament Chemical Vapour Deposition system was used to deposit diamond film over Silicon substrate. A constant residence time (t_r = 1010 sec) for precursor's gases (H_2 +CH_4) at total mass flow rates of 200, 300 and 400 sccm was selected with two different concentrations of CH_4; to compare the quality of deposited diamond. To analyze the morphology, growth rate, crystal orientation and quality of deposited diamond, standard characterization techniques were utilized. Surface morphology and fracture cross-section images of SEM reveal that deposited coatings exhibit similar surface morphology and crystal orientation but improved growth rate at all total mass flow rates. By increasing CH_4 concentration at t_r = 1010 sec increased the growth rate but deteriorated the quality of deposited diamond. The results obtained indicate that by adjusting 't_r' coating deposited at total mass flow rate of 100 sccm represent a similar trend in its properties for forthcoming like wise 200, 300, 400 sccm and so on. Present approach enable us to evaluate the diamond coating properties at higher mass flow rates by keeping constant 't_r' without the execution of original line of experiment.

BP-65 Improved Adhesion and Tribological Properties of Hard Graphite-Like Hydrogenated Amorphous Carbon Films Grown by a Remote Plasma on Steel Substrates, *T. Zaharia (t.zaharia@tue.nl)*, Eindhoven University of Technology, Netherlands, *R. Groenen*, N.V. Bekaert S.A., Belgium, ***R. van de Sanden***, Eindhoven University of Technology, Netherlands

Recently we reported on a novel form of hard graphite-like hydrogenated amorphous carbon deposited by an expanding thermal remote plasma in an Ar – C_2H_2 environment [1, 2]. The graphite-like films deposited on Si and steel substrates are dense (~2.0 g/cm^3) and very smooth, with RMS roughness below 4 nm for film thicknesses above 1µm, which makes them ideal candidates for tribological applications.

However, dense a-C:H material commonly leads to high compressive stress, which in turn causes poor adhesion on metallic substrates. The influence of a Ti metallic interlayer in between M2 steel substrates and the hard graphite-like films is investigated by monitoring adhesion with the Rockwell C test and the scratch test as a function of carbon film thickness, interlayer thickness and deposition temperature. It is shown that a sputtered Ti interlayer deposited at substrate temperatures of 200 – 250°C and with an adjusted thickness dependant on the carbon film thickness improves the adhesion drastically. This can be explained by a more densely packed film structure at higher temperatures and by a roughening effect of the top Ti surface with increasing thickness, due to grain coarsening. The wear rates of the a-C:H/Ti/M2 steel stack against a 100Cr6 ball counterpart in a ball-on-disk test were found to be very competitive, in the order of 2.5×10^{-17} m^3/Nm.

[1] S.V. Singh et al., Appl. Phys. Lett. **92** (2008) 221502.

[2] S.V. Singh et al., J. Appl. Phys. **107** (2010) 013305.

BP-66 Structure Characterization and Antibacteria Behavior of TaN-Ag, TaN-Cu and TaN(Ag,Cu) Nanocomposite Thin Films, ***Y.-J. Lin***, *J.-H. Hsieh (jhhsieh@mail.mcutedu.tw)*, *S.-Y. Hung*, Ming Chi University of Technology, Taiwan, *C. Li*, National Central University, Taiwan

TaN-(soft metal) nanocomposite thin films have been shown to have good mechanical properties. This study aims at comparing the antimicrobial behaviors of TaN–Cu, TaN-Ag, and TaN-(Ag,Cu) nanocomposite films. These films were deposited by reactive co-sputtering on Si. They were then annealed using RTA (Rapid Thermal Annealing) at 400°C to induce the nucleation and growth of metal particles in TaN matrix and on film surface. After being characterized using XRD, FESEM, and TEM, the samples were tested for their anti-bacterial behaviors against Gram-negative and Gram-positive bacteria. It is found that TaN-Ag is more effective against E. Coli (Gram-negative), while Cu ion or TaN-Cu is more effective against Staphylococcus aureus (Gram-positive). For TaN-(Ag,Cu), a synergistic effect is observed. This film is effective against both types of bacteria. The wider application is expected.

Fundamentals and Technology of Multifunctional Thin Films: Towards Optoelectronic Device Applications
Room: Town & Country - Session CP

Symposium C Poster Session

CP-2 AZO Coatings Deposited by Reactive HiPIMS for Modified TCO Properties on Polymeric Web, *P. Barker (p.barker@mmu.ac.uk)*, ***P. Kelly***, *G.T. West*, Manchester Metropolitan University, UK, *J.W. Bradley*, University of Liverpool, UK, *H. Assender*, University of Oxford, UK

The potential to produce coatings with much enhanced properties has made high power impulse magnetron sputtering (HiPIMS) an area of great interest with the surface engineering community in recent years. Many papers and conference presentations are coming from the academic community but, at present, industry is slow to take up the technology due to known or perceived processing issues (low deposition rates, power supply instabilities, difficulties with reactive process control, etc.). Also, as yet, few applications have emerged to convince industry that this technology merits the significant investment required to move from lab-scale to production-scale processing.

Previous work carried out by this group has shown that the thermal load experienced at the substrate is low when operating in HiPIMS mode, compared to DC and pulsed DC sputtering. It has also been seen that modifications are being made to thin film properties when produced by

HiPIMS. AZO coatings have, therefore, been deposited under systematically varied conditions of pulse frequency and pulse width, selected to also vary the degree of ionisation in the plasma and incident at the substrate. The coatings were then characterised in terms of their structural, optical and electrical properties using SEM, EDX, XRD, optical spectroscopy and a Hall probe and the interrelationships between deposition parameters and film properties were explored. Further, different methods of reactive sputter control were tested in an effort to make HiPIMS sputtering onto polymeric web a reliable option for industrial processing.

The work presented here shows that TCO coatings with industrially relevant optical and electrical properties can be readily deposited onto thin, polymeric web. Although this is currently only on laboratory scale systems, transfer to a development-scale roll to roll system is in progress.

CP-4 Study of the Physical Properties of PLD Grown Cobalt Doped Nanocrystalline $Zn_{0.9}Cd_{0.1}S$ Thin Films, ***A.K. Chawla***, *S. Singhal, H.O. Gupta, R. Chandra (ramesfic@iitr.ernet.in)*, Indian Institute of Technology Roorkee, India

Here we report a systematic study of structural, optical, and magnetic measurements on $Zn_{0.9}Cd_{0.1}S$:yCo films in the concentration range of 0.005 *y* 0.05 M using pulsed laser deposition technique. Structure, composition analysis, and optical measurements revealed that Cobalt is incorporated into the lattice, as Co^{2+} substituting Zn^{2+} ions, forming a solid solution with cubic structure instead of Cobalt precipitates. Low temperature magnetization measurements reveal a paramagnetic behaviour. UV-Vis measurements showed a red shift with respect to undoped sample in the energy band gap with increasing Cobalt concentration. Photoluminescence measurements confirmed the substitution of Cobalt ions in the tetrahedral crystal field by showing the characteristic peaks.

CP-6 Thermal Properties of C-Si-O Composite Thin Films Deposited by PBII Method, ***S. Abe***, *N. Moolsradoo (nutthanun.moo@kmutt.ac.th), S. Watanabe*, Nippon Institute of Technology, Japan

DLC films are meta-stable amorphous films that exhibit unique combinations of properties such as high hardness, low friction coefficient, and good wear resistance, etc. However, DLC films have several known limitations, such as high internal stress, low thermal stability. In order to solve these problems, enhance the film properties, Si has been incorporated into the amorphous hydrocarbon films. Our study aimed to study the effects of silicon incorporation on the thermal properties of C-Si-O composite thin films deposited by PBII method. The films were deposited by PBII method with gaseous mixtures of C_2H_2:TMS:O_2 on Si (100) wafers. The flow rate ratio range between C_2H_2 and TMS were from 10:1 to 100:1, while oxygen was kept constant at 1 sccm. The deposition pressure range was from 2-6 Pa. The bias voltage was set 0 kV, at RF power of 300 W. The total deposited thickness of the films was approximately 500 nm. An annealing temperature range of 200-600°C was investigated under high vacuum, air atmosphere and argon atmosphere for 1 hour. The film structure was analyzed using Raman spectroscopy. The thermal properties were analyzed using Differential Thermal Analysis (DTA) and Thermogravimetry (TG). From the results deposited at 2 Pa pressure, the results show that the silicon incorporation is good thermal properties under high vacuum.

CP-7 Influence of Substrate Temperature on Electrical and Optical Properties of Al-Doped ZnO Thin Film, *S.-C. Her (mesch@saturn.yzu.edu.tw)*, ***T.-C. Chi***, Yuan Ze University, Taiwan

The increasing use of transparent conductive oxides (TCO) films in electronics, optoelectronics and information technology devices such as displays, solar cells and sensors has promoted the study of Zinc oxide (ZnO) films. In this regards, aluminum-doped ZnO (AZO) films with high optical transmittance and low electrical resistivity have attracted significant attention in recent years. In this work, aluminum-doped ZnO films were deposited on glass substrate at substrate temperatures from room temperature to 275^{o}C by radio frequency magnetron sputtering. The effect of substrate temperature on the electrical and optical properties together with the surface morphology was investigated. Electrical properties including the resistivity, carrier concentration and mobility of AZO films were evaluated by Hall effect measurements at room temperature. Optical properties including transmittance and reflectance were measured with a Perkin-Elmer Lambda UV/Visible/NIR spectrometer. The crystalline structure and preferred orientation of the AZO films were investigated by X-ray diffraction (XRD). Scanning electron microscopy (SEM) and atomic force microscopy (AFM) were used to study the surface morphology and roughness of the deposited films. At low substrate temperature (25^{o}C) AZO films have high resistivity ($3.01x10^{-2}$ Ωcm) with small carrier concentration ($3.3x10^{19}$ cm^{-3}), while the one prepared at higher temperature (275^{o}C) has low resistivity ($2.14x10^{-3}$ Ωcm) with large carrier concentration ($1.57x10^{20}$ cm^{-3}). The increase of substrate temperature enhances the doping efficiency yielding to films with a lower resistivity and a wider band gap energy. It was observed that all the AZO films deposited in the substrate temperature range from room temperature to 275^{o}C were preferentially oriented in the c-axis or (002) plane. The average of the optical transmittance for all the films was close to 81% over the visible wavelength range from 400nm to 800nm. Present work shows that the enhancement of the AZO film performance with high transparency and low resistivity can be achieved by increasing the substrate temperature.

CP-8 Temperature Effect on the Optical and Mechanical Properties of Silver Thin Film Deposited on Glass Substrate, ***S.-C. Her*** *(mesch@saturn.yzu.edu.tw), Y.-H. Wang*, Yuan Ze University, Taiwan

Silver films with high reflectance and low absorption in the visible wavelength region have been widely used in optical applications. Examples are transparent heat mirrors for the reduction of heat load in cars and buildings and for other energy applications such as solar cell. In this investigation, silver optical thin films were prepared on the glass substrate at various temperatures by electron-beam vapor deposition. The reflectance of Ag thin films was measured by a Perkin-Elmer Lambda spectrophotometer in the visible wavelength region of 450-680 nm. The experimental measurements of reflectance were validated with the numerical results using the Essential Macleod software. The surface topology and cross section structure of the films were examined by means of atomic force microscope (AFM) and scanning electron microscope (SEM), respectively. The effects of the substrate temperature on the reflectance were presented through a parametric study. The average reflectance of silver films over the visible wavelength range decreases form 99.26% to 91.15%, while the substrate temperature is increasing from 22^{0}C to 300^{0}C. The dispersion curve shows that the reflectance of the silver film increases with the increase of the wavelength in the visible range. The surface morphology of the films revealed that the grain size and surface roughness increased with the increase of the substrate temperature. More energy is supplied to the deposition particles at higher temperatures resulting in the higher migration mobility, which in turn favors the recrystallization. The films prepared at high substrate temperature have a crystalline structure and the films prepared at low temperature have an amorphous structure. Nanoindentation tests were employed to determine the hardness and Young's modulus of the film. The measured hardness and Young's modulus of the silver thin film were found to depend on the penetration depth. It can be observed that the Young's modulus increases with increasing substrate temperature. This increase is attributed largely to the effects of crystalline structure of the film at higher temperature.

CP-9 Charge Trapping Induced Frequency-Dependence Degradation in n-MOSFETs with High-k/Metal Gate Stacks, ***C.-H. Dai*** *(m953050006@student.nsysu.edu.tw)*, National Sun Yat-sen University, Taiwan

This letter investigates the reliability issues of HfO_2/Ti_xN_{1-x} metal-oxide-semiconductor field effect transistor (MOSFETs) in terms of static and dynamic stress. The results indicate threshold voltage (V_T) instability under dynamic stress is more serious than that under static stress, owning to transient charge trapping within high-k dielectric. Using C-V techniques verified that electron trapping under dynamic stress was located in high-k dielectric near the source/drain (S/D) overlap region, rather than the overall dielectric. Furthermore, the V_T shift clearly increases with an increase in dynamic stress operation frequency. This phenomenon can be attributed to the fact that electrons injecting to the S/D overlap region have insufficient time to de-trap from high-k dielectric. We further investigated the impact of different Ti_xN_{1-x} composition of metal-gate electrode on charge trapping characteristics, and observed that V_T shift decreases significantly with an increase in the ratio of nitride. This is because the nitride atoms fill up oxygen vacancies and reduce the concentration of traps in high-k dielectric.

CP-10 Electrical and Optical Characterization of Fluorine Doped Tin Dioxide Film Grown by Spray Method, *M. Oshima (swc3900@student.miyazaki-u.ac.jp)*, Univeristy of Miyazaki, Japan, *K. Naomi*, ***K. Yoshino***, University of Miyazaki, Japan

Transparent conduction oxides (TCOs) have high electrically conducting and high visible transmittance with widely used as transparent electrode for flat panel displays including liquid crystal display, organic light emitting diodes and plasma displays. The most important TCOs film in practical applications nowadays is Sn-doped In_2O_3 (ITO)(1). SnO_2 is an alternative potential candidate of ITO thin films due to its cheap and abundant raw material(2). Thus, we focused on this material. SnO_2 is also a promising material for applications including gas sensors, photovoltaic solar energy conversion, and electrochromic devices. SnO_2 behaves like an n-type semiconductor with a wide energy gap (≈ 3.8eV) and has a tetragonal structure similar to the rutile structure.

In our previous paper(3), FTO (0 ~ 5 mol%) films were grown on glass substrates by the spray pyrolysis method at 500˚C. The F-doping caused the resistivity to decrease and the carrier concentration to increase. The undoped and F-doped SnO_2 films were all n-types, which indicated that fluorine atoms can act as donor impurities. The lowest resistivity of 1.4×10^{-3} Ωcm was obtained at a fluorine concentration of 4 mol%.

In the present study, transparent conducting F-doped SnO_2 films were successfully prepared on glass substrates by spray pyrolysis method in order to find out the effect of high F-doped concentration. The best electrical and optical properties, average transmittance of 82 % and resistivity of 3.9×10^{-4} Ωcm, carrier concentration of 4.7×10^{20} cm^{-3}, mobility of 34 cm^2/Vs, were achieved with fluorine doing concentration of 17 mol% at substrate temperature of 500°C.

(1) H. Chen, X. Wang, Y. H. Yu, Z. L. Pei, X. D. Bai, C. Sun, R. F. Huang, L. S. Wen, Appl. Surf. Sci 158 (2000) 134.

(2) S. Takaki : Reports on Ashai Glass Co., Ltd. Research Center, 50 (2007) 105.

(3) M. Oshima, Y. Takemoto, K. Yoshino, Phys. Status Solid (C) 6 (2009) 1124.

CP-11 Improving the Visible Transmittance of Low-e Titanium Nitride Based Coatings for Solar Thermal Applications, ***M. Yuste*** *(miriam.yuste@icmm.csic.es), R. Escobar Galindo, O. Sánchez, J.M. Albella*, Instituto de Ciencia de Materiales de Madrid, Spain

Low-emissivity (*low-e*) coatings on glass are nowadays extensively used for energy saving applications in architectural windows and on solar thermal collectors. In this work we studied the feasibility of TiN-based layers, deposited by reactive magnetron sputtering, as cost-effective low-emissivity coatings. By changing the deposition parameters, different compositions of the films (measured by Glow Discharge Optical Emission-GDOES and Rutherford Backscattering Spectroscopy- RBS) and different textures and surface morphologies (X-Ray Diffraction-XRD and Scanning Electron Microscope-SEM) can be observed. These changes allow tuning the optical properties of the coatings, in particular, the transmittance (T) in the visible range, measured by Spectroscopic Ellipsometry (SE) and the emissivity (ε), measured both directly by an emissometer and indirectly by Fourier Transform Infrared Spectroscopy (FTIR). In order to improve the visible transmittance of TiN single layers we have proposed three strategies:

- Doping with aluminium, the T of the TiN films improves in a 15% but at the expenses of increasing their ε by a factor 1.3.

- Post-deposition annealing treatments up to 500°C improve in a 10% the T at room temperature while keeping the ε.

- Multilayers structures (TiO_2/TiN/TiO_2) present the best results improving in a 30% the T of the TiN single layers while keeping the ε.

Hence, based on the control of the optical properties, and taking into account other properties such as thermal stability and long term durability, it is then possible to design selective coatings to be used in industrial solar thermal applications.

CP-13 Processing of TiO_2 Films by dc Magnetron Sputtering and Pulsed dc Magnetron Sputtering., ***L.C. Fontana*** *(fontana@joinville.udesc.br)*, Universidade do Estado de Santa Catarina, Brazil, *J. Lin, J.J. Moore*, Colorado School of Mines

TiO_2 thin film has attracted extensive attention in terms of its interesting thermal, electronic and optical properties in recent years. The properties of the magnetron sputtered TiO_2 thin films are determined by the phase and microstructure of the films, which can be modified and optimized by usefully controlling the ion bombardment on the growing thin films. TiO_2 oxide films are deposited by means of two processes: continuous dc magnetron sputtering and pulsed dc magnetron sputtering. The influence of plasma generated bombardment of ions on TiO_2 film growth in pulsed dc Magnetron-Sputtering by controlling the negative substrate bias voltage and the oxygen partial pressure was investigated. An electrostatic quadrupole plasma mass spectrometer was employed to measure the energy of ions in the plasma. The correlation between the energy delivered to film during deposition and the film texture, microstructure, electrical and mechanical properties is investigated.

CP-14 The Band Diagram Constructed by Scanning Surface Potential Microscopy (SSPM) in n-ITO/p-Si Heterojunction Solar Cells, *P.-C. Juan (pcjuan@mail.mcut.edu.tw)*, Center for Coatings and Laser Applications, Taiwan, *C.-H. Liu*, National Taiwan Normal University, Taiwan, ***J.-F. Dai***, Ming Chi University of Technology, Taiwan, *C.-L. Lin*, Feng Chia University, Taiwan

Indium tin oxide (ITO) was deposited on silicon substrate to form an ITO/Si heterojunction for solar cell applications. Before metal top electrode was formed, different oxygen contents in helium ambient were added in the postannealing temperatures of 400°C, 500°C, and 600°C during rapid thermal annealing (RTA). The result shows the optical bandgap of ITO thin films increases with increasing postannealing temperature and/or film thickness, but the bandgap decreases with adding 5% oxygen in the helium gas. The wider bandgap under high temperature annealing and without oxygen added in the helium gas results in better rectifying characteristics for pn heterojunction. The work function of ITO thin films was measured by using the scanning surface potential microscopy (SSPM). The work function of ITO (RTA = 400°C) is 4.55 eV. The temperature-dependent current-voltage characteristics were also measured and the barrier height between ITO and silicon is extracted to be about 0.16 eV. Therefore, the band diagram before and after two materials contacting with each other can be constructed. From the band diagram proposed, an inversion layer near the silicon surface is easily formed when the ITO contacts with p-type silicon substrate. It is consistent with the reverse rectifying characteristics at the ITO/p-Si interface. Finally, the optoelectronic characteristics such as cell efficiency of ITO/Si heterojunction solar cells are measured and can be well explained by the positions of energy levels of the band diagram.

CP-15 Optical Optimized Transparent Electrode for Thin Film Solar Cell by Atomic Layer Deposition, *C.-N. Hsiao (cnhsiao@itrc.org.tw), C-.C. Yu, P.-K. Chiu, C-.C. Kei,* ***D. Chiang***, National Applied Research Laboratories, Taiwan, *H.-C. Pan*, Gintech Energy Corporation, Taiwan

Optical optimized Al doped ZnO nanolaminates were deposited on glass and Si wafer by atomic layer deposition as a transparent electrode for thin film solar cell . The corresponding properties of the films were investigated by in-situ quartz balance, ellipsometry, spectrometry, Hall-effect measurement, and high-resolution transmission electron microscopy. It was found that the optical, electrical and structural properties were significantly dependent on the growth temperature. For the relatively low temperatures growth condition (< 200˚C), the optical optimized 2% Al doped ZnO nanolaminates transparent electrode with high mobility allows film resistivity in the low 10^{-3} W-cm range and a high transparency > 86% over a wide spectrum, from 400 to 1300 nm. Furthermore, atomic-scale HRTEM (HAADF) revealed that a secondary inter-phase formed between the Al_2O_3/ZnO interface. In addition, to estimate the reliability of thin film solar cell modules with the ALD AZO transparent electrode, an international standard IEC61646 certified test was performed. The results of efficiency, environmental, and mechanical testing of photovoltaic (PV) modules will be discussed.

CP-16 Helical SiO_2 Film for Indiscriminatively Circular Polarization Handedness Inversion, *Y.-D. Kim, Y. Zou,* ***J.-J. Kim***, *J.-B. Kim, C.-K. Hwangbo (hwangbo@inha.ac.kr)*, Inha University, Korea

Polarization converters have been widely used in optical systems. Semiconductor quantum dots or optical tunnelings have been used as circular-to-linear and linear-to-circular converters. A semiconductor guiding layer, a thin-film grating or a [prism/MgF_2 columnar thin film/air] configuration etc. have been used as a linear polarization converter. However, the study on the handedness conversion of circular-polarized light is rare. Since helical films fabricated by oblique angle deposition are known as excellent candidates for circular polarization elements including sources, reflectors, filters, and detectors, they may be used as a circular polarization converter.

In this study, the circular polarization conversion reflectance is studied for [prism/SiO_2 helical thin film/air] configuration for the first time according to our knowledge. A circular polarization conversion reflectance from right(left)-circular polarization to left(right)-circular polarization was measured and calculated for a [prism/SiO_2 helical thin film/air] configuration under total internal reflection condition. It is found that the handedness of an incident circular-polarized light can be reversed with the highest circular polarization conversion reflectance of 92.2% at an incidence angle of 57.8±0.1°. Principal refractive indices of the helical film were derived by fitting the measured circular polarization conversion reflectance to the calculated one.

CP-17 The Electrical Impedance Spectra Characterization of Electrochromic Glass, ***W.-D. Jheng***, National Chin-Yi University of Technology, Taiwan, *C.-K. Lin (cklin@fcu.edu.tw)*, Feng Chia University, Taiwan, *C.-C. Chen*, National United University, Taiwan

The electrochromic (EC) glass was fabricated by the sputter deposition process. The EC glass has the configuration glass/ITO/WO_3/1M $LiClO_4$-PC/ ITO/glass. When the voltage (-3.5V) was applied to the device, the active layer of the assembled device changed from almost transparent to a translucent blue color (colored). The average transmittance in the visible region of the spectrum for a 100 cm^2 EC device was 73% in the bleached state. The device with 140 nm WO_3 as the active layer has an average transmittance in the colored and bleached states of 11.9% and 54.8%, respectively. The transmittance spectra results showed a clear color change in the device was observed when the applied voltage was below -3V (colored) and above 2V (bleached). The characteristics of the EC glass were determined using UV–VIS transmittance spectra, cyclic voltammetry, and electrochemical impedance spectrum equipment. Different logotypes were presented onto electrodes by voltage control when the device was applied a positive voltage state ("NCUT") and applied a negative voltage state ("NUU"), respectively. EC glass structure was simulated using an equivalent circuit where ω_1 and ω_2 represent the working electrodes, and ω_3, ω_4 represent the electrolyte and counter electrode. In the circuit, the ohmic impedance includes ITOs resistance and transport wire resistance (R_0). The working parts of the ITO/WO_3 and WO_3/electrolyte interfaces are presented as $C_1//R_1$ and $C_2//R_2$. The electrolyte presents as $C_3//(R_3+W)$. The counter part of ITO/electrolyte is presented as $C_4//R_4$.

CP-18 Tantalum Oxide Films Prepared by Magnetron Sputtering for All Solid State Electrochromic Devices, ***S.-C. Wang***, Southern Taiwan University, Taiwan, *K.-Y. Liu, J.-L. Huang (jlh888@mail.ncku.edu.tw)*, National Cheng Kung University, Taiwan

In this study, inorganic-solid-state electrolyte tantalum oxide thin films were deposited by D.C. reactive magnetron sputtering to improve the leakage and deterioration of the traditional liquid electrolyte of electrochromic device. The parameter of O_2 atmospheres (the flow rate range : 1~20sccm) and powers (35~100W) were conducted to prepared the tantalum oxide films with various compositions, microstructures, optical properties and electrochromic properties. The results indicated that tantalum oxide thin films were amorphous, near stoichiometric, porous with loose fibrous structure, and highly transparent in nature. As the oxygen flow rate and power increased, the refractive index increased however the current density and optical transmission change as the film decreased. At the oxygen flow rate of 3sccm and 50W, the transmission change between colored and bleached states at a wavelength of 550nm was 56.7%. The all solid electrochromic device was manufactured as the multilayer of Glass/ITO/WO_3/Ta_2O_5/NiO_x/ITO/Glass. The optical transmittance difference of the device increased as the applied voltage increase and the maximum change reached 66.5% in the applied voltage of ±5V.

CP-19 Effect of Annealing Temperature on the Microstructure and Photoluminescence of Low Resistivity Si/Si-N/Ta-N Thin Films Using Magnetron Sputtering, *C.-K. Chung (ckchung@mail.ncku.edu.tw), T.-S. Chen,* ***N.-W. Chang****, M.-W. Liao*, National Cheng Kung University, Taiwan

The silicon (Si) is characterized as having a poor efficiency of light emission and only produces light outside the visible range due to its indirect low bandgap material. However, the Si-based nanostructures show the quantum confinement effect, luminescence center and surface chemistry effect to enhance the efficiency and to produce emission of visible light. A lot of studies have been devoted to the fabrication of porous Si, erbium-doped Si and Si embedded in dielectric matrix of Si-O or Si-N together with furnace annealing. But, these Si nanostructured films were high resistivity and non-conducting. In the article, the effect of annealing temperature on the microstructure and photoluminescence of low-resistivity Si/Si-N/Ta-N three-layer thin films deposited by magnetron sputtering and followed by rapid thermal annealing (RTA) has been investigated. Grazing Incidence X-ray Diffraction, Fourier transform infrared transmittance spectra, energy dispersive spectroscopy, scanning electron microscopy and photoluminescence (PL) spectrum were utilized to characterize the evolution of microstructure and PL behavior of multilayer films at different annealing temperature. The main emission peak of PL at about 550 nm was observed and had red shift with increasing annealing temperature. The Si nanocrystals were formed by the post annealing of a Si/Si-N/Ta-N at 90°C. It suggests that the observed PL is originated from electro-hole pair recombination in Si nanocrystals or luminescence center in the film. The relationship between the annealing temperature, microstructure and photoluminescence behavior of Si/Si-N/Ta-N multilayer films is discussed and established.

CP-20 Surfactant Assisted Growth of SnO_2 Thin Films for Gas Sensing Applications, ***K. Khun Khun***, *A. Mahajan (dramanmahajan@yahoo.co.in), R.K. Bedi*, Guru nanak dev University, Amritsar, India

Porous nanostructured SnO_2 films have been prepared using an ultrasonic spray pyrolysis technique in conjunction with cationic, anionic and non ionic surfactants namely CTAB (Cetyl trimethyl ammonium bromide), SDS (sodium dodecyl sulphate) and PEG (polyethylene glycol) respectively. The effect of surfactants on the structural, electrical, optical and gas sensing properties of SnO_2 films were investigated by using different techniques such as X-ray diffraction (XRD), Field emission scanning electroscope microscopy (FESEM), two probe technique and Photoluminiscence (PL) studies. The results reveal that the addition of surfactants in the precursor solutions leads to reduction in crystallite size with significant changes in porosity of SnO_2 films. PL studies of the films show emissions in the visible region which exhibit marked changes in the intensities upon variation of surfactants in the precursor solutions. The prepared films were tested for their sensing behaviour towards chlorine and the results reveal that the films prepared in conjunction with cationic surfactant CTAB exhibits a good sensing response towards chlorine at low operating temperatures.

CP-21 Structural Evolution and Photocatalytic Activity of Pulsed Magnetron Sputtered Titania-Based Coatings, *N. Farahani, P. Kelly (peter.kelly@mmu.ac.uk), G.T. West, M. Ratova,* Manchester Metropolitan University, UK, *C. Hill,* Cristal Global, UK, ***J. Kulczyk-Malecka***, Manchester Metropolitan University, UK

It is well known that, depending on deposition conditions, the structure of titania coatings may be amorphous, anatase or rutile, or a mixture of phases, and that the anatase phase is the most promising photocatalyst for the degradation of organic pollutants. The formation of anatase depends on the energy delivered to the growing film, which in turn depends on the operating parameters chosen. In this study, coatings have been deposited onto glass substrates by pulsed magnetron sputtering (100 – 350 kHz) both from metallic targets in reactive mode and directly from oxide powder targets. The as-deposited coatings were analysed by scanning electron microscopy (SEM), X-ray diffraction (XRD) and micro Raman spectroscopy. Selected coatings have been annealed at temperatures in the range of 100 - 800 ºC and re-analysed. The photocatalytic activity of the coatings has been investigated through measurements of the degradation of organic dies, such as methyl orange, under the influence of UV light. For both sets of coatings, the influence of deposition parameters, such as pulse frequency, duty and magnetron configuration on the as-deposited and post-annealed structures and properties has been investigated. Further sets of coatings have been produced both from metallic and powder targets in which the titania is doped with a range of transition metal elements. These coatings have also been analysed and the influence of the dopant element on photocatalytic activity has been investigated.

CP-23 Characterization of IZO-Based Thin Film Transistors Fabricated Using a Novel Two-Step Deposition Process, ***W. Kim***, *S.-H. Lee, J.-H. Bang, H.-S. Uhm, J.-S. Park (jinsp@hanyang.ac.kr)*, Hanyang University, Korea

Future active matrix display systems with enhanced performances are likely to be larger than they currently are. With the rapid progress in display technology, there has been increasing interest in developing oxide-based thin film transistors (TFTs) and many studies have been focused on variety oxide semiconductors that can be used as channel layers of the oxide-TFTs. Among those, sputtering-produced amorphous indium-zinc-oxide (a-IZO) thin films exhibit high electron mobility even when it is deposited at room temperature. Also, their conductivity can be controlled by varying the oxygen partial pressure, the sputter power, and the composition of target material. It is possible that a-IZO thin films are used both as a channel layer and as source/drain (S/D) layers of TFTs. To use the a-IZO thin film as a channel layer, it is often deposited in oxygen ambient to reduce the carrier concentration. This manner, however, may significantly increase the electrical resistivity of a-IZO films, leading to the deterioration of a-IZO TFT's performance.

In this study, we suggest a novel two-step deposition process, by which a-IZO TFTs with excellent on/off current ratios can be achieved without deteriorating their TFT performance. The a-IZO TFTs were fabricated with a bottom gate structure. An n-type Si (100) wafer with a low resistance (below 0.002 Ωcm) was used as a gate, and a gate oxide layer (300 nm) was formed by thermally oxidizing the Si substrate . Then, a-IZO channel layer was deposited on the gate oxide layer via the RF sputtering method by following the two-step deposition procedure. The 1st step deposition was done at a relatively low oxygen partial pressure (i.e., $O_2/Ar < 5$ %) formed to get a higher mobility. The 2nd step deposition was accompanied without stopping the vacuum, only by increasing the oxygen partial pressure (i.e., $O_2/Ar > 10$ %) to maintain low off-current levels. The source/drain contact area was defined by photolithography and the source/drain regions uncovered by photoresists were plasma-treated to reduce the contact resistances. The a-IZO films used for the source/drain contacts were deposited via the same RF sputtering system under a pure Ar environment. For all the deposited IZO films, the electrical, optical, and chemical analyses were carried out and the results were characterized in terms of various O_2/Ar ratios and plasma treatment conditions. The device characteristics of the a-IZO TFTs fabricated by the proposed two-step method were compared those fabricated by the conventional single deposition process. The results showed that the on/off current ratio was significantly improved by the proposed two-step process.

CP-24 Effects of Additive Hydrogen Gas on the Instability Due to Air Exposure in ZnO-Based Thin Film Transistors, *J.-H. Bang,* ***S.-H. Lee****, W. Kim, H.-S. Uhm, J.-S. Park (jinsp@hanyang.ac.kr)*, Hanyang University, Korea

Thin film transistors (TFTs) made by an amorphous Si (a-Si) have been important elements in the flat-panel display. However, a-Si TFTs have critical problems such as light sensitivity and low mobility (< 1 $cm^2/V\times s$). To resolve these problems, use of oxide semiconducting materials as a channel layer for TFT has recently been introduced. The channel materials of most oxide TFTs are comprised of zinc oxide (ZnO) and various compounds based on ZnO. Among those, ZnO is one of the most promising candidates for the transparent TFT applications since it has good crystallinity even when prepared at low temperature and it also has a widely range conductivity from metallic to insulating. When ZnO films are exposed to air, however, they often show unstable electrical properties (e.g., their electrical resistivities significantly increase), resulting in the degradation of the ZnO-based TFT's device performance. It was also recently observed from our experiment and other group's works that the electrical properties of hydrogen-incorporated ZnO films showed to be less sensitive to the air exposure. This was believed to be due to the role of hydrogen atoms that limited the adsorption of oxygen at the ZnO surface. However, this issue has scarcely been studied.

Here, we have investigated the effects of additive gases (such as H_2 and N_2), which are added during ZnO deposition, on the variation in the electrical resistivity of ZnO films and the device characteristic of ZnO-based TFTs due to the long-term air exposure. Thin films of ZnO (including ZnO:H and ZnO:N) used for channel of TFT were deposited at room temperature via RF magnetron sputtering by varying the mixing ratio of the additive gases. The ZnO-based TFTs with a bottom gate structure, which consisted of heavily-doped Si wafer (gate), plasma-enhanced CVD -produced SiO_x (gate insulator), and sputtered Al layers (source/drain), were fabricated using a lift off method. All the ZnO films and ZnO-based TFTs prepared were exposed to air for a long time up to 5 days. The variations in the structural, chemical, electrical, and optical properties of ZnO films due to air exposure were monitored by field-emission scanning electron microscopy (FESEM), atomic force microscopy (AFM), x-ray diffraction (XRD), and secondary ion mass spectroscopy (SIMS). In addition, the I-V characteristics of ZnO-based TFTs and their device parameters (such as threshold voltage, field-effect mobility, and on/off current ratio) were measured and characterized in terms of the air exposure time and the condition of gas addition. Finally, all the experimental results were physically explained by discussing the role of additive gas atoms.

CP-26 CuInSe$_2$ Thin Film Photovoltaic Absorber Formation by Rapid Thermal Annealing of Binary Stacked Precursors,
J. Koo, *S.-C Kim, H. Park, W.-K. Kim (wkim@ynu.ac.kr)*, Yeungnam University, Korea

Chalcopyrite $Cu(InGa)Se_2$-based materials have demonstrated the potential of high efficiency thin film solar cells, yielding around 20% cell efficiency. Conventional method to fabricate CIGS absorber follows either elemental coevaporation of individual elements (i.e., Cu, In, Ga and Se) or reactive annealing of metallic precursors (i.e., Cu-Ga-In). The reactive annealing of metallic Cu-Ga-In precursors under Se or H_2Se is a likely method of producing effectively large area $Cu(InGa)Se_2$. However, Ga accumulation near the Mo side of substrate/Mo/CIGS structure is often observed during the selenization of Cu-Ga-In precursors yielding phase-separated $CuInSe_2$ and $CuGaSe_2$ which subsequently lead to lower open-circuit voltages.

In this contribution, rapid thermal process (RTP) using stacked binary (metal-Se) precursors, e.g., glass/Mo/In_xSe_y/Cu_xSe, was explored to reduce the reaction time of $CuInSe_2$ formation drastically, while maintaining compositional depth uniformity. Various binary stacked precursors, including In_2Se_3/CuSe and InSe/CuSe, were prepared onto Mo-coated glass substrates. The reactive annealing of metal precursors was performed in a rapid thermal process system consisting of a quartz tube reactor with an inner diameter of 62 mm, quartz sample tray and infrared (IR) heater under a Se atmosphere. The quartz sample tray held up to six 1 cm x 1 cm samples. The IR heater ramped temperature rapidly, requiring only 1 min to reach 1,000˚C from room temperature. At a fixed annealing temperature of 550˚C, it was confirmed that reaction time of 2 min was sufficient enough to form $CuInSe_2$ by completely consuming binary reactants. The longer reaction time of 5~10 min caused the formation of $MoSe_2$ at $CuInSe_2$/Mo interface.

Precursor and $CuInSe_2$ structures were characterized by x-ray diffraction (XRD) and scanning electron microscope (SEM). Bulk composition and compositional depth profiles of the films were measured by inductively coupled plasma optical emission spectroscopy (ICP-OES) and secondary ion mass spectrometry (SIMS), respectively.

CP-27 Galvanic Corrosion Behaviour of Al Based Coatings in 0.6 M NaCl Solution,
O.A. Fasuba, *A. Yerokhin (a.yerokhin@shef.ac.uk), A. Matthews, A. Leyland*, University of Sheffield, UK

In engineering design, care is taken to avoid dissimilar metal contact that cause galvanic corrosion in aqueous environments. Engineers and designers often use coatings to minimize the effect of galvanic attack. Cadmium-based coatings provide excellent barrier and sacrificial corrosion protection on steel, as well as desirable physical and mechanical properties of self-healing and anti-seizure; however, such coatings are effectively banned from many applications due to the toxic nature of both coating and application technique. Ever more stringent environmental regulations lead to an increasing need to develop coatings with equally good corrosion resistant behaviour to that of cadmium, which are also environmentally benign. Aluminium-based coatings can exhibit corrosion potentials similar to cadmium, such that (if the coating is damaged) aluminium will preferentially corrode instead of the exposed substrate. Traditional corrosion evaluation techniques (such as salt spray testing) are useful in screening coating behaviour (ie. acceptable performance or not) but reveal little of the underlying complex electrochemical phenomena that lead to the observed behaviour. Therefore, this study examines the electrochemical behaviour of a selection of commercially available Al based coatings on steel in 0.6 M NaCl solution, to provide in-depth information on the corrosion processes involved, and their evolution with time.

The corrosion performance of the coatings was assessed by various electrochemical techniques. Open-circuit potential (OCP) stability measurements were carried out for a period of 2 hours, against the resting potential of each coating in 0.6 M NaCl solution. Potentiodynamic polarization scanning was performed at a rate of 1.667mV/s starting at –0.2V vs. OCP and ending at 0V vs. SCE. In the galvanic corrosion tests, uncoated steel was the working electrode while the coated steel substrates were used as the counter electrode, the reference being a saturated calomel electrode (SCE). The data acquisition rate was 0.1 points/second for a duration of 2 hours at 0V vs. OCP. SEM images and EDX analysis were also used to characterise the morphology, elemental composition and the physical degradation of the coatings. Results obtained indicate that thermally sprayed Al coatings give high corrosion current densities with polarisation behaviour similar to that of cadmium. Electroplated and IVD aluminium coatings showed passivation and periodic breakdown and regrowth of the passive film over a range of applied potentials, while coatings containing aluminium particles in a chromate/phosphate inorganic binder give OCP values very close to that of steel.

CP-28 In Situ Thermal Residual Stress Evolution in ZnO Thin Films Deposited by Magnetron Sputtering on Si,
P.-O. Renault *(porenaul@univ-poitiers.fr), C. Krauss, E. Le Bourhis, P. Goudeau,* University of Poitiers, France*, E. Barthel,* SVI, Aubervilliers, France*, S.Y. Grachev, A. Benedetto*, SGR, Saint Gobain, France

Zinc Oxide is a material of technological importance for its practical and potential applications for short wavelength optoelectronic devices and transparent conductive oxide films, such as in UV-lasers, blue to UV light-emitting diodes and solar cells electrodes. This oxide is also used in glass stacking as a UV spectrum filter and can provide other promising technological applications thanks to its adjusting photoluminescence properties. The advantage of the magnetron sputtering technique is the achievement of polycrystalline ZnO films deposition on large flat glass area without intentional substrate heating. However, it results in residual stresses which can be detrimental when occurrence of spontaneous delamination, or under scratch during processing or in service. The control of their mechanical reliability can then be achieved by an in depth comprehension of the residual stresses build up or relaxation mechanisms occurring in the films in relation with the material structure.

Residual stress evolution in sputtered ZnO films has been studied in-situ in a furnace by synchrotron X-ray diffraction. The films sputter deposited on (001) Si substrates were thermally cycled from 25°C up to 700°C and down to 25°C . X-ray diffraction 2D patterns were captured continuously during the heating, plateau and cooling ramps. The corrections carried out for compensating the furnace drift are presented. The obtained stress state is observed to change from compressive to tensile upon cooling. Stress amplitudes increase up to 370°C and, then stress relaxation is detected. The overall behaviour is discussed in terms of structure changes induced during the heat treatment. This work is done in the framework of an ANR project named Merethif.

CP-29 X-ray Photoelectron Spectroscopy Depth Profiling of La$_2$O$_3$/Si Thin Films Deposited by Reactive Magnetron Sputtering,
C.V. Ramana (rvchintalapalle@utep.edu), R.S. Vemuri, University of Texas at El Paso*,* ***V. Kaichev,*** Boreskov Institute of Catalysis, Russia*, V. Kochubey,* Institute of Semiconductor Physics, Russia*, A. Saraev,* Novosibirsk State University, Russia*, V.V. Atuchin*, Institute of Semiconductor Physics, Russia

Lanthanum trioxide (La_2O_3) is one among the most promising high-*k* dielectric materials to replace SiO_2 and Si_3N_4 in advanced metal-oxide semiconductor devices in gate stack. La_2O_3 can be prepared by various techniques; however the film properties are strongly dependent on the fabrication conditions. Reactive magnetron sputtering deposition is widely used for the preparation of high quality transition multivalent metal oxide films with reproducible parameters and controlled thickness. The technique is preferred since it usually offers a high deposition rate for oxide films and a possibility to control the chemical composition of the film by reactive atmosphere in vacuum chamber. The aim of the present study is to understand the surface structure and evaluate the chemical parameters of La_2O_3 films deposited on Si substrates by reactive magnetron sputtering. La_2O_3 thin films were deposited onto Si(100) substrates in an argon/oxygen atmosphere using a high purity La target (99.9%). Structural parameters of the films were estimated by reflective high energy electron diffraction (RHEED) method at electron energy of 50 keV. All the films show no diffraction pattern indicating their amorphous nature in the near surface layers. Chemical state examined by the X-ray photoelectron spectroscopy (XPS), SPECS device, monochromatic Al *Ka* radiation before and after Ar^+ ions (2.4 keV, 10 mA/cm^2, 2, 15, 30 min) sputtering indicates the stoichiometric film formation. Chemical nature of the species was identified with using binding energy (BE) difference parameter DLa = BE (La $3d_{5/2}$) - BE (O *1s*). The C 1s signal disappeared after 2 min ion bombardment. So, it may be concluded that multicomponent C *1s* spectra found for initial film surface is related to top surface hydrocarbons and carbonate species. For initial surface the atomic ratio [O]/[La] exceeded noticeably the ratio characteristic of La_2O_3, that is an indicator of presence of CO_x groups at the surface. The ratio [O]/[La] decreases from 3.66 to 1.41 with increasing duration of ion bombardment revealing removement of CO_x and partial oxygen loss. Formation of carbonates at the La_2O_3 surface is confirmed also by complex shape of O *1s* spectra. The intensity of high binding energy component is decreasing with increase of ion sputtering time.

CP-30 Microstructure and Dispersive Optical Parameters of Thermally Evaporated Nickel Films, *C.V. Ramana (rvchintalapalle@utep.edu),* University of Texas at El Paso, ***V.V. Atuchin****, T.I. Grigorieva, V.N. Kruchinin,* Institute of Semiconductor Physics, Russia*, D.V. Lychagin,* Tomsk State University of Architecture and Building, Russia*, L.D. Pokrovsky*, Institute of Semiconductor Physics, Russia

Nickel (Ni) films are widely used in electrochemistry, microelectronics, energy and nanotechnology. In integrated optics, the nanometric Ni films are used as a source for doping $LiNbO_3$ substrate and optical waveguide fabrication by thermal diffusion. Because effective refractive indices of the waveguide modes are strongly dependent on the optical profiles in doped layer, precise control of Ni film thickness (*h*) is needed in the range *h*~10-50 nm. Ellipsometry can be successfully applied for nondestructive determination of the thickness of a dielectric and semi-transparent metal film when optical constants of the material are known. Regrettably, noticeable scattering was found for optical constants reported earlier in literature for Ni films and crystals. As it seems, this scattering appeared due to different film quality or crystal surface preparation. The focus of the present work is centered on Ni film fabrication by thermal evaporation, evaluation of their optical parameters with spectroscopic ellipsometry, and compares the results with those determined for Ni single crystal . Nickel single crystals (99,995%) were grown by directional solidification from machined polycrystalline blanks in graphite mold. Laue X-ray back reflection method was used for crystal orientation. Specimens were sliced from the single crystal by means of an acid saw. The specimen with the smoothest polished surface was studied by spectroscopic ellipsometry method. Nickel films were fabricated by thermal evaporation method in vacuum below 10^{-5} Torr. The substrate temperature was *T*=100 °C. For precise determination of optical parameters, thick Ni film (*h*~100 nm by as determined from optical interferometry) was prepared on silica substrate. To increase the metal adhesion, the substrate was subjected to RCA chemical cleaning just before insertion into vacuum chamber. Structural parameters of Ni films were studied with reflection high-energy electron diffraction (RHEED). Thermally evaporated Ni films are polycrystalline. Spectral dependencies of refractive index *n*(l) and extinction coefficient *k*(l) were determined with the help of spectroscopic ellipsometry in the spectral range, l~250-1030 nm. The *n* and *k* increase continuously with l. Such a behavior is typical for refractive metals. The dependencies *k*(l) determined for the film and crystal surface are very close. The curves *n*(l), however, are close in the shape but the refractive index of Ni film is slightly higher than that determined for single crystal. This refractive index gap ~0.1 between the curves may be appeared due to different surface state of Ni film compared to single crystal (100) surface.

CP-31 Effect of Nitrogen Pressure on the Growth, Microstructure and Optical Properties of TiN Thin Films, *C.V. Ramana (rvchintalapalle@utep.edu), N. Esparaja, V. Rangel,* ***S. White****,* University of Texas at El Paso*, A.L. Campbell*, Wright-Patterson Air Force Base (WPAFB)

Transition metal nitrides (TMNs) are widely used as diffusion barriers in microelectronic applications, heat and corrosion resistance coatings. The unique optical properties of TiN films such as selective spectral range optical transmission and reflection make these materials interesting for application in solar-control windows and optical filters in addition to the traditional electronic and ceramic devices. However, the microstructure of TiN films is very sensitive to the growth conditions, specifically the reactive nitrogen pressure. On the other hand, controlled growth, texture, and composition of the layers can significantly influence their properties, phenomena and performance In present work, TiN films were fabricated using reactive radio frequency magnetron sputter deposition onto silicon (100) and quartz substrates. The nitrogen flow ratio in reactive gas mixture (Ar/N_2) was varied in a wide range. It was found that the crystal structure, texture and optical quality of the grown TiN layers are dependent on the nitrogen ratio in reactive gas mixture during deposition. TiN coatings shown initially the mixture of (111) and (002) texturing to a completely (111) followed by completely (002) texture with increasing nitrogen content. Correspondingly, the optical quality of the TiN coatings varies depending on the preferred orientation. Chemical composition profiles indicate that the nitrogen incorporation into the layers and the associated chemistry determines the functional physical properties of the coatings. The results will be presented and discussed.

CP-34 Large Area Colloidal Crystals for Photonic Applications, ***S. Portal*** *(sabineportal@hotmail.com), E. Cabrera, O. Arteaga, M.-A. Vallvé,* Universitat de Barcelona, Spain*, J. Ferre-Borrull,* Universitate Rovira i Virgili, Spain*, J. Ignés-Mullol, E. Bertran*, Universitat de Barcelona, Spain

Large area colloidal crystals were prepared in one deposition step using a large trough Langmuir-Blodgett system. They were constituted of spherical particles of metal oxide prepared by sol-gel method from hydrolysis of metal ethoxide precursor in ethanol. Particles of different materials were synthesized (titania, silica) with a wide range of size from 50 nm to 1 micron with a narrow dispersion (<10%).

Langmuir-Blodgett self-assembled monolayers of the synthesized particles were deposited on 25-100 cm2–substrates of silicon and glass. Depending on the size distribution, the particle monolayers were characterized by either hexagonal or disordered compact structures.

Morphological properties (particle roughness, shape, surface pattern) were characterized by Atomic Force Microscopy and Scanning Electron Microscopy. Transmittance spectra and ellipsometry measurements provided the optical properties of the colloidal films, which were connected to the degree of their structural order and compactness. The effects of film characteristics on wettability were evaluated by contact angle measurements. Colloidal films can find application in photonics but also as smart surfaces with controllable photo-switched wettability and photocatalytic properties. They are also promising for applications in bioengineering and photovoltaic cells.

CP-35 Diamond Like Carbon/Metal Nanocomposite Films for Solar Harvesting Applications, *H. Zoubos,* University of Ioannina, Greece*, S. Kalogirou, G. Constantinidis, P.C. Kelires,* Cyprus University of Technology, Cyprus*,* ***P. Patsalas*** *(ppats@cc.uoi.gr)*, University of Ioannina, Greece

Diamond-Like Carbon (DLC) has been long studied as a material for surface protection against wear and corrosion; in addition due to the vast range of its optical properties it has been applied in anti-scratch layers in photovoltaics and optical systems. The combination of its exceptional mechanical and optical properties with its reported high thermal conductivity makes it a promising candidate for solar energy harvesting in solar trough collectors. However, its optical transparency is a major drawback for such applications, because the optical absorption spectrum of DLC does not cover the whole solar spectrum.

In this work we incorporated metal nanoparticles into DLC in order to extend its optical absorption into the visible spectral range. We have grown a variety of DLC:Me (Me=Ag, Cu, Ti, Zr, Ni) nanocomposites of varying metal and sp^3 volume fractions by pulsed laser deposition. A detailed study of their optical properties has been performed using optical reflectance and transmittance measurements as well as spectroscopic ellipsometry. The optical properties of the DLC films have been correlated with their structural features such as the metal and sp^3 volume fractions (measured by in-situ Auger electron spectroscopy) and density (measured by in-situ electron energy loss spectroscopy). In addition, their mechanical performance and adhesion to various materials used for solar trough collectors have been evaluated by nanoindendation and scratch testing. Finally, the various DLC:Me films have been thermally (in a vacuum furnace and in ambient) and optically (using a solar simulator) annealed and the changes in their integrity and optical performance have been evaluated, in an effort to identify their potential for realistic applications in solar harvesting.

CP-36 Temperature Effect on $Cu(InGa)Se_2$ Thin Film Photovoltaic Absorber Formation by Reactive Annealing of Metal Precursors, ***H. Park****, J. Koo, J.-S. Han, W.-K. Kim (wkim@ynu.ac.kr)*, Yeungnam University, Korea

The reactive annealing of metallic Cu-Ga-In precursors under Se or H_2Se is a likely method of producing effectively large area $Cu(InGa)Se_2$. However, Ga accumulation near the Mo side of substrate/Mo/Cu(InGa)Se_2 structure is often observed during the selenization of Cu-Ga-In precursors yielding phase-separated $CuInSe_2$ and $CuGaSe_2$ which subsequently lead to lower open-circuit voltages. Cu(InGa)Se_2 films formed by selenization of metal precursors are readily delaminated from Mo layers during CdS chemical bath deposition due to their poor adhesion. It has been suggested that a $MoSe_2$ layer may affect the adhesion at the interface of Cu(InGa)Se_2 and Mo. In particular, a $MoSe_2$ layer oriented parallel to the surface of the Mo layer shows poor adhesion because hexagonal $MoSe_2$ compounds are stacked by weak Van der Waals interactions.

In our research group, the reactive annealing of metal precursors was performed in a rapid thermal process (RTP) system consisting of a quartz tube reactor with an inner diameter of 62 mm, quartz sample tray and infrared (IR) heater. The quartz sample tray held up to six 1 cm ´ 1 cm samples. The IR heater ramped temperature rapidly, requiring only 1 min to reach 1,000°C from room temperature. CuGa-In precursors were prepared on Mo-coated thin sodium-free Corning 7059 glass (SFG) of 0.7mm thickness by sequentially or simultaneously sputtering CuGa alloy with 24wt% Ga and elemental In targets. Total thicknesses of precursors were intended to be 600 ~ 700 nm. The atomic compositions of the precursors were confirmed to be Cu/(In+Ga) = 0.9 ~ 1.0 and Ga/(In+Ga) ~ 0.3.

In this paper, the effects of annealing temperature and ramp rate on the properties of Cu(InGa)Se_2 fims deposited by rapid thermal annealing were systematically investigated, with particular attention paid to the formation of $MoSe_2$ and compositional depth profiles.

CP-38 Transportation Model Establishment of InGaZnO TFT by Using Vacuum System Measurement, *Z.-Z. Li,* Minghsin University of Science and Technology, Taiwan*, **Z.-X. Fu**, Y.-T. Chou, P.-T. Liu (ptliu@mail.nctu.edu.tw),* National Chiao Tung University, Taiwan*, B.-M.. Chen*, Minghsin University of Science and Technology, Taiwan

The effect of annealing atmosphere on electrical metastability of a-InGaZnO TFT is investigated. The generation of oxygen vacancies by the annealing in a vacuum led to an increased I_{off} and large V_{th} shifts, while N_2 and O_2 ambience effectively improve the device performance. A physical mechanism is also reasonably proposed. Amorphous transparent conductive oxide (a-TCO) has attracted lots of attention for its superior electrical performance and insensitivity characteristics to visible light. One of the most popular candidates of a-TCO material nowadays is amorphous indium gallium Zinc Oxide (a-IGZO). However, some fundamental transport mechanisms still need to be clarified, otherwise it will limit the technology development for realistic application. In addition, previous studies reported thermal annealing process was able to critically dominate the electrical performance of a-IGZO TFT, but the process factors in the annealing process have not be specified completely. In this study, the effect of annealing atmosphere (pure N_2, pure O_2, and vacuum) will be studied to explore the optimum annealing conditions for the sputter-deposited a-IGZO TFT. Electrical reliability also will be investigated further by analyzing electrical behavior after gate bias stress in the ambient air and a vacuum. In summary, experimental results indicated the effects of annealing atmosphere on electrical metastability of the a-IGZO TFT under gate bias stresses with different voltage polarities. Annealing temperature would improve the front channel properties while the annealing atmosphere would modify vacancies at the back channel. For the O_2-annealed and N_2-annealled a-IGZO TFT, the magnitude of the V_{th} variation was similar in atmosphere and vacuum during positive gate bias stress, because of the lack of oxygen vacancy in backchannel. However, H_2O would stay on the surface of a-IGZO and resulted in different V_{th} variations in atmosphere or vacuum during negative gate bias stress.

CP-41 Electron Microscopy Analysis of the Growth and Interface Structure of Sputter-Deposited ZrO_2 Thin Films, ***C.V. Ramana*** *(rvchintalapalle@utep.edu), R.S. Vemuri, A. Ferrer*, University of Texas at El Paso

Zirconium oxide (ZrO_2) is an important material with a potential for a wide range of technological applications. The outstanding chemical stability, electrical and mechanical properties, high dielectric constant, and wide band gap of ZrO_2 makes it suitable for several industrial applications in the field of optics, electronics, magneto-electronics, and optoelectronics. ZrO_2 is frequently used as a high refractive index material in multilayer optical coatings in high power laser systems. ZrO_2 is employed in superplastic structural ceramics that demonstrate excellent strength and fracture toughness. ZrO_2 has been considered as a promising dielectric to replace SiO_2 in advanced metal oxide semiconductor (MOS) devices in gate stack. However, it is well known that the electrical and optical properties of ZrO_2 thin films are highly dependent on the film-substrate interface structure, morphology, and chemistry, which are in turn controlled by the film-fabrication technique, growth conditions, and post-deposition processes.

The objective of the present work is to better understand the growth and local structure, interface structure, and chemical reactions at the ZrO_2-Si interface using electron microscopy. The ultimate goal is to minimize the interface diffusion using the surface nitridation approach. In the present work, ZrO_2 thin films have been prepared by the radio-frequency magnetron sputter-deposition onto Si(100) substrates as a function of growth temperature (T_s) varied in a wide range of 30-500°C. The growth behavior, surface structure and morphological features, interface structure, and chemical analysis of surfaces and interfaces have been examined by the high-resolution transmission electron microscopy (HRTEM) and high-resolution scanning electron microscopy (HR-SEM). HRTEM and HRSEM are considered to be the best capabilities to examine the ultra-microstructure of the ZrO_2-Si interface. The results indicate that the effect of T_s on the surface structure, interface layers and morphology of ZrO2 films is significant. ZrO_2 films grown at 30°C are amorphous without IL formation. An increase in T_s results in the formation of nanocrystalline ZrO_2 films. A significant amount of interface mixing occurs at higher temperatures (T_s=500°C) where the clear distinction between ZrO_2 and Si is not possible. The grain sizes determined are in the range 5-40 nm, where the temperature-dependence is clear. Efforts are made to explain the quantitative information, obtained based on the electron microscopy results, making use of the existing models to account for growth behavior and interface structure.

CP-42 High Transparent Soluble Polyimide/Polyimide–Nanocrystalline-Titania Hybrid Optical Materials for Antireflective Applications, *Y.-Y. Yu (yyyu@mail.mcut.edu.tw), W.-C. Chien,* ***H.-H. Yu***, Ming Chi University of Technology, Taiwan

In this study, a new synthetic route was developed to prepare polyimide–nanocrystalline-titania hybrid materials with a relatively high titania content. A soluble polyimide with carboxylic acid end groups (6FDA–6FpDA–COOH) was first synthesized from 4,40-(hexafluoroisopropylidene) diphthalic anhydride (6FDA), 4,40-(hexafluoroisopropylidene) dianiline (6FpDA), and 4-aminobenzoic acid (4ABA). Such end groups could undergo an esterification reaction with titanium butoxide and provide organic–inorganic bonding. A homogeneous hybrid solution was obtained through the mole ratio of titanium butoxide/carboxylic acid, water/acid content, and a mixed solvent system. Then, the polyimide/TiO_2 hybrid thin films were prepared by sol-gel process. The effects of TiO_2 content (up to 90 wt%) on the hybrid film properties and the optimum operating conditions were also investigated. HRTEM results indicated the formation of nanocrystalline-titania domains of around 5–10 nm in the hybrid films. TGA and DSC analysis showed that the decomposition temperature of polyimide was about 468°C. The T_d increased as the titania content in hybrid thin films increased. FTIR spectra indicated that the amidization was complete and the cross-linking Ti-O-Ti network formed. N&k and UV-vis analysis showed that the prepared hybrid films had the good optical properties and high refractive index 1.961. Moreover, the prepared polyimide/titania hybrid thin films were further applied to develop a three layer antireflective (AR) coating on the glass and PMMA substrate. The results showed that the average reflectance of the AR coating on the glass and PMMA substrate was 0.495 and 0.267%, respectively. The transparency at 550nm was greater than 90% for both AR coatings on the glass and PMMA substrates.

CP-43 Preparation and Characterization of P3HT:$CuInSe_2$:TiO_2 Thin Film for Application on Hybrid Solar Cell, *Y.-Y. Yu (yyyu@mail.mcut.edu.tw), W.-C. Chien,* ***S.-H. Chen***, Ming Chi University of Technology, Taiwan

This investigation reports the preparation and characterization of the conductive polymer regular poly(3-hexylthiophene) (rrP3HT) and copper indium diselenide ($CuInSe_2$) and titania (TiO_2) nanocrystals and their application in hybrid solar cells. Quantitative area calculation of the ^{1}H NMR spectra showed that the regularity of the prepared rrP3HT was 93.82%. The rrP3HT was further blended with different contents of $CuInSe_2$ and TiO_2 nanoparticles and spin cast onto the ITO glass. The prepared nanocomposites were characterized by SEM, AFM, TEM, UV-vis, FTIR, PL, and XRD analysis. TEM and XRD analysis showed that the prepared $CuInSe_2$ and TiO_2 nanoparticles had a high degree of crystallinity. UV-vis and PL spectra of the prepared P3HT:$CuInSe_2$:TiO_2 nanocomposites indicated that the absorption and emission spectra increased and decreased with increasing amount of titania, respectively. SEM and AFM images showed that no phase separation could be observation for the prepared P3HT:$CuInSe_2$:TiO_2 films. Solar cells with a device structure of ITO/NiO/P3HT:$CuInSe_2$:TiO_2/Ca/Al were then produced by evaporation of NiO ,Ca and Al as the back contact. Analysis of solar cells showed that the incident photon to converted electron efficiency (IPCE) and energy conversion efficiency (h) increased with the increase in $CuInSe_2$ content. The maximum value of IPCE and h could be obtained as the TiO_2 content was 25wt%.

CP-46 Electrical and Morphological Properties of Metal Doped-TiO_2 Sol-Gel Thin Films, *R. Valaski,* Inmetro, Brazil, ***M. Cremona*** *(cremona@fis.puc-rio.br),* Pontifícia Universidade Católica do Rio de Janeiro, Brazil, *C. Arantes, C. Legnani, W. Quirino, C. Achete*, Inmetro, Brazil

TiO_2 is n-type semiconductor with a large gap which has been successfully used in several applications as photovoltaic, organic photovoltaic and electrochromic devices due to its stability and electronic features. Among the different techniques to produce TiO_2 films the sol-gel methods stand out due to be an easier and cheaper process for large area films production without controlled atmosphere or more sophisticated experimental apparatus. However the TiO_2 resistivity must be decreased considerably to become its utilization easier and wider. The TiO_2 resistivity can be modified and controlled through the precursor solution and post annealing. However, the resistivity decreasing in this case is not large enough for applications as in electrodes development, although feasible results had been obtained in organic photovoltaic devices with TiO_2 as intermediate layers. A well established way to decrease the material resistivity is the doping process with metal atoms. This technique was used in the present work. Besides the TiO_2 doping process with metals as Al and Zn we also investigated the influence of the material used as source of this metals. As metal source nitrates and chlorates due to their higher solubility in the solvent of TiO_2 precursor solution were used. The TiO_2 carrier charge mobility, carrier charge density and resistivity were 1.5×10^1 $cm^2/V.s$, 9.5×10^{12} cm^{-3} and 5.0×10^4 Ω.cm, respectively, for a 40 nm TiO2 film annealed for one hour at 550ºC. Al-TiO_2 precursor solution doped films presented carrier charge mobility, carrier charge density and resistivity 1.2×10^3 $cm^2/V.s$, 3.1×10^{12} cm^{-3} and 1.9×10^3 Ω.cm, respectively for the same film thickness and annealing conditions. When the precursor solution was doped with Aluminum Nitrate (0.3 mM) the carrier charge density increased to 1.5×10^{14} cm^{-3}. Nevertheless, in this case, the resistivity was the same of pure TiO_2 due to the decreasing in the carrier charge mobility. The addition of Aluminum Chlorate in TiO_2 precursor solution seems to influence more the morphology that the electronic film features. In order to elucidate these questions, XRD and XPS measurements were carried out as well Al-TiO_2 and Zn-TiO_2 doped films were developed and characterized with different chlorates and nitrates concentrations. The influence of annealing condition changes was also investigated.

CP-47 Preparation of Impurity-Doped ZnO Transparent Electrodes Suitable for Thin-Film Solar Cell Applications by Various Types of Magnetron Sputtering Depositions, *T. Minami, J. Nomoto, T. Hirano,* ***T. Miyata*** *(tmiyata@neptune.kanazawa-it.ac.jp)*, Kanazawa Institute of Technology, Japan

This paper describes the influence of the type of magnetron sputtering deposition (MSDs) on the characteristics of impurity-doped ZnO thin films for applications as transparent electrodes in thin-film solar cells. An r.f. power-superimposed d.c magnetron sputtering deposition (r.f.+d.c.-MSD) that produced a decrease in deposition damage and obtainable resistivity as well as an increase of deposition rate is demonstrated. Transparent conducting Al- and Ga-doped ZnO (AZO and GZO) thin films were deposited using a magnetron sputtering apparatus with an oxide target, and both an d.c. and an r.f. (13.56 MHz) power supply was applied either separately or in combination. The oxide targets used were commercially available high-density-sintered rectangular targets (127 mm×275 mm). A substrate of OA-10 glass (Nippon Electric Glass Co., Ltd.) with an area of 200 mm×200 mm was placed parallel to the target surface at a substrate-target distance of 90 mm. Sputtering depositions were carried out at a deposition temperature of 200ºC in a pure Ar gas atmosphere at 0.2 Pa. For transparent conducting AZO and GZO thin films prepared by various types of MSDs, the surface morphology and the crystallinity obtained by supplying r.f. power such as in r.f.-MSD and r.f.+d.c.-MSD outperformed those obtained with d.c.-MSD. A higher deposition rate and lower resistivity exhibited in the AZO and GZO thin films prepared by r.f.+d.c.-MSD were obtained in comparison with those found with r.f.-MSD and d.c.-MSD, respectively. To evaluate the light scattering characteristics suitable for applications in thin-film solar cells, surface texturing of the samples was carried out by wet-chemical etching in a 0.5% HCl solution. Subsequently, surface morphology observation and measurements of the optical transmittance and the diffusive component of the surface-textured AZO and GZO thin films were also performed. The high transmittance and high haze properties obtained by supplying such r.f. power as in r.f.-MSD and r.f.+d.c.-MSD outperformed those obtained with d.c.-MSD. The influence of the type of MSD described above may be attributable to decreases of the amount and activity of oxygen reaching the substrate surface; a lower electric field reflects lower sputter voltage in r.f.-MSD and r.f.+d.c.-MSD. Thus, the demonstrated low-damage and high-rate preparation of impurity-doped ZnO transparent electrodes on low temperature substrates by r.f.+d.c.-MSD are suitable for solar cell applications.

CP-48 PL and EL Characteristics of Rare Earth-Activated $BaLa_2O_4$ Phosphor Thin Films with or without Co-doping of Bi, *T. Miyata (tmiyata@neptune.kanazawa-it.ac.jp), Y. Nishi, J.-I. Ishino,* ***T. Minami***, Kanazawa Institute of Technology, Japan

This paper describes the PL and EL characteristics of newly developed rare earth (RE)-activated $BaLa_2O_4$ oxide phosphor thin films with or without the co-doping of Bi and prepared by magnetron sputtering depositions. $BaLa_2O_4$ phosphor thin films were prepared on thick $BaTiO_3$ ceramic sheets by either a conventional or a combinatorial radio frequency (r.f.) magnetron sputtering (rf-MS) deposition method using a powder target, which was a mixture of oxide powders. In combinatorial rf-MS depositions, $BaLa_2O_4$:Bi,RE phosphor thin films with either Bi or RE content that varied across the substrate surface were deposited using a powder target divided into two parts. The sputter depositions were carried out under the following conditions: atmosphere, pure Ar or Ar+H_2; pressure, 6 Pa; r.f. power, 100 W; and substrate temperature, 350ºC. The thickness of all deposited phosphor thin films was approximately 1.5 µm. After the depositions, postannealing was carried out in a pure Ar or a reducing gas atmosphere at a temperature up to 1100ºC. TFEL devices were fabricated by depositing an Al-doped ZnO thin-film transparent electrode and an Al thin-film back electrode on the phosphor thin-film emitting layer and the $BaTiO_3$ ceramic sheet, respectively. As an example, multicolor PL emissions were always observed from $BaLa_2O_4$:Bi,Eu phosphor thin films prepared with appropriate Bi and Eu contents and postannealed at 1000-1100ºC. However, the spectral shape of the PL emissions observed from the postannealed $BaLa_2O_4$:Bi,Eu phosphor thin films were considerably affected by the postannealed atmosphere. In addition, multicolor EL emissions were obtained in TFEL devices fabricated using postannealed $BaLa_2O_4$:Bi,Eu thin films prepared by varying either the Bi or Eu content. The observed blue emission band peaking at a wavelength around 420 and 450 nm may reflect the transition in Eu^{2+} and the $6s^2$-$6s^16p^1$ transition in Bi^{3+}, respectively. The multiple sharp emission peaks involving red emissions peaking around 610 and 620 nm are assigned the transition in Eu^{3+}. It can be concluded that multicolor PL and EL emissions, which were observed from $BaLa_2O_4$:Bi,RE phosphor thin films prepared by varying either Bi or RE content, allow the control of emission color over a wide range. In addition, $BaLa_2O_4$ is very promising as new host materials for oxide phosphor applications.

CP-49 Exciton Wavefunction Coupled Surface Plasmon Resonance for In-doped ZnO Nanowires with Aluminum Cylindrical Micropillars, ***C.-H. Fang***, *Y.-T. Liang, J.-C. Wang, T.-E. Nee (neete@mail.cgu.edu.tw)*, Chang Gung University, Taiwan

Zinc oxide (ZnO) has attracted intensive research effort in recent years, due to its unique properties and versatile applications. Besides, ZnO is naturally of *n*-type conduction due to a large number of native defects. Recently, the researches of ZnO electrical conductivities are focused on the synthesis of *p*-type ZnO using various techniques and dopants. Recent work on the conservation of surface plasmon and light through period metal arrays has elucidated the propagation of surface plasmon resonance (SPR) behavior. In this paper, we discuss the SPR dispersion relations with various Al cylindrical micropillars by measuring the surface charge displacements. Optical characterization of exciton coupled with SPR for indium-doped ZnO nanowires with Al cylindrical micropillars has been also investigated.

From photoluminescence spectra, it is found that In-doped ZnO nanorods have a blue emission at 425 nm, which resulted form the ZnO band-to-band transition with SPR coupling effect. Prior to the arrays of samples were annealed, a broad green emission centered at 500 nm was observed, which is attributed to ZnO native point defects. The relatively strong green band emission results from the radiative recombination that arises from the ionized oxygen vacancy. Compare the In-doped ZnO on Si substrate, the enhancement of PL intensity for In-doped ZnO with deposited Al cylindrical micropillars can be attributed to strong coupling interaction with SPR and exciton over a broad temperature range. These experimental results indicate that Al cylindrical micropillars can significantly affect carrier confinement and enhance the quantum efficiency of In-doped ZnO/Al heterostructures due to the interaction of SPR coupling between In-doped ZnO nanowire and Al film. The rate equation models are invoked to corroborate the anomalous temperature behaviors. All the calculations are agreement with the experimental observations. The temperature-dependent mechanism of ZnO band-to-band transition with SPR coupling effect will be discussed in detail as well.

CP-50 Preparation and Post Annealing Effect on Physical Properties of Nanostructure ZTO Thin Films, ***V.K. Jain*** *(vipinjain7678@gmail.com),* University of Rajasthan, India, *P. Kumar,* National Physical Laboratory, India, *P. Jain,* Indian Institute of Technology, India, *S. Srivastav, S. Agrawal, Y.K. Vijay*, University of Rajasthan, India

Transparent conducting oxide (TCO) films have been widely used in the field of optoelectronics. Recently, Zinc Tin Oxide (ZTO) films have been considered as possible alternative to ITO films due to less expensive, more abundant, and more stable against hydrogen plasma which makes them appropriate for using as anode in flat-panel displays. Zinc tin oxide (ZTO) thin films were deposited on glass substrate with varying concentrations ($ZnO:SnO_2$ - 100:0, 90:10, 70:30 and 50:50 wt.%) at room temperature by flash evaporation technique. These deposited ZTO film were annealed at 450°C in vacuum. These films were characterized to study the effect of annealing on the structural and optical properties. Atomic force microscopy (AFM) and Scanning electron microscopy (SEM) images manifest the surface morphology of these ZTO thin films. The apparent growth of surface features revealed the formation of nanostructured ZTO thin films. The small value of surface roughness (root mean square R_{RMS}) ensures the usefulness in optical coatings. The optical transmittance found to be decreased however blue shift has been observed after annealing. The optical band gap was also found to be decreased for both types of films with increasing concentration of SnO_2.

Biomedical Coatings
Room: Town & Country - Session DP

Symposium D Poster Session

DP-1 A Study on Cell Adhesion and Hemocompatibility of CN_x Coated on Carbon Nanotubes, *M.L. Zhao, Y.C. Yue,* ***D.J. Li*** *(dejunli@mail.tjnu.edu.cn)*, Tianjin Normal University, China

Due to carbon nanotubes (CNTs) unique properties and potential applications in a variety of biomedical and biological systems and devices, significant progress has been made in the effort to overcome some of the fundamental and technical barriers toward bioapplications. Recently, the investigation of CNTs in biomedical applications has primarily focused on preventing nonspecific protein adsorption and identifying particular proteins by surface modification and promoting cell growth as a culture medium by utilizing their uniquely individual shapes and electrical properties. CNTs have no toxicity and maintain their intrinsic cytoimmunity function. Recently, however, tissue compatibility of CNTs need further improvement. There have been few studies of hemocompatibility for CNTs.

In considering tissue compatibility and hemocompatibility improvement of CNTs, nano-thick carbon coatings, such as diamond-like carbon (DLC) and carbon nitride (CN_x), appear to have an advantage because promising studies of DLC supporting its biomedical applications. As a comparable to DLC in structural as well as mechanical and tribiological properties and probable positive effect on biocompatibility due to the presence of nitrogeon, however, CN_x has not been paid attention to biocompatibility so far, especially for the hemocompatibility investigations. CN_x coated CNTs should be a [app:ds:potential] biocompatible material for use to improve biocompatibility of CNTs, which is not only due to its excllent properties such as high chemical inertness and wear resistence, but also due to its chemical composition containing only carbon, hydrogen and nitrogen, which is biocompatible.

In this work, CN_x with different N concentration were coated on CNTs by chemical vapor deposition (CVD). This study compared and investigated cell adhesion and hemocompatibility on CNTs with and without CN_x coating using contact angle test, cells adhesion testing, platelet adhesion testing, and hemolytic rate testing. The results showed that the fibroblasts exhibited much better spindle-shape or polygon morphology with round nucleus on CNT with CN_x coating than those on CNTs without CN_x coating. Cell numbers on CNTs with CN_x coating were continuous to increase with incubation time. No toxicity reaction can be observed during culture. Blood tests showed that hemolytic rate and number and adhesion rate of platelet of on CNT with CN_x coating were lower than MWCNT without CN_x coating. This result indicated CN_x coated on CNTs possessed good tissue and blood compatibility. We believe that CN_x coated on CNTs can improve biocompatibility of CNTs due to wettability increasing.

DP-2 Characterization and Antibacterial Performance of ZrCN/Amorphous Carbon Coatings Deposited on Titanium Implants, ***Y.-Y. Chang*** *(yinyu@mail2000.com.tw),* Mingdao University, Taiwan, *H.-L. Huang*, China Medical University and Hospital, Taiwan, *H-.Y. Kao,* Mingdao University, Taiwan, *C.-H. Lai, T.-M. Shieh*, China Medical University and Hospital, Taiwan

Titanium(Ti)-based materials have been used for dental/orthopedic implants due to their excellent biological compatibility, superior mechanical strength and high corrosion resistance. The osseointegration of Ti implants is related to their composition and surface treatment. A better anti-bacterial performance of Ti implant is beneficial for the osseointegration and for avoiding the infection after implantation surgery. In this study, nanocomposite ZrCN/amorphous carbon (a-C) coatings with different carbon contents were deposited on a bio-grade pure Ti implant material. A cathodic-arc evaporation system with plasma enhanced duct equipment was used for the deposition of ZrCN/a-C coatings. Reactive gas (N_2) and C_2H_2 activated by the zirconium plasma in the evaporation process was used to deposit the ZrCN/a-C coatings. WDS was used to characterize the composition of the deposited ZrCN/a-C coatings. The crystalline structure and bonding states of the coatings were analyzed by XRD and XPS. To verify the susceptibility of implant surface to bacterial adhesion, Staphylococcus aureus (S. aureus), one of the major pathogen frequently found in the implant-associated infections, was chosen for in vitro anti-bacterial analyses by a fluorescence staining method employing Syto9 and bacterial viability agar tests. In addition, the biocompatibility of human gingival fibroblast (HGF) cells on coatings was also evaluated by a MTT test assay. The results suggested that the ZrCN/a-C coatings with carbon content higher than 13 at.% can improve antibacterial performance with compatible biological response.

DP-3 Modification of the Surface of Porous Polymer Fibrous and Membranes by Deposition of Multifunctional Bioactive Nanostructured Films, ***D.V. Shtansky*** *(shtansky@shs.misis.ru), A.N. Sheveiko, P.V. Kiruykhantsev-Korneev,* National University of Science and Technology "MISIS", Russia, *N.A. Gloushankova,* Cancer Research Center of RAMS, *A.S. Grigoryan*, Cental Research Dental Institute

While polytetrafluoroethylene (PTFE) is widely used for implants in restorative surgery, its surface shows hydrophobic properties, cells do not attach the PTFE surface, and the interfacial bonding between the polymer surface and the surrounding bone is poor or does not exist at all. An effective way to promote the formation of bone-like layer on the polymer implant surface is the deposition of bioactive film. The present work is focused on the investigation of the structure and properties of multifunctional bioactive nanostructured films (MuBiNaFs) deposited on the surface of PTFE. Particular attention was paid to the various PTFE substrate pretreatments to improve adhesion. It was shown that unlike ion implantation with energy density of 226 J/sm^2, ion etching with energy density of 363 J/sm^2 results to polymer destruction and origin of citotoxicity. MuBiNaFs were deposited by magnetron sputtering of composite targets based on the $TiC_{0.5}$ or (Ti,Ta)C phases with various inorganic additives CaO, TiO_2, ZrO_2, $Ca_3(PO4)_2$, Si_3N_4, and $Ca_{10}(PO_4)_6(OH)_2$. The film morphology and phase composition were examined using X-ray diffraction, scanning electron microscopy, and Raman spectroscopy. The films were characterized in terms of their adhesion to PTFE substrate, hardness, elastic modulus, elastic recovery, wettability, electrochemical characteristics, friction and wear both under physiological solution (100 ml H_2O + 0.9 g NaCl) and Dulbecko modified Eagle medium with Fetal calf serum. In vitro studies showed that human fibroblasts well adhered and spread on the surface of polymers coated with MuBiNaFs. In vivo studies using rat hip defect model and rabit calvarian defect model demonstrated a high osteointegration potential of MuBiNaFs/PTFE implants.

DP-4 Stable Superhydrophilic Surfaces on Titanium Substrates, *R. Fleming,* ***M. Zou*** *(mzou@uark.edu)*, University of Arkansas

A method of producing superhydrophilic surfaces on titanium substrates via sandblasting and dip-coating with colloidal silica nanoparticles is presented. The surface exhibits a high level of hydrophilic stability, as it stays superhydrophilic for an excess of 40 days and through multiple wetting-dewetting cycles. The combination of microscale roughness from the sandblasting and nanoscale roughness from the silica particles results in a micro-nano binary structure, which greatly enhances the hydrophilicity of the titanium samples. Due to the simplicity and ease of implementation of this method, this surface is suitable for potential use in a variety of applications, such as prosthetic dentistry and other biomedical fields.

DP-5 Allylamine Plasma Enhanced Cytocompatibility of Porous NiTi Bone Implants, *S.L. Wu,* City University of Hong Kong*, X.M. LIU,* Hubei University, China*, K.W.K. Yeung,* ***T. Hu****,* City University of Hong Kong*, Z.S. Xu,* Hubei University, China*, J.C.Y. Chung, P.K. Chu (paul.chu@cityu.edu.hk)*, City University of Hong Kong

It is generally agreed that the surface properties of biomedical implants such as surface topography, roughness, and chemical composition play a crucial in cell recognition and bone healing. In addition, the interaction between hyaluronan produced by the cells and matrix hyaluronan-binding proteins and cell-surface hyaluronan receptors significantly influences cell behavior such as cell migration, cell-cell adhesion, and cell differentiation because hyaluronan acts as a mediator and modulator during the initial steps of cellular adhesion [1, 2]. Since hyaluronan is negatively charged, a positive charge on the biomaterials surface is needed to attract hyaluronan. The introduction of amino groups is one of the important surface strategies to introduce positive charges in the aqueous environment. In this work, a thin polymeric allylamine (P-PPAAm) layer is deposited on the surface of a porous NiTi scaffold to enhance the cytocompatibility using a pulsed radio frequency (RF) plasma containing allylamine vapor and NH_3 as the precursor gas. *In vitro* tests reveal that P-PPAAm functionalized surface enhances adhesion and proliferation of both endothelial cells and osteoblasts. This can be attributed to the formation of a high density of positively-charged amino groups on the exposed surface of the porous NiTi scaffold and it consequently promotes attachment of hyaluronan and cell adhesion.

References

[1] Knudson CB, Knudson W, Hyaluronan-binding proteins in development, tissue homeostasis, and disease. Faseb Journal 1993; 7(13): 1233-1241.

[2] Toh WS, Lee EH, Guo XM, Chan JKY, Yeow CH, Choo AB, Cao T. Cartilage repair using hyaluronan hydrogel-encapsulated human embryonic stem cell-derived chondrogenic cells. Biomaterials 2010; 31(27): 6968-6980.

DP-6 Antibacterial with Silver-Embedded Silica/ Polyethylene Nanocomposite*,* ***C.-H. Chien****, K-.H. Chen,* National Tsing Hua University, Taiwan*, Y.-C. Pu, C.-M. Liu,* Industrial Technology Research Institute Taiwan*, H-C. Shih (hcshih@mx.nthu.edu.tw)*, National Tsing Hua University, Taiwan

In this study, an ionic silver was uniformly incorporated into Silica framework by sol-gel process, which introduce controlled Al ions to play a significant role in overall Silica matrix. The interaction between $[AlO_4]^-$ tetrahedral structure and Ag^+ result in uniform Ag^+ distribution by electrostatic force, and then Ag^+ embedded Al-O-Si structure is revealed. The Ag^+ embedded Al-O-Si structure is then annealing by O_2 atmosphere range from the temperature 600 to 900 ^oC. We utilized as-prepared Ag-embedded silica to hybrid with Polyethylene(PE), which show excellent antibacterial behavior by reason of having the minimum inhibition concentration(MIC) value 350 ug/l against E.coil as well as slowly release silver ions into ethanol and H_2O. The UV-visible spectrum illustrates to be colorless pattern when Ag^+ embedded Al-O-Si structure mix with polyethylene. These consequences provide prospective development in biomaterial, which obviously demonstrate the outstanding superiority in homogeneity and lower reactive temperature.

DP-10 Microscopical Observation of Osteoblast Growth on Micro-arc Oxidized Titanium Dioxide*,* ***H.-T. Chen****,* Feng Chia University & China Medical University Hospital, Taiwan*, C.-J. Chung (cjchung@seed.net.tw),* Central Taiwan University of Science and Technology & Taipei Medical University, Taiwan*, T.-C. Yang,* Feng Chai University, Taiwan*, C.-H. Tang,* China Medical University, Taiwan*, K.-C. Chen, J.-L. He*, Feng Chai University, Taiwan

Titanium alloys known for their excellent physical properties and biocompatibility has therefore been considered as ideal metals for orthopedics and dental implants. In our previous studies, we had developed an anatase (A) rich and rutile (R) rich titanium dioxide (TiO_2) coating, respectively, on β-Ti alloy surface by using micro-arc oxidation (MAO) technique. It is also noticeable that the R rich TiO_2 coating not only achieved better *in-vitro* biocompatibility but also *in-vivo* osteogenesis performance. However, microscopical aspect on the interaction between osteoblast and TiO_2 layer was lack. A focused ion beam (FIB) technique was used in this study for cross-sectional sampling of the osteoblast cell that grown on the TiO_2 layer, followed by using energy dispersive spectrometer (EDS) and transmission electron microscope (TEM) for investigating how the TiO_2 coating influence osteoblast cell growth.

Experimental results revealed that the osteoblast adhered more tenaciously and grew conformably with a larger extent on the R rich TiO_2 specimen than on A rich TiO_2 and raw β-Ti specimens. In addition, the number of adhered and proliferated cells on R rich TiO_2 specimen was visually greater than that on both A rich TiO_2 and raw β-Ti specimens. By observing EDX profile along FIB-cut cross-section, the nitrogen and sulfur elements (as the biological feature of osteoblast cell) were both detected in the cell body and interior space of TiO_2 layer. This supports the hypothesis that the osteoblast cell could well grow into porous structure of MAO-TiO_2 coatings. Moreover, the well-conformal growth of the osteoblast cell on R rich TiO_2 specimen rather than A rich and raw β-Ti alloy specimens confirms that the R rich TiO_2 coating formed by MAO technique can serve as a novel surface modification technique for β-Ti alloy implants for orthopedics and dental implant applications.

DP-11 ***In vivo*** **Osseointegration Performance of Titanium Dioxide Modified Polyetheretherketone Using Arc Ion Plating***,* ***H.-K. Tsou****,* Feng Chia University & Taichung Veterans General Hospital, Taiwan*, M.H. Chi,* Feng Chai University, Taiwan*, Y.-W. Hung,* Taichung Veterans General Hospital & National Chung Hsing University, Taiwan*, C.-J. Chung (cjchung@seed.net.tw),* Central Taiwan University of Science and Technology & Taipei Medical University, Taiwan*, J.-L. He*, Feng Chai University, Taiwan

Polyetheretherketone (PEEK) resembling human cancellous bone in biomechanical performance has been extensively used for implant materials. However, its bio-inertness and hydrophobic surface properties provide poor osseointegration. A surface modification method using arc ion plating (AIP) technique is developed to produce highly osteoblast compatible titanium dioxide (TiO_2) coatings onto PEEK substrate in this study. The TiO_2 modified PEEK was implanted into the femurs of New Zealand white rabbits to evaluate its *in vivo* performance. The osseointegration response and shear strength of the bone/implant interface using histological observation and push-pull testing are carried out in this research..

The results showed that utilizing AIP technique can successfully prepare TiO_2 coatings onto bullet-type PEEK substrates, for use as implant materials. After a long implantation period (4 weeks, 8 weeks and 12 weeks) of animal experiments, no signs of inflammation were detected in any of the substrates. The formation of newly regenerated bone occurred more prominently in TiO_2 modified PEEK based on microstructure observation of bone/implant interface. In addition, the shear strength of the bone/implant interface increases with increasing implantation period, what's more important is that the TiO_2 modified PEEK exhibited superior bone bonding performance than the bare PEEK. It is also noticeable that the rutile-rich TiO_2 coatings achieved better osseointegration than anatase-rich coatings. Therefore, the AIP-TiO_2 can be considered to serve as a novel surface modification method for spinal interbody fusion PEEK cages.

DP-12 Corrosion Behavior of Ag-Ti(C,N) Coatings for Biomedical Applications*,* ***G. Ramírez*** *(enggiova@hotmail.com),* Universidad Nacional Autonoma de Mexico*, N. Manninem, S. Carvalho,* Universidade do Minho, Portugal*, S.E. Rodil,* Universidad Nacional Autonoma de Mexico*, M. Henriques, I. Carvalho*, Universidade do Minho, Portugal

Application of thin films in the biomedical field represents an attractive challenge due to the multiple situations where they may improve or even functionalize implant surfaces. Implant failure is a huge problem, which involves repeated surgeries and consequently considerable economical resources, this failure can be attributed to a variety of factors including: excessive wear and wear debris, corrosion process of the implant, bacterial biofilm formation, etc….

The aim of the present work is to study the electrochemical behavior of silver doped TiCN thin films deposited by DC unbalanced reactive magnetron sputtering, on simulated biological fluids.

The obtained Ag-Ti(C,N) based coatings were characterized in terms of composition and structure as well as in terms of corrosion in two different electrolytes that simulated biological conditions: NaCl 0,89% and phosphate buffer saline (PBS). Both solutions are isotonic to the human body, but PBS also contains phosphates. The electrochemical response was evaluated using potentyodynamical and electrochemical impedance spectroscopy (EIS), the latter as a function of immersion time.

The results showed that the electrochemical response depends not only on the amount of silver incorporated, but also on the Ti-C-N phases present. Without silver, the TiCN films showed similar response than the stainless steel substrate. Silver incorporation up 14 at% gave better corrosion resistance, but above this value, the TiCN films decomposed into a two phase material, where amorphous carbon nitride was predominant and then the corrosion resistance was decreased. Similar behavior was observed when the EIS spectra were analyzed as a function of the immersion time. However, it is important to note that the film dissolution, liberating Ag ions might be beneficial to promote an antibacterial response that inhibit bacterial attachment on the surface. This was studied using two bacterial strains *Candida Albicans* and *Staphilococus Epidermis* and evaluating the percentage of growth inhibition on each surface.

DP-13 Silver Diffusion and Ionization Mechanisms on Antibacterial Ag(Au)-TiCN Coatings, *I. Carvalho,* Universidade do Minho, Portugal, ***R. Escobar Galindo*** *(rescobar@icmm.csic.es),* Instituto de Ciencia de Materiales de Madrid, Spain, *S. Calderon, M. Henriques,* Universidade do Minho, Portugal, *C. Palacio,* Universidad Autónoma de Madrid, *A. Cavaleiro,* Coimbra University, Portugal, *S. Carvalho*, Universidade do Minho, Portugal

Ag(Au)-TiCN coatings were deposited onto Stainless Steel 316L aiming at the evaluation of silver ionization on antibacterial activity and adhesion of the *Staphylococcus epidermidis*. Samples were prepared by DC unbalanced reactive dual magnetron sputtering using two targets, Ti and Ti+Ag in an Ar, C_2H_2, N_2 atmosphere. Silver pellets were placed on the erosion zone of the Ti target in order to obtain a silver content between 0 to 9 at. %. Additionally, with the purpose of accelerates silver ion release to enhance the antibacterial effect of the films, Au pellets were added to the Ti-Ag target. Compositional depth profiling of the coatings have been obtained by GDOES. Phase formation will be analysed by XRD. Samples were in previous contact with the media used to perform biofilm formation (Tryptic Soy Broth). Inductively coupled plasma optical emission spectrometry (ICP-OES) was used to determine the content of silver ions in the TSB medium. Moreover the surface chemical and morphological modifications of the coatings were analyzed by XPS, ARXPS and HR-SEM. Adhesion was assessed by epifluorescence microscopy and Biofilm activity was determined by measuring the amount of formazan salts formed after the biofilm reaction with XTT and the amount of total biomass formed was determined after crystal violet staining.

DP-15 Photocatalytical Performance of Silver Containing Titania Films by Reactive Sputtering, ***C.-C. Hsieh***, *M.-S. Wong (mswong@mail.ndhu.edu.tw),* National Dong Hwa University, Taiwan, *H.-H. Chang*, Tza Chi University, Taiwan

Titanium dioxide (TiO_2) has received great attentions because of its high reactivity under UV light irradiation ($\lambda < 380$ nm). When TiO_2 is doped with silver, its photocatalytic and bacteriacidal activities can be extended and enhanced in the visible light [1]. Reactive magnetron sputtering and cosputtering techniques were used to prepare various silver containing titania samples, which include two different types, Ag/TiO_2 double layer and Ag-TiO_2/TiO_2 multilayer. The as-deposited and annealed samples were characterized for composition, structure, morphology and photocatalytic characteristics. The results indicate the photocatalytic performance of the Ag/TiO_2 double-layered films is not proportional to the amount of silver on the surface of titania due to shielding effect. In the other hand, the Ag-TiO_2/TiO_2 multilayers exhibit improved photocatalytic activities under visible light. The SEM observation of surface morphology of the annealed multilayers reveals a unique three-dimentional net-like nanocomposite structure, which largely increases the specific surface area of the sample for catalytic reaction [2]. Furthermore, silver nanoparticles are uniformly distributed in the nanostructure, which could decrease the probability of e^-/h^+ recombination and enhance antibacterial effect [3]. The Ag-TiO_2/TiO_2 multilayers exhibit excellent photocatalytic and bacteriacidal activities in the visible light.

[1] O. Akhavan, Journal of Colloid and Interface Science 336 117-124 (2009)

[2] Hyeong Jin Yun, Hyunjoo Lee, Nam Dong Kim and Jongheop Yi, Electrochemistry Communications 11 363–366

(2009)

[3] W. Su, S.S. Wei, S.Q. Hu and J.X. Tang, Journal of Hazardous Materials 172 716-720 (2009)

DP-16 Corrosive Nature of Orthopedic Implant Alloys: Influence of Protien and Corrosion Mechanisms, ***M.T. Mathew*** *(mathew_t_mathew@rush.edu),* Rush University Medical Center, *R. Pourzal,* University of Duisburg-Essen, Germany, *J. Hallab,* Rush University Medical Center, *A. Fischer,* University of Duisburg-Essen, *J. Jacobs, M.A. Wimmer*, Rush University Medical Center

The corrosive behavior of metallic implants is of concern as it affects the biocompatibility and longevity of artificial devices. In orthopedics, as of 2003 data, approximately 202,500 primary total hip replacements (THR) were performed in the US . About 450, 000 total knee replacements (TKRs) are conducted annually in the US . Chemical reactions and transport mechanisms of released metal ions may cause adverse reactions in the periprosthetic tissue as well as remote organs. Recently, there has been a growing number of reports of abnormal soft-tissue masses, often described as 'pseudotumors', linked to metal-on-metal (MoM) joints. While the general corrosive behavior of Ti6Al4V alloy and CoCrMo-alloys are well explored, the influence of in vivo proteins on surface chemistry and the resulting corrosive kinetics and mechanisms are not well understood. In this study, the corrosive behavior of the mild steel (control metal), Ti (Ti6Al4V) and CoCrMo alloy were studied as a function of immersion time. The electrolytes were, 2.4% NaCl solution, ringer solution and bovine calf serum (biologically simulated synovial fluid) and in a controlled environment such as temperature (37°C) and dissolved oxygen level. The open circuit potential (OCP), Potentiodynamic curve, and Electrochemical Impedance Spectroscopy (EIS) was employed in characterizing the corrosive behavior. The EIS results were modeled using Z-view software. In this study, it is hypothesized that CoCrMo alloy exhibits inferior corrosion resistance in bovine calf serum (BCS) compared with protein-free solutions due to a change in corrosion kinetics.

DP-17 Thick Polycrystalline Diamond Layers for Biomedical Application, ***M. Fijalkowski*** *(mateuszfijalkowski@o2.pl),* Technical University of Lodz, Poland, *A. Karczemska,* Technica University of Lodz, Poland, *J.M. Lysko,* Institute of Electron Technology, Poland, *A. Bolshakov, D. Sovyk, V. Ralchenko*, Russian Academy of Science, Russia

Thick polycrystalline diamond layers are used in the biomedical applications mostly because of such properties as the highest thermal conductivity, remarkable biocompatibility, chemical resistance, good optical properties and high electrical breakdown voltage. Nowadays one of the most popular separation technique is the electrophoresis, which uses an electric field for the separation of charged particles. Biomolecules, such as DNA or proteins, migrate inside the microchannels (forced by the electric field) and are separated due to the differences in electrical charges and molecular masses. The microchannels are filled by a buffer. In this paper properties of a diamond electrophoretic chip manufactured by replica method using a Si mould are presented. Electrophoretic separations were performed in small microchannels (40 wide and 250µm depth) built-in diamond film. The designed microstructure of the mould was made with use of the 4" diameter and 3mm thick silicon wafer. Standard photolithography, with the single mask was used for the pattern transfer on the photoresist layer and chemical solutions were used to etch SiO_2/Al layers. Plasma etching (Bosch process) with high aspect ratio (depth-to-width) was used to produce ridges on Si to be converted to deep trenches in deposited diamond. The 0.5 mm thick polycrystalline diamond film was grown on the Si mould by MPCVD (Microwave Plasma Chemical Vapor Deposition) method. After diamond deposition the Si has been etched away to produce the diamond plate with channel system on the substrate side. Bio-samples of extremely small volumes were introduced from lateral cross-channels to the central micro-fluidic channel, where the electrophoresis takes place. Joule heating is a major problem during the conventional electrophoresis processes. Small size of the microchannels and application of material with good thermal properties made it possible to minimize this phenomenon. Moreover in further investigations due to very high thermal conductivity of diamond we will be able to apply higher electrical field and provide biomedical investigations faster. The buffer temperature characteristics and Raman spectroscopy temperature measurements inside the microchannels are the main subject of this paper.

DP-19 Tribocorrosion of Multi-Layered ZrN/(Ti,Al)N Thin Coatings Deposited by Magnetron Sputtering, ***O. Jimenez-Aleman*** *(o.jimenezaleman@gmail.com), M. Flores, E. Rodriguez*, Universidad de Guadalajara, Mexico

PVD thin films for biomedical applications are required to meet a combination of properties in order to ensure their good performance. To mention some, mechanical, corrosion and wear resistance result very important. Surface modification through PVD processes (magnetron sputtering in particular) represented the option to deposit a series of multilayered coatings based on transition-metal nitrides. In this paper results on the deposition and properties of multilayered ZrN/TiAlN coatings are presented. A TiAlN monolayer coating was deposited also for comparison. Coatings were deposited in a mixture of Ar/N_2 atmosphere onto a selection of substrates. The structure and morphology of the coatings were studied by means of X-ray Diffraction and Scanning Electron Microscopy respectively. The elemental composition and the surface chemistry such as the bonding environment were obtained by XPS. The microhardness was measured by composite microhardness tests whereas adhesion of the multilayers was estimated using the scratch test method. Wear properties were carried out by means of reciprocating sliding experiments using alumina counterparts and different normal loads. Corrosion resistance was studied by open circuit potentials (OCP) and potentiodynamic (PD) polarisation experiments in a saline solution. The combined corrosion-wear degradation of coatings is discussed based on tribocorrosion studies of substrates immersed in a Ringer solution. Improvement of corrosion and wear resistance by utilisation of multilayered coatings is also discussed.

DP-21 Tribocorrosion Behavior of $TiAlPt_xN$ Coatings in a Ringer´s Solution, ***M. Flores*** *(martin.flores@red.cucei.udg.mx), O. Jimenez,* Universidad de Guadalajara, Mexico*, J. Garcia,* Universidad Panamericana, Mexico*, E. Rodriguez,* Universidad de Guadalajara, Mexico*, L. Huerta*, Universidad Nacional Autonoma de Mexico

Tribocorrosion is a material degradation process due to the combined effect of corrosion and wear. The $TiAlPt_xN$ coatings can improve the corrosion and wear resistance of materials for biomedical applications. The tribocorrosion behavior of $TiAlPt_xN$ coatings and $TiAlPt_xN/TiAlPt_x$ multilayers immersed in a corrosive environment was investigated. The coatings were deposited on 316L stainless steel and Ti6Al4V alloys by magnetron sputtering. The period size of multilayers was 350 nm and the total thickness was 4.2 microns. The corrosion was studied using open circuit potential (OCP) measurements and potentiodynamic polarization techniques in a Ringer ´s solution. Tribocorrosion tests were performed using a reciprocating ball- on- flat geometry where the sliding contact is fully immersed in a Ringer ´s solution. The counterbody was a 10 mm diameter alumina ball. The loads used were from 1 to 5 N, the oscillating frequencies were 1 and 5 Hz. The potentiodynamic polarizations and OCP measurements were performed during, and after the sliding test. The composite microhardness, nanohardness and the scratch resistance were measured as function of the Pt content in the films. The structure and composition of multilayers were studied by means of XRD and XPS techniques respectively. The surface topography and worn surface were studied by means of optical microscopy and profilometry. The microhardness, scratch resistance and wear depend of the Pt content within the multilayers. The wear mechanism and synergy effect of the tribocorrosion tests are reported.

DP-22 The Tribocorrosion Behavior of Cp- Titanium Deposited by Micro Arc Oxidation at Different Frequencies, ***E.E. Demirci*** *(e_ebrudemirci@homail.com), E. Arslan, Y. Totik,* Atatürk University, Turkey*, O. Baran,* Erzincan University, Turkey*, I. Efeoglu*, Atatürk University, Turkey

Micro Arc Oxidation (MAO) has been considered as a new technique to form ceramic coatings on Titanium alloys for tribocorrosion resistances. A number of studies have been carried out for using of micro arc oxidation (MAO) technology for depositing ceramic coatings on titanium alloys. However, very few have focused on the behaviour of tribocorrosion of the MAO process parameters. In this study, the Cp-Titanium was coated by using Micro arc oxidation technique with different frequencies parametres and tribocorrosion behavior of coatings studied using different electrochemical test techniques including open circuit potential (OCP) measurement and potentiodynamic polarization tests under sliding contact in 1 M NaCl solution. Potentiodynamic polarization measurements were conducted to determine the tribocorrosion resistance of the samples and Scanning electron microscopy (SEM) was employed in order to characterize corrosive-wear damage. The results showed that which frequency parameter was the most significant factor affecting on the coatings's tribocorrosion resistance.

Tribology and Mechanical Behavior of Coatings and Thin Films
Room: Town & Country - Session EP

Symposium E Poster Session

EP-1 Textured Coatings with Ag_3VO_4 Solid Lubricant Reservoirs, ***S. Schwartz***, Valparaiso University*, B. Luster, D.P. Singh, D. Stone,* Southern Illinois University, Carbondale*, M. Baben, J.M. Schneider,* RWTH Aachen University, Germany*, K. Polychronopoulou, C. Rebholz,* University of Cyprus*, P. Kohli, S.M. Aouadi (saouadi@physics.siu.edu)*, Southern Illinois University, Carbondale

Silver oxovanadate (Ag_3VO_4) powder was synthesized by a simple wet chemical route. The synthesized Ag_3VO_4 precipitate resulted from the reduction of Ag_2VO_5 in solution phase. Differential scanning calorimetry (DSC) and x-ray diffraction (XRD) were used to evaluate the thermal and structural properties of the precipitant, respectively. The silver oxovanadate was then subsequently investigated as a potential solid lubricant by burnishing it onto textured VN. The textured vanadium nitride (VN) coatings were created by depositing VN on an Inconel substrate by unbalanced magnetron sputtering and then etched; using reactive ion etching; through a mask to create a periodic array of micro-sized dimples on the surface. The effectiveness of this new design was tribologically tested against Si_3N_4 balls at different temperatures. A significant decrease in the wear rate and coefficient of friction was achieved and was maintained due to the micro-sized depressions on the surface acting as reservoirs to replenish Ag_3VO_4 to the sliding contact throughout the tribological tests. After wear testing, Raman spectroscopy and XRD was performed to identify the phase composition that was tribochemically formed at the surface.

EP-2 Formation of Micro- and Nanostructured Phases in Ni-Cr-B-Si-Fe Coatings Improving Their Protection Functions, ***D. Pogrebnjak*** *(apogrebnjak@simp.sumy.ua), N. Bratushka, M.V. Il'yashenko, G.V. Kirik, P. Shypylenko,* Sumy State University, Ukraine*, L. Alotseva, V. Prohorenkova,* East-Kazakstan State Technical University, Kazakhstan*, V. Pshyk, A. Demianenko*, Sumy State University, Ukraine

Using the plasma-detonation technology, coatings of 80 to 150 µm thickness on a steel 3 substrate were fabricated. To improve properties of these coatings and decrease their porosity, we repeated a plasma-jet melting, which melted the layer up to 45 to 50 µm. A plasma-detonation gun "Impulse- 6" with 0.3 msec pulse duration and $10^6 Wt/cm^2$power flux was employed. We used a powder fraction of 28 to 43 µm size, the Russia standard (Ni was the base, Cr was 10 to 14 wt.%, B was 2.9 to 3.2; Si = 2,5, Fe was to 6wt.%). Samples were 10 x 20 mm and reached 4 mm thickness. After deposition they were cut for analysis and corrosion wear and nano- and microhardness tests. After deposition, we found a nanocrystalline γ-phase based on Ni and a micro-crystalline phase based on CrN3 (of 50 to 150nm size) in the coating. Regions with nanograins having different crystallographic orientations were found in the nanocrystalline phase.

Using HRTEM and XRD analysis, we investigated the phase composition and grains sizes of these phases. RBS and EDS were employed to perform an element analysis both over the coating depth and over transversal cross-section.

It was demonstrated that doping of the coating, which was realized in the process of deposition, reached the whole coating depth (though we observed also the regions without Mo – TEM analysis). After melting, the coating nano- and microhardness was 8.1GPa. Before irradiation, it was 6.8 GPa. The wear resistance increased almost by a factor of three, in comparison with the substrate and by a factor of 1.7 in comparison with the non-melted Ni-Cr-B-Si-Fe coating. The mass-transfer processes and redistribution of impurities in the coating due to the repeated melting were investigated.

EP-3 Tribological Properties and Thermal Stability of C-Si-O Composite Thin Films Deposited by PBII Method, ***N. Moolsradoo*** *(nutthanun.moo@kmutt.ac.th), S. Abe, S. Watanabe*, Nippon Institute of Technology, Japan

DLC films are meta-stable amorphous films that exhibit unique combinations of properties such as high hardness, low friction coefficient, and good wear resistance, etc. However, DLC films have several known limitations, such as high internal stress, low thermal stability. In order to solve these problems, enhance the film properties, Si has been incorporated into the amorphous hydrocarbon films. Our study aimed to study the effects of silicon and oxygen incorporation on the tribological properties and thermal stability of C-Si-O composite thin films deposited by PBII method.

The films were deposited by PBII method with gaseous mixtures of C_2H_2:TMS:O_2 on Si (100) wafers. The flow rate ratio range between C_2H_2 and TMS were from 10:1 to 100:1, while oxygen was kept constant at 1 sccm. The deposition pressure range was from 2-6 Pa. The bias voltage was set 0 kV, at RF power of 300 W. The total deposited thickness of the films was approximately 500 nm. An annealing temperature range of 200-600°C was investigated under high vacuum, air atmosphere and argon atmosphere for 1 hour. The film structure was analyzed using Raman spectroscopy. The hardness and elastic modulus were measured by a nano-indentation hardness tester. The tribological properties were measured using a ball-on-disk friction tester under air condition. From the results deposited at 2 Pa pressure, hardness and elastic modulus of films decreases with silicon incorporation, believed to be partly due to the changes in the microstructure, indicates that increasing graphite dominance, as could be concluded from Raman analysis. For annealed films under high vacuum, results also decreases with silicon incorporation. The films at flow rate ratio of 10:1 are stable and low friction coefficient of 0.04, due to high hardness and elastic modulus.

EP-5 Analysis of Mechanical Properties and Structure of a-C:H DLC Thin Films, ***A.N. Berthelsen*** *(anb@inano.au.dk), S. Louring, N.D. Madsen,* Aarhus University, Denmark*, B.H. Christensen, K.P. Almtoft, L.P. Nielsen,* Danish Technological Institute, Tribology Centre, Denmark*, J. Bøttiger*, Aarhus University, Denmark

Amorphous hydrogenated carbon thin films were deposited by reactive magnetron sputtering, using a CemeCon industrial scale unit. The films were deposited from two carbon targets in a mixed argon and acetylene atmosphere. In order to investigate the influence of hydrogen on the mechanical properties and structure of the films the acetylene flow rate was varied. Furthermore the effect of substrate bias voltage was investigated.

The hardness and elastic modulus of the coatings were measured by nanoindentation, and were in the range from 2 to 21 GPa and 30 to 215 GPa respectively. Raman analysis indicated that a optimum in hardness occurred when the highest structural disorder in the sp^2 matrix was present. This disorder probably originates from C-C sp^3 sites distorting the matrix. A combination of nanoindentation and Raman spectroscopy was used to calculate the compressive stress in the films, and showed that the hardest films were the most stressed, with compressive stress values peaking at 5.5 GPa. Post-deposition annealing at 430°C of the films showed a significant reduction in the stress from 5.5 GPa to 1 GPa, while almost no loss in hardness was observed. The stress reduction was attributed to a relaxation of the film, where bond angles and bond lengths change to a more stable configuration. The stress reduction was thus not caused by a graphitization, where C-C sp^3 sites are converted into C-C sp^2. Also, the relaxation was not attributed to hydrogen emission from the films, since NRA measurements revealed an almost constant hydrogen content of the annealed films.

EP-6 Nano-Impact Test on a TiAlN Pvd Coating and Correlation Between Experimental and Fem Results, ***K.-D. Bouzakis*** *(bouzakis@eng.auth.gr), S. Gerardis, G. Skordaris,* Aristoteles University of Thessaloniki, Greece, CERTH, Greece & IPT, Germany, *E. Bouzakis*, Aristoteles University of Thessaloniki, Greece, CERTH, Greece & IPT, Germany, Greece

Nano-impact test on PVD coatings is an efficient method for investigating film failure mechanisms. During this test, the coating is subjected to repetitive impacts by a diamond indenter, inducing high local deformations and stresses into the film material, which may lead to coating failure.

In the paper, coated specimens with a TiAlN PVD film were investigated by nano-impact tests. The nano-impacts were conducted at several loads and for various test durations. For explaining the attained results, the nano-impact test was simulated by a developed three dimensional FEM model, considering a piecewise linear plasticity material law. The film elasto-plastic properties, used in the FEM-calculations, were determined by nanoindentations and analytical evaluation of the related results. During the nano-impact indenter penetration, it was assumed that the coating material at the FEM model node regions can withstand the applied load up to a maximum value, which corresponds to the coating rupture stress. Over this load limit, the related nodes are disconnected from the neighboring finite elements. If all nodes of an element are disconnected, the element is released for simulating a crack formation and it becomes an inactive separate entity. In this way, the stress fields developed in the film material and its coating fracture progress in terms of imprint depth versus the repetitive indenter penetrations are analytically described. The attained results converge sufficiently with the experimental ones. The developed nano-impact FEM-simulation predicts the film failure initiation and evolution, which depend on the impact load.

EP-10 Comparison of Gas Nitrided and Powder-Pack Borided AISI 4140 Steel Behaviour in Terms of Tribological Properties, *L. Lopez,* ITESM, Mexico, ***J. Solis*** *(josesolis@infinitum.com.mx),* SEP-DGEST-ITTLA/ITESM, Mexico, *U. Figueroa, E. Oseguera,* ITESM, Mexico, *O.A. Gomez*, SEP-DGEST-ITTLA/ITESM, Mexico

Termochemical processes such as nitriding and boriding have proven to improve surface mechanical properties such as hardness and wear strength among others. However, on one hand, it is not recommended to apply nitriding in some high carbon steels because of the well known flaking and spalling problems when a mechanical load is applied. On the other hand, boriding has positioned as a promising process due to its flexibility in terms of materials application and high performance. In the present work, a comparison of some mechanical properties of nitrided and borided AISI 4140 was carried out. AISI 4140 steel substrates were low pressure gas nitrided with three different time intervals. Production of boriding layer at the surface of the low alloy steel, in turn, was applied in solid medium, i.e. pack boriding at 950°C for 5h. Surface treated samples were characterized by Vickers microhardness testing, energy dispersive spectroscopy, x-ray diffraction, scanning electron microscopy and atomic force microscopy. As to tribological behaviour, standard pin-on-disc wear tests were conducted at ambient temperature (20-24ºC) and dry sliding.

EP-11 Optimized DLC Films for High-Performance Racing Engine Applications, ***O. Coddet*** *(o.coddet@platit.com),* Platit AG, Switzerland, *B. Torp,* Platit Scandinavia, Denmark, *G. Bulaja,* Platit Inc., USA, *C. Galamand,* Platit AG, Switzerland, *G. Huffman,* Calico Coatings, USA, *T. Cselle*, Platit AG, Switzerland

The research efforts on Diamond-Like Carbon (DLC) films have strongly increased over the last decade. Those coatings exhibit a wide range of attractive properties such as a low friction coefficent, a high wear resistance as well as good thermal and chemical stabilities. However, the main issues in tribological applications are related to smoothness, heat transfer and abrasion resistance especially under severe conditions like in an automotive engine.

For that reason, we have investigated amorphous hydrogenated silicon-doped carbon (a-C:H:Si) films deposited on various substrate materials. The DLC films were grown by using a combined PVD and Plasma Enhanced Chemical Vapor Deposition (PECVD) technique with the help of the LARC® technology.

The adhesion strategy, the transition layer as well as the film structure have been tuned to match the application requirements on various components like lifters and valves. The tribological properties were investigated by a pin-on-disc test at room temperature and up to 400°C. Hardness and elastic modulus were measured and considered as an additional reference in terms of coating quality. Finally, results of the spintron and dyno testing will be detailed for the mentioned applications.

EP-15 Structural, Surface and Mechanical Properties of a-C:H:Si:F and a-C:H:Si:Cl Films Produced by PECVD, *T. Matiello, R. Turri, M.B. Appolinario, R. Martins,* State University of São Paulo - UNESP, Brazil, *C.U. Davanzo,* UNICAMP, Brazil, *W.H. Schreiner,* State University of Paraná, Brazil, *N. Cristino da Cruz, E. Rangel, J.R. Bortoleto,* ***S.F. Durrant*** *(steve@sorocaba.unesp.br)*, State University of São Paulo - UNESP, Brazil

Fluorinated and chlorinated amorphous hydrogenated carbon films also containing silicon were produced by plasma enhanced chemical vapor deposition from hexamethyldisiloxane-argon mixtures together with either sulfur hexafluoride or chloroform. Chemical structure and composition were examined using infrared reflection-absorption spectroscopy (IRRAS) and X-ray photoelectron spectroscopy (XPS). Infrared spectra show the presence of silicon-containing functionalities and XPS allows quantification of the degree of halogenation of the films. Thus correlations may be made between surface contact angles, measured using a goniometer, film composition, and surface roughness obtained via atomic force microscopy. Nano-indentation was used to investigate the nano-hardness, elastic modulus and stiffness of the films as a function of the degree of fluorination or chlorination.

EP-17 The Study on the Mechanical Properties of Perfect Lattice and Sputtering of Al/Cu Multilayer Thin Film by Molecular Dynamics Simulation, *J.-C. Huang (Jc-huang@mail.tnu.edu.tw),* ***Y.-C. Liao***, Tungnan University, Taiwan

The multilayer films have been widely accepted and applied in the fields of coating technology and industrial application. However, the complex behaviors of multilayer formation attract much interest in academic research, and become a topic that one should not ignore. The goal of this paper is to study the influence of multilayer microstructure on mechanical properties and adhesion by molecular dynamics (MD). The microstructure of Al/Cu nano-multilayer coatings were fabricated into simulated perfect lattice stacked with the monocrystalline aluminum and copper, and deposited by sputtering process with simulation separately. To investigate the binding strength between each layer and mechanical properties, two kinds Al/Cu nano-multilayer coatings with different microstructure were tested in nano-tensile. As results, the microstructure and the thickness of Al/Cu nano-multilayer coatings could deeply affect the binding strength and adhesion.

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

Symposium F Poster Session

FP-2 The Preparation and Photo-Sensing of Thermal Evaporated ZnS/ZnO Core-Shell Nanowires, ***Y.-W. Cheng***, National Cheng Kung University Taiwan, *H.-C. Shih,* Chinese Culture University, Taiwan, *C.-P. Liu (cpliu@mail.ncku.edu.tw)*, National Cheng Kung University Taiwan

In this study, we report that the high-density ZnS/ZnO core-shell nanowires were successfully synthesized on a Si substrate using thermal evaporation at a temperature of 1000°C for 1 hr. A field emission scanning electron microscope (FESEM) shows that the ZnS/ZnO core-shell nanowires have a diameter of 50 to 100 nm and a length of several micrometer. An x-ray diffraction (XRD) pattern shows the planes of (100), (002), (110) for the ZnS/ZnO core-shell nanowires. An x-ray photoelectron spectroscopy (XPS) gives Zn_2p_3, S_2p_3 and O 1s. A high-resolution transmission electron microscope (HRTEM) shows that both of ZnS and ZnO are of single crystalline hexagonal wurtzite with a common growth direction of [0002]. An energy dispersive x-ray spectrometer (EDS) indicates peaks of Zn, S and O. The cathodoluminescence (CL) spectra shows that ZnS/ZnO core-shell nanowires exhibit a green emission. The conductivity of ZnS/ZnO core-shell is better than the ZnS nanowire. The photo-sensing measurement demonstrates the ZnS/ZnO core-shell nanowire-based photodetectors have both high sensitivity and low response time, which proves that ZnS/ZnO core-shell nanowires have potential application in future UV photodetectors.

FP-4 Defects and Oxygen Incorporation in TiAlN, *M. to Baben (to_baben@mch.rwth-aachen.de), L. Raumann,* ***J.M. Schneider***, RWTH Aachen University, Germany

In literature, theoretical studies on phase stability and structure of oxynitrides are rare which limits understanding as well as application of this material system. The aim of this study is to contribute towards understanding of the influence of oxygen on stability and elastic properties of TiAlN.

Using ab initio calculations, defects in TiAlN as well as oxygen incorporation in TiAlN were studied. Vacancies, substitutions, interstitials and combinations thereof in different configurations have been investigated in terms of crystal energies, enthalpies of formation and bulk moduli.

The enthalpies of formation per vacancy are 2.5 eV, 2.0 eV and 3.4 eV for Ti, Al and N, respectively. The enthalpy of formation of the second metal vacancy is 0.3 - 0.5eV higher than for the first, while a second nitrogen vacancy has the same enthalpy of formation as the first one. No indication for interaction of vacancies was observed. Irrespective of the kind of vacancies, the bulk modulus B is reduced linearly with the number of vacancies. Compared to stoichiometric TiAlN B decreases by 7 % when the stoichiometry is changed to $(Ti,Al)_1N_{0.94}$ or $(Ti,Al)_{0.94}N_1$.

The energy of mixing of TiAlN and hypothetical isostructural TiAlO is negative which may imply the possibility to form TiAlNO in NaCl structure. The influence on enthalpy of formation of metal vacancies is calculated as well as on enthalpy of formation of interstitial oxygen. It is shown that oxygen on the nitrogen sublattice leads to spontaneous incorporation of interstitial oxygen. Possible reasons are discussed.

Thin films of TiAlNO are prepared using High power impulse magnetron sputtering of a TiAl target in mixed nitrogen and oxygen atmosphere. It is shown that high oxygen flux leads to the formation of amorphous films. The influence of temperature on structure, composition and elastic properties is determined.

FP-5 Aluminum Films with Protruding Nanoislands by Thermal Evaporation, ***R. Fleming***, *M. Zou (mzou@uark.edu)*, University of Arkansas

Nano-textured surfaces (NTSs) can reduce friction and adhesion forces due to the decrease in effective contact area and thus have potential to be applied to micro-electro-mechanical systems to increase their reliability. Here, we report a novel NTS consisting of aluminum nanoislands protruding from a continuous aluminum film on silicon substrate, deposited by thermal evaporation. This surface combines the favorable tribological properties of nanoscale surface-texturing with the enhanced strength provided by a continuous film as compared to isolated nanoislands deposited on a substrate. Characterization of this novel aluminum surface includes scanning electron microscopy, transmission electron microscopy, atomic force microscopy, x-ray diffraction, and energy-dispersive x-ray spectroscopy. Tribological test results showed improved frictional performance as compared to a smooth silicon surface.

FP-8 The Nano-Depth Profiling Analysis of La-Substituted $BiFeO_3$ Multiferroic Thin Films Sputtered on Silicon Surface with Different Postannealing Temperatures, *P.-C. Juan (pcjuan@mail.mcut.edu.tw),* ***C.-W. Hsu***, Ming Chi University of Technology, Taiwan, *C.-H. Liu*, National Taiwan Normal University, Taiwan

Metal-ferroelectric (lanthanum-substituted $BiFeO_3$)-insulator (HfO_2)-silicon (MFIS) structures has been fabricated by the co-sputtering technique. The purpose of the insulator layer is to prevent the reaction and interdiffusion between the ferroelectric layer and silicon substrate. La^{3+} substituted for Bi-site was investigated by x-ray photoelectron spectra (XPS) and x-ray diffraction (XRD) patterns. The La 3d, O 1s, and Si 2p core-level XPS spectra after postannealing were characterized. The XPS spectra shows that Bi^{3+} is gradually replaced by La doping in $BiFeO_3$ thin films when the annealing temperature increases from 500^0C to 700^0C. The nano-depth profiles of the interface between the insulator layer and silicon surface were carefully examined by adjusting the Ar sputtering rate. The measured Fe $2p_{1/2}$ peak can be fitting into two peaks, which are Fe^{2+} and Fe^{3+} states. The Fe^{2+}/Fe^{3+} ratio shows different with varying the La doping amount, especially at silicon surface and film itself. The C-V memory windows of MFIS structures as functions of insulator film thickness, DC power for La during deposition, postannealing temperature were measured and compared. The memory window increases with increasing HfO_2 insulator thickness due to the effect of charge injection. The temperature-dependent leakage current of MFIS structures with La-substituted BFO compared to that with pure BFO as the ferroelectric layer is improved. The hopping electron between Fe^{2+} and Fe^{3+} states is the origin of leakage current mechanism is proposed.

FP-9 Two-Step Synthesis and Electrical Transport Properties of Tungsten Oxide Nanowires Bundles, *T. Hsieh (zziz.tw@gmail.com),* ***L.-W. Chang***, *C.-C. Chang,* National Tsing Hua University, Taiwan, *B.J. Wei,* National Chung Hsing University, Taiwan, *H-C. Shih*, National Tsing Hua University, Taiwan

Uniform tungsten oxide ($W_{18}O_{49}$) nanowires were simply synthesized by thermal chemical vapor deposition (CVD) without using any catalyst in a tube furnace via the two-step process 8 00 and 1000°C, respectively. The nanowires have diameters of 15–20 nm and lengths of several micrometers. Morphology, composition, and crystal structure were characterized by scanning electron microscopy (SEM); x-ray diffraction (XRD); transmission electron microscopy (TEM); and energy-dispersive x-ray (EDX), and Raman. SEM images of high-density $W_{18}O_{49}$ nanowires clearly demonstrate that the nanowires have a uniform one-dimensional morphology high aspect ratio. The result of XRD, TEM, and EDX confirmed the formation of $W_{18}O_{49}$ nanowires (lattice constants, a = 1.832 nm; b = 0.3784 nm; c = 1.403 nm) containing W and O atoms, with [010] as the major growth direction. The vapor-solid (VS) mechanism is responsible for the growth of $W_{18}O_{49}$ nanowires in this experiment since no catalyst were used. We investigated the temperature dependence electrical transport properties of individual $W_{18}O_{49}$ nanowires. The conductivity is 2.6 $\Omega^{-1}cm^{-1}$ at 290K and 42.4$\Omega^{-1}cm^{-1}$ at 500K, respectively. The electron activation energy was calculated to be about 0.26eV.

FP-10 Position and O_2 Concentration Effects on Growth of Carbon Nanotubes (CNTs) by DC-PECVD at Low Temperature, ***H. Wang***, *J.J. Moore (jjmoore@mines.edu)*, Colorado School of Mines

Vertically aligned carbon nanotubes were synthesized using FeNi or Fe sputtering catalyst layers on glass substrates by direct current-plasma enhanced chemical vapor deposition (DC-PECVD) method at low temperature. Electronic field had different intensities in different positions of a PECVD chamber, and strong electronic field produced high concentration of reactive radicals, which enhanced CNTs growth. Therefore, CNTs exhibited different growth rates in different positions due to different intensities of electronic field. With increasing in concentration of O_2 the growth rate of CNTs increased. Adding O_2 can remove amorphous carbon from CNTs and enhance CNTs growth, while adding H_2 can lead to high activity and wetting ability of metal catalyst and enhance growth of CNT. But O_2/H_2 ratio was a key factor on CNTs growth. In DC-PECVD, the CNTs were well aligned vertically. FeNi thin film catalysts exhibited higher activity and better wetting ability than the Fe island thin film catalysts. This article discussed the growth mechanisms of CNTs based on plasma physics, position of substrate, concentration of O_2 and H_2, and catalysts.

FP-11 Novel Nanoplate Thin Film Solar Cell Using Amorphous Silicon-Based Materials, ***B.-F. Hsieh***, *J.-W. Fan, S.-T. Chang (stchang@dragon.nchu.edu.tw), C.-Y. Lin*, National Chung Hsing University, Taiwan

One of the disadvantages of amorphous silicon (a-Si) thin film solar cells is the light induced degradation owing to Staebler-Wronsky effect. One possible way of minimizing the degradation in an amorphous silicon thin film solar cell is to reduce the thickness of the intrinsic amorphous silicon layer. This lead to the multi-junction concept, by stacking several solar cells the thickness of the component cells can be reduced. For the low bandgap absorber layer amorphous silicon-germanium (a-SiGe) thin film are often used. However, the efficiency of a-SiGe thin film solar cells is limited due to deterioration of the electronic properties of a-SiGe with increasing Ge alloying and the introduction of large band offsets between the a-SiGe thin film intrinsic layer and p-layer and n-layer. To overcome some of these problems the bandgap profiling of the intrinsic layer has been introduced [1]. In Ref. [2], it is reported that introducing novel designs for profiling the intrinsic a-SiGe layer to optimize the performance of solar cells. Based on their simulation results we proposed the new profile, which shows a strong reduction in recombination losses in the intrinsic layer compared to conventional profiles. In order to separate the way of light absorption and carries transport, a novel nanorod structure for pn junction solar cell with a nanorod structure is proposed as shown in Ref. [3]. Additionally, more and more fabrication work about inorganic semiconductor photovoltaic technology combined with a nano structure was appeared. However, different from crystal silicon solar cell, drift mechanism is the dominate transport of carriers for amorphous silicon thin film cell. The drift force caused by built-in electrical field was not involved in their research. Different nanorods in a row of array are to combine to form a nanoplate. Such a nanoplate structure is proposed in our study. In this work, the thin film solar cell with amorphous silicon-carbon p-layer and a-SiGe i-layer grown on n-type a-Si nanoplate array was investigated using TCAD simulations. Impact of key geometric parameters such as absorber thickness, nanoplate height/width on the performance of solar cell will also be explored.

Reference

[1] J. Zimmer, H. Stiebig, and H. Wagner, J. Appl. Phys. 84, 1998, pp. 611-617.

[2] Pieters B.E., Zeman M., Swaaij R.A.C.M.M. van, and Metselaar W.J., Thin Solid Films 451 -452C, 1997, pp. 294-297.

[3] Kayes B.M., Atwater H. A., Lewis N.S., J. Appl. Phys., 97 (2005) 114302.

FP-12 Recycling of Used DLC-Coated WC/Co Dies for Practical Dry Stamping, ***T. Aizawa*** *(taizawa@sic.shibaura-it.ac.jp),* Shibaura Institute of Technology, Japan*, Y. Morita*, Nano-Coat and Film LLC, Japan

Diamond-like carbon (DLC) coating has been widely used for protection of dies, punches and tools from friction and wearing. Even in the progressive stamping, where a series of die units are aligned to form a metallic sheet to products, DLC films coated onto the drawing dies, shearing and bending punches successfully work within the specified time of life. Further, nano-laminated DLC coating is also utilized to prolong the tool life for stamping dies and punches up to 100, 000 times stamping in continuous. In addition to research and development to prolong the tool life, considering the practical stamping cases for battery cases or DVD parts, re-coating is also needed to reuse the die substrate and tool materials.

In the present study, our developing rf/dc oxygen ashing apparatus is first applied to efficient removal of used DLC coated dies, punches and tools. Different from conventional dc-plasma ashing, the interlayer between main DLC coating and substrate is also removed efficiently without severe damage to substrate. In the present experiment, original mirror-shaped WC (Co) substrate surface is reproduced even after removal processing via rd/dc plasma ashing. Next, nano-laminated DLC film is re-coated onto the recycled substrate. This recycled DLC coated dies and tools are further used in the further steps of progressive stamping. Quality of stamped products is compared

FP-15 The Effect of Thickness on Structure and Properties of Tantalum Thin Films Deposited by Modulated Pulse Power Magnetron Sputtering, ***S. Myers****, J. Lin, J.J. Moore (jjmoore@mines.edu),* Colorado School of Mines*, W.D. Sproul,* Reactive Sputtering, Inc.*, S. Lee*, US Army ARDEC Benet Labs

Tantalum thin films have been of importance since the early 1960's for their use in fabricating resistors and capacitors. Tantalum is of particular interest today because it is a strong candidate to replace electrodeposited (ED) chromium coatings used for various tribological applications, such as the interior lining of large caliber gun barrels. Typically, coatings used for this application require thicknesses 100 µm or more. Modulated pulse power (MPP) magnetron sputtering is a promising deposition technique to deposit thick films due to the ability to generate high metal ion fluxes with low ion energies. Thin and thick tantalum coatings ranging from 2 – 100 µm were deposited by MPP at 2 kW, 5 mTorr and – 50 V substrate bias. The microstructure and properties of the coatings were characterized by glancing incident angle X-ray diffraction and conventional X-ray diffraction, nanoindentation, scratch test and scanning electron microscopy. The effect of the coating thickness on the coating residual stress, phase formation, grain size, surface roughness and mechanical properties will be presented in detail.

FP-16 Graphene Layers Deposited by Hot Wire CVD, ***C. Corbella*** *(corbella@ub.edu), J. Badia-Canal, V.-M. Freire, E. Bertran, J.-L. Andújar*, Universitat de Barcelona, Spain

Graphene layers have been grown on monocrystalline silicon (c-Si) wafers by chemical vapour deposition (CVD) thermally activated in a hot wire process. The depositions were performed at 2.5 mbar using acetylene as gas precursor, which was diluted in a hydrogen atmosphere. In a previous step, a Cu film was deposited on the c-Si by magnetron sputtering (PVD) to enhance the growth of graphene. PVD and CVD processes were held consecutively in the same reactor. A graphite heater activated the decomposition of the hydrocarbon precursor and increased the substrate temperature up to 800ºC. The other variables considered in this work are the gas flow ratio and the distance between sample and heater. Raman spectroscopy assessed the synthesis of carbon in graphene form, by showing the graphene-characteristic 2D band, as well as the D and G peaks. Also, the morphology of the samples was characterized by atomic force microscopy (AFM) and scanning electron microscopy (SEM). These techniques were used to study the extension and surface quality of the layers. The results, which are discussed in terms of the technological parameters of deposition, suggest the feasibility of hot wire CVD to produce graphene layers on metallic substrates.

FP-18 Analysis of the Inorganic Component of Autogenous Tooth Bone Graft Material, ***S.-C. Jin****, S.-G. Kim (sgckim@chosun.ac.kr), J.-H. Byeon, Y.-K. Kim,* Chosun University, Korea*, S.-Y. Kim,* Yeungnam University, Korea*, I.-W. Um*, Dentist - Private Practice, Korea

This study was performed to evaluate the inorganic components and surface structure of recently developed autogenous tooth bone graft materials used in clinics. Using extracted fresh teeth and samples treated as autogenous tooth bone graft materials, we analyzed the weight reduction after heat treatment and performed scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), and X-ray diffraction analysis (XRD). Each sample was classified as the crown, the root, and the total tooth powder for analysis. After heat treatment, there were weight reductions of approximately 4.7%, 28.7%, and 29.5% in the enamel, the root (dentin and cementum), and the total tooth, respectively.

The results of the EDS analysis of sample 1 showed that the calcium/ phosphorus (Ca/P) ratio of the enamel was approximately 1.54, the Ca/P ration of the dentin was approximately 1.02, and the Ca/P ratio of the cementum was approximately 0.96. The results of the EDS analysis on the crown, root, and total tooth powder of sample 2 showed that the Ca/P ratios of the total tooth were 1.46 and 1.24, which were comparable to the values of tricalcium phosphate (TCP) and octacalcium phosphate (OCP). The crown portion had a ratio of 1.75, which was comparable to the hydroxyapatite (HA) value, and the root portion had a ratio of 1.32, which was similar to the amorphous calcium phosphate (ACP) value. In XRD, HA and TCP were detected in all samples. We confirmed that the dental crown portion was primarily composed of high-crystalline calcium phosphate while the root portion was composed of poor-crystalline calcium phosphate. Favorable bony remodeling by osteoconduction could be anticipated if the dentin and cementum portion of the tooth, which was the largest portion of the tooth, was used as the bone graft materials because they contained low-crystalline apatite.

FP-19 Non-Catalytic Method to Prepare Organized Nickel–Carbon Nanofibers on Nanopatterned Silicon Substrates, ***A.-A. El Mel****,* Université de Nantes, France*, W. Xu, C.-H. Choi,* Stevens Institute of Technology*, E. Gautron, B. Angleraud, A. Granier, P.-Y. Tessier (Pierre-Yves.Tessier@cnrs-imn.fr)*, Université de Nantes, France

The incorporation of metal or metal carbide nanoparticles into or onto carbon nanofibers (CNFs) has recently highlighted new applications of carbon structures at the nanoscale. These nanofibers are considered as a promising candidate for sensors application at the nanoscale. Nickel-carbon composite nanofibers (c-Ni/CNFs) are attractive for various applications due to their promising properties. The elaboration of this type of material is considered as a challenge in the field of nanoscience. The purpose of this work is to report a new, easy and cheap method in order to prepare organized c-Ni/CNFs. This method consists in combining two plasma processes PVD and PECVD (Physical Vapor Deposition and Plasma Enhanced Chemical Vapor Deposition) for direct growth of horizontal and aligned c-Ni/CNFs on silicon nanopatterned substrate prepared by laser interference lithography. Before integrating these nanofibers in complex nanodevices we characterize it by various analysis techniques. The observation of these nanofibers with scanning electron microscopy demonstrates their very high length (up to several millimeters) and their good flexibility. Their diameter is about 150 nm. Micro-Raman spectroscopy performed on a single nanofiber, after being dispersed on a silicon substrate, shown that the carbon phase was amorphous. The chemical composition of the nanofibers was determined by XPS, and the presence of nickel nanoparticles was demonstrated by high resolution transmission electron microscopy imaging. After the optimization of the growth of the nanofibers, the impacts of the deposition time and of the dimensions of the nanopatterned silicon substrate on the growth of the nanofibers are studied. By controlling these two parameters (deposition time and the dimensions of the nanopatterned substrate) it is possible to control the diameter of the nanofibers between 80 nm (the lower value reached by this process) and 400 nm. This synthesis technique gives the opportunity of synthesizing nickel/carbon nanofibers with a very high length, with a controlled diameter and microstructure.

FP-20 Stable Electron-Emission from a Tip-Type Carbon Nanotube-Based Emitter via Formation of Interlayers, ***J.-P. Kim****, H.-B. Chang, Y.-R. Noh,* Hanyang University, Korea*, J.-U. Kim,* Korea Electrotechnology Research Institute, Korea*, J.-S. Park (jinsp@hanyang.ac.kr)*, Hanyang University, Korea

X-ray tubes using cold cathodes as electron source has recently attracted great attention in a wide range of applications, especially in x-ray radiography such as diagnostic medical imaging and embedded-type radiation brachytherapy, because they have a lot of advantages, including possibility of miniaturization, fast response, low power consumption, and low fabrication cost, over the x-ray systems using conventional thermionic cathodes. Carbon nanotubes (CNTs) have been considered to be one of the most promising materials for point-type cold electron sources due to their mechanical and chemical stability as well as superior electron emission properties. The CNT-based field emission cold cathodes have been fabricated either by direct growth of CNTs on substrates or by indirect technique. The direct growth by CVD process has several problems, such as difficulties in controlling each CNT, the complexity of the fabrication process, and high growth temperature. The indirect printing method, by contrast, is a relatively simple process and can be done for a lower cost than the direct growth method, but also has many technical limitations including non-uniform dispersion of the CNT powders, poor adhesion between the substrate and the CNT layer, and emission degradation by residues of binder.

Here, we present a novel method of fabricating CNT-based field emitters, which adhere strongly to a sub-micron sized tungsten (W) tip substrate, by forming interlayers between the CNT and the W-tip substrate. The interlayers were built up by depositing thin films of aluminium (Al) and hafnium (Hf) on conical-type W-tip substrates via RF magnetron sputtering, prior to CNT growth. Multi-walled CNTs with diameters of 5 - 20 nm were deposited on the species of interlayer/W-tip at room temperature using an electrophoretic deposition method and then they were thermally treated using an inductively coupled plasma-chemical vapor deposition system at various temperatures. For all the samples, scanning electron microscopy, high-resolution transmission electron microscopy, and Raman spectroscopy were used to monitor their morphologies, microstructures, and crystal qualities. X-ray photoelectron spectroscopy was also measured to observe the chemical binding states of CNTs and interlayers. Furthermore, the field-emission properties of the fabricated CNT-emitters, such as turn-on fields for field emission, maximum emission currents, current fluctuations, and long-term stabilities, were characterized. The results conclusively indicated that highly stable electron-emission could be achieved from tip-type CNT-emitters via formation of proper interlayers.

FP-21 Small Angle Neutron Scattering (SANS) Characterization of Electrically Conducting Polyaniline Nanofiber/Polyimide Nanocomposites, ***A.R. Hopkins*** *(alan.r.hopkins@aero.org),* The Aerospace Corporation*, S.J. Tomczak,* AFRL/RZSM, Edwards Air Force Base*, V. Vandana,* AFRL/PRSM, Edwards AFB*, A.J. Jackson*, NIST

Nanocomposites of polyaniline nanofibers and polyimide were fabricated and studied using small angle neutron scattering (SANS). The immiscible nature of the conformationally dissimilar polyaniline nanofiber and polyimide host is established by a series of experiments involving neutron scattering. Based on these techniques, we conclude that the crystal structure of the polyimides is not disrupted, and that there is no mixing on a molecular level between the two components. The morphology of the conducting salt component was analyzed by SANS data and was treated by two common models: Debye-Bueche (D-B) and inverse power law (IPL). Due to deviations in the linear curve fitting over a large scattering range, neither the D-B nor the IPL model could be used to characterize the size and shape of all PANI-0.5-CSA/polyimide blend systems. At 1 and 2% concentration, the D-B model suggested salt domains between 20 and 70 Å with fractal geometries implied by the IPL model. As salt concentrations are increased to 5%, the structures are observed to change, but there is no simple structural model that provides a suitable basis for comparison.

FP-24 Effects of Tip-Curvatures and Selective Growth on Electron Emission Behavior in Conical-Type Carbon Nanotube Field-Emitters, *Y.-R. Noh, J.-P. Kim,* ***H.-B. Chang****, J.-S. Park (jinsp@hanyang.ac.kr)*, Hanyang University, Korea

Recently, carbon nanotubes (CNTs) have been researched to develop a cold cathode electron source in x-ray system for medical applications such as diagnosis and brachytherapy of cancers. In order to realize a high-resolution x-ray image by using CNTs, their field-emission properties should be enhanced and, at the same time, the fine focusing of the electron beam should be required. For this purpose, tip-type CNT-emitters were proposed by our previous works, where the CNTs were directly grown on conical-type metal-tip substrates. The results showed that the tip-type CNTs had much better electron-emission properties and smaller beam areas than conventional CNTs that used flat-type substrates like Si wafer. However, the peel-off phenomenon of the CNTs after a prolonged operation occurred at the summit part of the tip, which led to the degradation of the emission current. For this reason, more studies on stable and sustaining electron emission from CNTs are still required for the practical use of CNT-emitters as cold cathodes. It is unfortunate, however, that this issue has hardly been considered in the literature.

In this study, we have aimed to develop a tip-type CNT-emitter that can provide highly stable and at the same time less fluctuated emission currents by investigating the effects of tip-curvatures and selective CNT-growth on their field-emission properties. The CNTs were directly grown on conical-type metal tips employing an inductively coupled plasma-chemical vapor deposition system. The conical tips were made through electrochemical etching of a tungsten wire and prepared to have different tip-curvatures (which were controlled by changing the conical angle of the tip from approximately 10^o to 180^o) by varying the etching time, the molarity of chemical (KOH), and the applied voltage between a anode and a cathode. Prior to growth of CNTs, a thin film of Ni as a catalyst was deposited and then treated using NH_3 plasma to form Ni islands for nucleation. Here, the area of the plasma-treated Ni layer was defined using a chemical etching method so that the CNTs were selectively grown only on the region where the Ni islands existed. For all the grown CNTs, their morphologies and microstructures were analyzed by scanning electron microscopy. Furthermore, their electron-emission properties including the current fluctuation and the long-term variation of emission current were measured and characterized in terms of tip-curvatures and selectively-grown CNT areas. In addition, to analyze the trajectory and beam size of electrons emitted from the CNTs, the field-emission microscopic images and the corresponding intensity profiles of brightness were extracted.

FP-25 Plasma Species Influence on the Properties of Oxynitrided Titanium Surface*,* ***C.A. Alves*** *(alvesjr@pq.cnpq.br),* Federal University of Rio Grande do Norte - Brazil*, D.C. Braz, J.C.P. Barbosa, R.C.S. Rocha,* UFRN, Brazil*, A. Nunes,* Federal University of Rio Grande do Norte - Brazil*, C. Krug*, Federal University of Rio Grande do Sul - Brazil

In this work, species as N_2^+, N_2, O and O^+ was analyzed by optical emission spectroscopy (OES) into the plasma of Ar-N_2-O_2 gas mixture. Argon and nitrogen flux was fixed in 2 and 4 sccm, respectively and varied the oxygen flux between 2 and 4 sccm. It was observed the influence of both gas and species concentrations in the surface properties after thermochemical plasma treatment. Surface tension measurements on the samples showed increasing in the dispersive coordinate proportionally to oxygen flow and it promoted an increasing in the angle contact. The DRX has presented a solid solution of nitrogen and titanium oxides (resultado importante?). The AFM measurements have shown different topographies and roughness values. Based on those characterization analysis it has been seen which a relation among luminous intensities and surface parameters. Nanohardness assays and elasticity module also presented variance accord to the luminous intensity of N_2^+ species.

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

Symposium G Poster Session

GP-2 Improvement on Corrosion Resistance of Austempered Ductile Iron via Low Temperature Duplex Coatings*,* *C.-H. Hsu (chhsu@ttu.edu.tw),* ***K.-H. Huang****, Y.-T. Chen,* Tatung University, Taiwan*, P.-L. Sun, C.-K. Lin*, Feng Chia University, Taiwan

Austempered ductile iron (ADI) is an attractive engineering material due to its excellent strength, toughness and the low cost. This study utilized electroless nickel (EN) and cathodic arc evaporation (CAE) technologies, with the known advantage of low processing temperature, to treat the ADI substrates. The eligibility of applying the EN and CAE-TiN duplex coatings on ADI, along with the coating properties, such as structure, roughness, and adhesion were evaluated and analyzed. Moreover, polarization tests were performed to further understand the effect of both the coatings on the corrosion behavior of ADI. The results showed that the unique microstructure of ADI did not deteriorate after EN and CAE treatments. Corrosion resistance of ADI in 3.5% NaCl solution could have a noticeable improvement via the use of EN/TiN duplex coatings.

GP-8 Fabrication and Mechanical Characteristics of Metal Matrix Composite with Homogeneously Dispersed Ceramic Particles*,* *E.-H. Kim, W.-R. Lee,* Changwon National University, Korea*, C.-G. Lee, M.-K. Lee, J.-J. Park,* Korea Atomic Energy Research Institute, Korea*, C.-S. Lee,* METIA Corporation, Korea*,* ***Y.-G. Jung*** *(jungyg@changwon.ac.kr)*, Changwon National University, Korea

Composites incorporating ceramic particles as reinforcement phase, namely metal matrix composites (MMCs), have been researched in efforts to enhance wear resistance, hardness, and elasticity of pure metal [1]. In order to optimize these advantageous properties, the ceramic particles must be individually dispersed in the metal matrix without any aggregation of particles. Therefore, in this work, titanium carbide (TiC) particles have been coated with nickel (Ni) to increase compatibility between TiC particles and metal matrix based on iron (Fe), leading to the improvement in the dispersion of TiC particles in the molten matrix. TiC particles were dispersed into the basic aqueous solution of pH 12, and then nickel nitrate ($Ni(NO_3)_2$) as a Ni precursor was added at the TiC suspension. The interaction between TiC particle and Ni precursor is driven by the attractive force of Ni anion and TiC particle with negative charge [2]. In this work, two different methods were employed for preparing the reinforcement particle: in one method, TiC particle was simply coated with the Ni precursor (process I); in the other method, an inoculant (ferrosilicon) was used as a core particle (process II), which has been generally used in the foundry industry to improve crystal growth of carbon. In process II, the Ni-treated TiC particles were coated onto the surface of the inoculant using an inorganic binder converted into the glass phase by sol-gel reactions. Then, the reinforcement particles prepared by above two processes were injected into the molten matrix of 1500°C. The dispersibility of TiC particles was evaluated using various analytic techniques, including mechanical properties of composite. The reinforcement particles prepared by process II showed more homogeneously and uniformly dispersion into the matrix than those by process I, maybe resulting from the specific gravity effect of reinforcement particle coated on the inoculant. However, the wear resistance and hardness of composite were significantly improved independent of process, compared with pure metal without the reinforcement phase. Consequently, MMCs with reasonable properties have been successfully prepared through the homogeneous dispersion of reinforcement particle in the matrix.

GP-9 Synthesis of Hydrogenated Amorphous Carbon Films with a Line Type Atmospheric-Pressure Plasma CVD Apparatus, ***M. Agemi*** *(msk516x.x@gmail.com), K. Kayama, M. Noborisaka,* Keio University, Japan*, A. Shirakura,* Kanagawa Academy of Science and Technology (KAST), Japan*, T. Suzuki*, Keio University, Japan

Hydrogenated amorphous carbon (a-C:H) films, which have various excellent properties, have been applied in mechanical and chemical fields and expected to expand the range of application. For example, a-C:H films have been found useful in food packaging and a protection material for concrete construction fields due to its excellent properties such as a gas barrier. But there are few studies of long-term outdoor use of a-C:H films as protection materials. In general, a-C:H films are synthesized by PECVD process under vacuum condition less than 100 Pa. But this synthesis process has problems such as high cost for vacuum devices, long deposition time and a limited synthetic area. Therefore, it is necessary to realize low-cost and high-speed synthesis to a large area. A line type atmospheric-pressure plasma CVD apparatus can solve these problems.

In this study, we synthesized a-C:H films on polyethylene terephthalate (PET) substrates, which have the highest gas barrier properties of the common polymer materials, with a line type atmospheric-pressure plasma CVD apparatus. The gas permeability of the films on PET was measured by a gas permeation tester, the surface of the films was observed by scanning electron microscope (SEM). In addition, we conducted an ultraviolet ray transmission measurement, an accelerated weathering test and cyclic fatigue test.

According to observation by SEM, the a-C:H films consisted of tiny particles which sizes were around 200 nm.

Ultraviolet permeability of the a-C:H films was 0-28 % in the ultraviolet range 320-400 nm, while ultraviolet permeability of uncoated films was 50-80 %.

GP-10 Influence of the Deposition Pressure on Properties of a-C:H Films Synthesized Using a Dielectric Barrier Discharge, ***R. Horikoshi*** *(horikoshi_r@yahoo.co.jp), K. Kayama, M. Noborisaka, Y. Tachimoto,* Keio University, Japan*, T. Watanabe,* Kanagawa Industrial Technology Center, Japan*, A. Shirakura,* Kanagawa Academy of Science and Technology (KAST), Japan*, T. Suzuki*, Keio University, Japan

a-C:H films have been applied in various fields such as machine components because of their excellent mechanical properties: high hardness, low friction coefficient and low wear rate. While a-C:H films are generally synthesized under vacuum condition (less than 10 Pa), new plasma sources which make possible low-cost deposition have been studied in recent years. Among them, a dielectric barrier discharge (DBD) has attracted much attention as a method to synthesize thin films operating at around atmospheric pressure. There are many studies on DBD processing at the atmospheric pressure (100 kPa). However, few data are available on the properties of a-C:H films synthesized under various pressures. If properties of films synthesized at these pressures are revealed, it is expected their application range will expand. Therefore we have aimed to synthesize a-C:H films under various pressures (1-100 kPa) and find out the effect of impressed voltage and gas mixture ratio on physical properties of the films at each pressure. In this study, we synthesized a-C:H films by a DBD. Acetylene gas was used as a source gas and nitrogen gas was used as a main plasma generation gas. The morphological surface of the films was observed by SEM, the hardness of the films was measured by nano-indentation test, the surface roughness (Ra) of the films was measured by AFM and the structure of the films was analyzed by FTIR. The films consisted of particles under any experimental conditions. The films synthesized at 1 kPa consisted of particles of uniform size and their surface roughnesses were 0.4-0.9 nm. On the other hand, the films synthesized at 100 kPa consisted of particles of various sizes and their surface roughnesses were 2.2-2.7 nm.

GP-12 Surface Texture and Stress State in Post Polished Cathodic Arc PVD Coatings, ***A. Pilkington*** *(antony.pilkington@rmit.edu.au), S.J. Dowey, J.T. Toton,* RMIT University and Defence Materials Technology Centre, Australia*, L. Ward,* RMIT University, Australia*, D. Griffett,* Cuttertec Pty, Australia*, E.D. Doyle*, RMIT University and Defence Materials Technology Centre, Australia

Advanced PVD coatings have enabled major productivity improvements for engineering tooling when applied to highly loaded cutting and forming tools. Cathodic arc deposition technology has become the most flexible technique for tribological coating production, offering high levels of coating adhesion with high deposition rates of 3-5 microns per hour from alloy cathodes onto HSS and carbide tooling. Macro-particles resulting from the arc evaporation process are well known to compromise the practical component or tool performance in terms of friction, high temperature oxidation resistance and wear modes. Post polishing of arc PVD coatings is often employed to improve the surface texture of high performance cutting tools. Two techniques used in industry are dry blasting with high velocity grit particles and nylon abrasive filament (NAF) brushing. Micro-blasting of materials is known to impart a degree of desirable compressive stress into the sub-surface region. In this work the effectiveness of the treatments were compared on arc deposited coatings of CrN, TiAlN and AlCrN deposited onto M2 substrates. The changes in surface texture parameters due to the post polishing treatments were measured using an infinite focus microscope. The removal of the macroparticles was quantified by number density and volume change after treatment. Residual stresses from the coating process were investigated by sin2 Ψ XRD techniques and by simpler coated beam deflection methods on thin substrates. Possible effects of the post-polishing on the residual stress state were compared by XRD measurement of lattice spacing. Changes in the tribology of coated samples with couples of metallic and ceramic counterfaces were investigated by a pin-on-disc wear testing apparatus over a range of loading conditions.

GP-13 Thermal Annealing Effect on Material and Electrical Properties of NbN_x Gates on HfO_2 Gate Dielectrics, ***S.-Y. Lin****, Y.-S. Lai (yslai@nuu.edu.tw)*, National United University, Taiwan

In this study, niobium nitride films were deposited by a magnetron sputtering system. The incorporation of nitrogen into the NbN_x films was controlled by $N_2/(Ar+N_2)$ flow ratios. NbN_x films were characterized by four point probe, grazing incident angle X-ray diffraction, scanning electron microscopy, and X-ray photoelectron spectroscopy. It is found that the resistivity increases whereas the crystallinity decreases as the $N_2/(Ar+N_2)$ flow ratio increases. The $NbN_x/HfO_2/Si$ capacitors were subjected to rapid thermal annealing at above 950°C and forming gas annealing at 400°C to study their effects on work function and thermal stability. The effect of nitrogen on the characteristics of NbN_x films, before and after annealing, was also demonstrated.

GP-15 Electrochemical Behavior of the Ti_6Al_4V Alloy Implanted by Nitrogen PIII, *G.S. Savonov (graziela@plasma.inpe.br),* Instituto Tecnologico de Aeronautica - ITA & Instituto Nacional de Pesquisas Espaciais - INPE, Brazil*, **M. Ueda**, R.M. Oliveira,* Instituto Nacionale de Pesquisas Espaciais - INPE, Brazil*, C. Otani*, Instituto Tecnologico de Aeronautica - ITA, Brazil

Plasma surface treatments have been used very often to enhance the surface properties of metallic materials. In this work, ion implantation of Ti_6Al_4V titanium alloy was carried out with nitrogen plasma immersion ion implantation in order to obtain improvements in its surface properties, such as corrosion resistance evaluated here. The microstructure and corrosion behavior of the implanted and unimplanted samples were examined, using SEM, XRD, GDOES and potentiodynamic polarization and impedance electrochemical spectroscopy tests in 0.6 M NaCl solution. It was verified that the nitrogen implantation by PIII created resistant layers to corrosive attacks. In corrosion tests by polarization, the implanted samples showed corrosion current densities reduction of about 10 times smaller than the Ti_6Al_4V alloy without treatment. Besides, it was also observed reduced passive current densities one order of the magnitude smaller. In all cases, the polarization curves were shifted to more positive values of potentials, indicating a better corrosion resistance of these PIII treated surfaces. The implantation process produced a thin TiN surface layer followed by Ti_2N and TiN_xO_y layer, detected on GDOES. The titanium nitride stoichiometric and non stoichiometric, TiN and Ti_2N, respectively were identified on diffraction patterns by XRD of the titanium alloy surfaces. The implanted samples exhibited corrosion behavior very similar on SEM images after nitrogen implantation. In these micrographs it was observed a compact and adherent oxidized layer, formed during the corrosion tests. These layers promoted an excellent polarization resistance of these Ti_6Al_4V surfaces on impedance spectroscopy tests also. This can be correlated with the formation of very thin, continuous nitride and oxinitride layer, which could retard chloride ions ingress into the substrate.

Work supported by FAPESP.

GP-17 Hydrophilicity of TiO_x Thin Films by Atmospheric Pressure Plasma Enhanced Chemical Vapor Deposition, ***S.-S. Kim** (kimss@iae.re.kr), J.-U. Shin, S.-C. Oh*, Institue for Advanced Engineering, Korea

Over the past 10 years, various methods have been employed to coat TiO_2 thin films on supporting substrates in order to realize important applications such as water and air purification and self-cleaning. Atmospheric pressure plasma enhanced chemical vapor deposition (AP-PECVD) processes are regarded as promising and cost-effective methods for the wide-area coating of sheets of steel, glass, polymeric webs, and other materials. In this study, TiO_x thin films were deposited by AP-PECVD with dielectric barrier discharge. The characteristics of TiO_x thin films were investigated as a function of the titanium tetraisopropoxide/H_2O/He flow rate. The TiO_x thin films were characterized by Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy, X-ray diffraction, and field emission scanning electron microscopy. The hydrophilicity of TiO_x thin films was investigated by a water contact angle test.

GP-19 Uniformity Enhancement of Incident Dose on Concave Surface in Plasma Immersion Ion Implantation Assisted by Pulsed Beam-Line Plasma, *Z.T. Zhu, X.B. Tian (xiubotian@163.com), Z.J. Wang, **C.Z. Gong**, S.Q. Yang,* Harbin Institute of Technology, China*, R.K.Y. Fu, P.K. Chu*, City University of Hong Kong, China

Plasma immersion ion implantation (PIII) is a promising surface treatment technique for the irregular-shaped components. However, it is difficult to achieve uniform implantation along the surface of a concave sample due to the propagation and overlapping effect of plasma sheath. In this paper, a new ion implantation process is presented for improving the dose uniformity, especially for enhancing the lateral dose of the samples with concavities. In PIII enhanced by beam-line plasma process, a pulsed beam-line plasma with a certain energy is introduced form an external source into the concavity to suppress the sheath propagation and consequently to improve the dose uniformity. The time-dependent evolution of the potential, electrical field and the particle movement surrounding the surface of concave sample is studied by a particle-in-cell (PIC) simulation during a single bias high voltage (HV) pulse synchronized with the pulsed beam-line plasma. The influence of the energy of induced beam-line ions, plasma density and the amplitude of bias HV pulse on the incident ion dose, angle and energy distribution is discussed. Compared with the traditional PIII process, the dose uniformity of the sample surface is improved obviously due to the increase of the ions implanted into the lateral surface.

GP-22 Liquid-Phase Deposition of Low-k Carbon Nitride Films, ***H. Kiyota** (hkiyota@ktmail.tokai-u.jp), M. Higashi, T. Kurosu, M. Chiba*, Tokai University, Japan

Low-*k* insulating materials with the relative dielectric constants lower than 2 have been required for modern ultra large-scale integration (ULSI) technology. So far, many efforts have been made to develop new low-*k* interlayers for multilevel interconnection in ULSI. Carbon nitride (CN_x) has a great potential for low-*k* material because of its excellent properties such as extreme hardness, high resistivity, and low dielectric constant. While the CN_x films have been studied by using various deposition techniques, the liquid-phase deposition has been attempted as an alternative deposition technique by using organic liquid containing nitrogen. In this work, we have studied composition, bonding structure, and electrical properties of CN_x films deposited using liquid acrylonitrile.

The CN_x films were deposited by application of DC bias voltage to n-Si substrates immersed in acrylonitrile. Continuous, uniform films are obtained by applying both positive and negative bias voltage. Measurements of X-ray photoelectron spectra (XPS) show the presence of C, N, and O as major components of the deposited films. The atomic ratios of nitrogen to carbon (N/C) are determined as 0.2 – 0.3 for the as-grown samples. While the films deposited under positive bias mainly consist of C and N, considerable amounts of oxygen and sodium are also contained in the films deposited under negative bias. From analysis of C 1s and N 1s spectra, the major bonding state of the CN_x film deposited under negative bias can be attributed to a mixed phase of C≡N and hydrogenated C=N bonds. On the other hand, the CN_x film deposited under positive bias consists of the partially hydrogenated C=N bond.

Metal-insulator-semiconductor (MIS) structures were fabricated using the CN_x insulating layers to evaluate the electrical properties of the deposited films. For the films deposited under positive bias, three distinct regions of accumulation, depletion, and inversion are shown in the *C-V* characteristics. On the other hand, MIS capacitor fabricated using the films deposited under the negative bias show anomalous behaviors such as a hysteresis shift in their *C-V* curves, suggesting that the CN_x films deposited under negative bias application are unsuitable for the dielectric material. The lowest relative dielectric constant of 2.6 was determined using the accumulation capacitance and the thickness of the CN_x film. Since the dielectric constant comparable to the existing low-*k* materials can be obtained, the liquid deposited CN_x film is a promising ultralow-k material that is required for the multilevel interconnection for ULSI circuits.

GP-23 Deposition of $In_{2-x}Fe_xO_3$ Films by Ultrafast Microwave Annealing Technique, *S.B. Qadri (qadri@anvil.nrl.navy.mil),* Naval Research Laboratory*, **C. Fahed**,* George Mason University*, N.A. Mahadik, H. Kim, M. Osofsky,* Naval Research Laboratory*, M.V. Rao,* George Mason University*, Y. Tian*, L. T. Technologies

Thin films of $In_{2-x}Fe_xO_3$ were deposited on glass substrates using ultrafast microwave annealing technique. It is well known that SiC is an excellent absorber of microwaves. Hence, microwave heating provides ultra-fast ramp rates (> 1000ºC/s) and very-high annealing temperature (up to 2100°C) conditions required for depositing $In_{2-x}Fe_xO_3$ films. In this method, microwaves (~ 1 GHz) from a source are amplified and directly coupled to the SiC through a microwave heating head. The indium iron oxide powder is placed on SiC sample. Since the sample is placed in microwave transparent surroundings, the microwaves are absorbed by the SiC sample only, leading to extremely high heating rates. This feature contrasts microwave annealing with resistive and inductive heating furnaces, where the heating source not only heats the sample but also the surrounding ambient. Similarly, as soon as the microwave source is turned off, the sample cools down rapidly because of cool ambient surrounding the sample. The glass substrate was placed directly on top of the hearth thus we were able to obtain deposited films. The structural, and transport properties of the films showed similar properties to that of the bulk samples.

GP-24 Incorporation of Silver Nanoparticles in DLC Films for Spatial Application, ***S.F. Fissmer**, L.V. Santos (santoslv@ita.br), M. Massi,* Technological Institute of Aeronautics, Brazil*, P.A. Radi*, Instituto Nacional de Pesquisas Espaciais - INPE, Brazil

The use of solid lubricant coatings with low friction coefficient began in the 90s with molybdenum disulfide MoS_2 and Diamond-Like Carbon (DLC) films. DLC is currently one of the major solid lubricants and is used in several areas, including spatial area. The main problem addressed here is the degradation of DLC films by atomic oxygen from orbits satellite altitudes between 100 and 300 km. The use of silver nanoparticles dispersed throughout the film provides passivity silver oxide layers which reduces the erosion of the film.

In this paper DLC films with silver nanoparticles were obtained from an adapted magnetron sputtering system. DLC film structures were analyzed by RBS to identify silver presence. AFM analysis was used to identify silver nanoparticle distribution and grain sizes. The grain size was identified in a ranging from 50nm to 150nm. Raman spectra revealed that silver didn't add any structural change in the film. After these analyses, the corrosion resistance of the films were tested in oxygen discharge using a RIE (*Reative Ion Etching*) reactor**.**

These corrosion tests were made in DLC films with and without silver and proved the efficiency of silver incorporation in DLC films. DLC films with silver had a corrosion rate five times lower (4nm/min) than the films without silver (16nm/min). Tribological studies of the films were investigated, in environment atmospheric and in vacuum, in order to verify whether the insertion of silver in film structure does not affect the film lubricant function and changes film morphology after the corrosion process.

GP-25 The Electrical Contact Resistance Endurance of Thin Silver Coatings Subjected to Fretting Wear: Influence of the Coating Thickness, *P. Jedrzejczyk,* Ecole Centrale de Lyon - LTDS, France*, **S. Fouvry** (siegfried.fouvry@ec-lyon.fr),* CNRS - ECL, France*, P. Chalandon*, PSA, France

The main requirement of the materials used in electrical connectors is to allow low and undisturbed electrical contact resistance. However due engine vibrations and thermal fluctuations fretting wear damages can be activated in the interface decaying the electrical conductance endurance. Since many years, different materials and coating configurations under fretting wear conditions were studied more or less extensively. Between them, the non-noble tin as well as noble gold coatings but very little have been addressed concerning the silver coatings. Keeping in mind the noble properties of silver, compared to tin, and its lower costs, compared to gold, this material can be considered as potentially interesting for electrical contact applications.

In this paper the electrical performance of pure silver coatings deposited on Ni interlayer and CuSn4 substrate, submitted to fretting conditions, are studied. Five different coating thicknesses; e = 1.3µm, 2µm, 3µm, 4µm and 5µm are considered. The step-by-step degradation process of the contact interface is investigated using interrupted tests and analytical surface expertises. We show that the electrical decay is directly correlated with the extent of surface degradation involving the silver elimination from the fretted interface and the constitution of a homogeneous Ni and Cu oxide insulating third body. In order to formalize the influence of the Ag coating thickness on the electrical lifetime, a quantitative approach is developed. It consists to report the electrical endurance (Nc) (i.e. when the electrical contact resistance overpasses a threshold value) as a function of the applied displacement amplitude. These "endurance electrical charts", so called Wöhler-like curves in reference to classical "fatigue" approach", are discussed and formalised. We show that above a threshold silver coating thickness, the electrical lifetime of studied contact is proportional to the coating thickness. This linear evolution is in fact consistent with the wear kinetic of the coating. Hence applying a local energy wear approach, the coating degradation but also the electrical endurance is formalised and the electrical endurance charts predicted.

GP-26 Plasma Nitrocarburizing of AISI 304 Stainless Steel Under Floating Potential, ***T.R. da Rosa*** *(thomas@ita.br),* Technological Institute of Aeronautics, Brazil, *L.C. Fontana, M. Tomiyama, J.H.C.P. Santos,* Universidade do Estado de Santa Catarina, Brazil, *H.S. Maciel*, Technological Institute of Aeronautics, Brazil

The plasma nitrocarburizing is considered a highly promising process for the surface modification of stamping parts because it can lessen distortion of the conformed lattice due to its lower treatment temperature (570–580ºC), and the treatment time for nitrocarburizing is far shorter than for nitriding.

In the present work, samples of austenitic stainless steel AISI 304 were submitted to a plasma nitrocarburizing process under floating potential in a graphite hollow cathode plasma. Experiments were carried out in two plasma working gas: 10% N_2 + 80% H_2 + 10% Ar + vaporized carbon and 20% N_2 + 70% H_2 + 10% Ar + vaporized carbon. The carbon vapor is obtained during the process by sputtering of the graphite hollow cathode surface. The hollow cathode was developed to allow the insertion of samples to be treated, with no contact with the cathode surface, thus characterizing a treatment under floating potential. A special configuration of the experiment allowed a nonuniform plasma heating such that a thermal gradient was produced along the sample. So, the microstructure of the layers formed could be evaluated for a range of temperatures (450 a 550ºC). In order to compare the processes, a condition of nitriding in the plasma working gas 20% N_2 + 70% H_2 + 10% Ar was investigated, also reproducing this temperature gradient. The techniques used for characterization of the samples were: X-ray diffraction, optical microscopy, scanning electron microscopy and microhardness vickers measurements.

The results show the formation of diffusion layers and the presence of phases of nitrides (ε-Fe_{2-3}(C,N), γ'-Fe_4(C,N), CrN) was detected in nitrocarburized samples of stainless steel AISI 304. They also indicate that plasma nitrocarburizing, in floating potential, is a feasible and effective process for the surface treatment of materials. It is alternative to conventional nitrocarburizing, forming thick and homogeneous composite layers, and can considerably increase the surface hardness of austenitic stainless steel AISI 304.

GP-28 The Characteristics of Interface for Pentacene/ZnO Hybrid p-n Junction Diode, ***J-B. Kwon****, H.-H. Kim, M.-S. Kim, J.-H. Han, D.-H. Lee, B.-H. O, S.-G. Lee, E.-H. Lee, S.-G. Park (sgpark@inha.ac.kr)*, Inha University, Korea

The purpose of this work is to show the improvement of hybrid p-n junction diode performance by making the hydrophobic n-ZnO film surface. One of the most effective ways to investigate hydrophobic surface properties is a contact angle measurement. A low contact angle between a solid surface and a water-drop indicates that the surface is hydrophilic and has a high surface energy. On the contrary, a high contact angle means that the surface is hydrophobic. In general, most of an inorganic oxide surfaces show hydrophilic state while most of organic semiconductors show hydrophobic states. This mismatch has negative influence on crystalline formation of organic semiconductor deposited on oxide substrates. Therefore, in this work, wet-etching and PDMS treatment were performed to change the hydrophilic characteristics of the ZnO surface into hydrophobicity, and we observed that these changes make some differences in a grain size of an pentacene deposited on surface-treated ZnO and improve electrical characteristics of pentacene/ZnO hybrid p-n junction diode.

The grain size of sputtered-deposited ZnO increased with increasing RF power. After wet-etching in BOE (6:1) and grafting PDMS contact angles of surface-treated ZnO were 103.5, 110.9 and 115.8° at 100, 200 and 300W of RF power, respectively. It is indicated that the more hydrophobic nature, the larger grain size it could have. We confirmed that the grain size of pentacene deposited on the hydrophobic ZnO had lager than as-deposited. When ZnO was deposited at the 100W of RF power, the current density of normal pentacene/ZnO diode was 2.6A /cm^2 at a forward bias of 12V, while that diode using surface treatment was about twice of 5.2A/cm^2. Turn-on voltages were approximately 2.5 and 4.8 V for as-deposited and surface-treated pentacene/ZnO , respectively.

We have investigated the characteristics of interface for pentacene/ZnO hybrid p-n junction diode. the grain sizes of pentacene on treated-ZnO were larger than as-deposited ZnO. and the current-density increased with increasing hydrophobicity. This study present improvement of the electrical characteristics of hybrid p-n junction diode using pentacene and ZnO.

GP-30 Improved Nucleation and Transition in Fast Response Liquid Crystal Displays by Atmospheric Plasma Treatments*,* ***G.M. Wu*** *(wu@mail.cgu.edu.tw), H.W. Chien, C.C. Huang*, Chang Gung University

The optically-compensated-bend (OCB) mode pi-cell s exhibit fast-response time and wide-viewing angle characteristics. However, OCB-mode requires a transition of the liquid crystal molecule from an initial splay state to the bend state configurations before it can provide quick operation. It may need a high voltage or take a long warm-up time to transform to the bend state. In this study, t he polyimide alignment films have been modified to reduce the splay-to-bend trans i tion time by atmospheric pressure plasma beam treatments . The proposed process method was demonstrated to be highly effective in improving the overall transition time. The number of splay-to-bend nucleation sites in the liquid crystal cell s could be increased dramatically by up to 20 times at the initial stage, and the improvement in the cell warm-up time was achieved at 45-7 1 % reduction at 5.5 V. The various plasma processing parameters were optimized at the plasma power of 700 W, plasma distance of 25 mm, and plasma scan speed of 600 mm/sec . In addition, we maintained the excellent optical properties and response time characteristics for the OCB mode liquid crystal displays.

GP-31 Nitriding of Tool Steels in Electron Beam Excited Plasma*,* ***P. Abraha*** *(Petros Abraha [petros@meijo-u.ac.jp]), J. Miyamoto*, Meijo University, Japan

We present the use of electron beam excited plasma in nitriding manufactured tool steels to increase the surface hardness to more than two times without altering the surface finish. The process eliminates the formation of the brittle and rough compound layer by hardening the process through diffusion of the plasma species in to the subsurface of the treated material. The applications of the process can be in areas of hard coating where adhesion of the coating material with the tool steel is of significant problem that needs to be addressed.

In this research, the sample tool material used was SKD 61 with a chemical composition of 0.36% C, 5.05% Cr, 1.21% Mo, 0.83% V, 0.92% Si, 0.43% Mn, 0.008% P, >0.001% S, Fe bal. The sample was heat treated, hardened and triple tempered to a hardness of 630 Hv. The sample was then treated in a nitrogen plasma produced by a beam current of 8 A under a working pressure of 0.4 Pa. The temperature was set at 500 degrees centigrade throughout the treatment time. The experimental set up includes bias terminals that reduce the ion density within the vicinity of the tool steel material. This is done to reduce nitriding due to ion and increase the chance of nitriding due to neutral species within the plasma.

The hardness distributions, thickness of the diffusion layer, surface roughness of the nitrided tool steels were examined to determine the mechanical and surface properties. The results of our experiments show that the surface hardness was increased to 1300 Hv, about two times more than the untreated one. The surface hardness is maintained to a depth of 30 micrometers and falls sharply and saturates to the hardness of the untreated samples in about 80 micrometers. The corresponding thickness of the diffusion layer also confirms the same results. The surface conditions were examined by scanning electron microscope and surface roughness measurements. The measured surface roughness was Ra=20 nm slight increase from the pretreatment value of 10 micrometers. However, there is no trace of the compound layer that is usually observed in the ion nitriding processes. This is also confirmed from the X-ray Diffraction peaks, as there is no visible Fe3N and Fe4N peaks observed. These results are attractive as they open new areas of application especially in the coating industry where adhesion remains to be the limiting factor in lots of the hard coatings applied to cutting tools and metal stamping punches.

Small-Scale Batch Nitriding of Tool Steels by Electron Beam Excited Plasma Source

Nitriding of cutting tools uniformly is an important criterion that has to be met for successful processing technique. A major difficulty of using plasma nitriding source for multiple batch-nitriding is the fixed positioning of the samples. The jigs and fixtures or just laying the sample on a solid surface compromises the exposure to the surrounding plasma.

GP-32 Multi-Functional ECR Plasma Sputtering System for Preparing Amorphous Carbon and Al-O-Si Films, *X. Fan, D. Diao (dfdiao@mail.xjtu.edu.cn), K. Wang,* ***C. Wang***, Xian Jiaotong University, China

Divergent and Mirror-confinement Electron cyclotron resonance (ECR) plasma sputtering system including a cylindrical double-target source with shutter slider which can continuously change the target area ratio was introduced in this paper, and kinds of film (single layer of pure and composite film as well as multi-layer film) deposition processes can be realized by using this multi-functional system. The Divergent ECR (DECR) and Mirror-confinement ECR (MCECR) sputtering system was first compared to prepared the highly concerned amorphous carbon films, which showed a normally friction coefficient around 0.15. Through adding substrate heating during film preparation, the tribological properties of DECR carbon films were improved with an obvious self-decreasing process of friction coefficient to 0.05 and a much longer wear life. The designed double-target source with shutter slider was first used to prepare the Al-O-Si thin films in this paper, in which the target area ratio of silicon to aluminum was changed from 0.5 to 2. A composite structure of Al-O-Si thin films with a transmittance up to 89% at 193nm wavelength was obtained with the multi-functional ECR plasma system.

Symposium T Poster Session
Room: Town & Country - Session TSP

TP Poster Session

TSP-2 Fabrication and Characterization of Nanocomposite Films, *S.-C. Her (mesch@saturn.yzu.edu.tw), T.-Y. Shiu,* ***S.J. Liu***, Yuan Ze University, Taiwan

Carbon nanotubes (CNT) with superior mechanical, electrical and thermal properties are excellent candidates for nano-reinforcing polymer-based composites. In this work, the multi-walled carbon nanotube (MWCNT) reinforced epoxy films were prepared on the backlite substrate by a hot-pressing process. To control the thickness of the film, a spacer of thickness 200um was employed. The analytical relationship among the moduli of the film, substrate and film/substrate system was derived basing on the beam theory, from which the elastic modulus of the film was determined by the three-point-bending test. Compared to neat resin films, an increase of 16% and 33% in elastic modulus were obtained when 1 wt% and 2 wt% of MWCNTs were added, respectively. Nanoindentation tests were employed to determine the hardness and Young’s modulus of the film in the nanometric scale. The measured hardness and Young’s modulus of the nanocomposite film were found to depend on the penetration depth. Experimental results show that the hardness and Young’s modulus of the film were decreasing with the increase of the indentation depth. In general, the modulus measured by the bending test represents the global and practical properties of the film, while the modulus measured by the nanoindentation test indicates the local and inherent properties. Experimental results revealed that the localized Young’s modulus obtained by the nanoindentation test is higher than the global Young’s modulus obtained by the three-point-bending test. The addition of the MWCNTs into epoxy matrix exhibits significantly improvement in the Young’s modulus of the nanocomposite film compared with pure epoxy.

TSP-3 Alumina Template Assistance in Pt/Sn Core-Shell Nano-Sphere Fabrication, ***C.-L. Chen***, *C.-C. Chen, Y.-S. Lai (yslai@nuu.edu.tw)*, National United University, Taiwan

In this work, platinum/tin (Pt/Sn) core-shell structures were deposited on anodizing aluminum oxide (AAO) substrate by sputtering technique. The Pt/Sn/AAO structures were characterized by scanning electron microscopy, atomic force microscopy, X-ray photoelectron spectroscopy, and X-ray diffraction. The AAO template with highly ordered nano-arrays served as nucleation sites on the sidewall. It was found that Sn atoms were clustered as island on AAO sidewalls, following the Stranski–Krastanov nucleation and growth model, due to its high surface energy. The island-shaped morphology of clustered Sn atoms adjacent to the AAO sidewall provided a rough surface for subsequent deposition of Pt catalysts. The activity area of Pt was measured by cyclic voltammetry. The dependence of chemical activity of catalysts on the Pt thickness and Sn/AAO morphology was explored.

TSP-10 Why Taking Creep Material Behavior Into Account is of Great Importance, ***P. Heuer-Schwarzer***, *N. Bierwisch (n.bierwisch@siomec.de)*, Saxonian Institute of Surface Mechanics, Germany

It is widely known, that many soft materials (e.g. polymers) show very significant time dependence with respect to their mechanical properties, especially with respect to Young’s modulus and Yield strength or Hardness.

In this work it will be shown how dramatic the influence of this dependency on the mechanical performance of real coating-substrate systems could be. In order to avoid failure due to flawed stability and life time prediction by ignoring this material behavior this dependence must be taken into account.

By doing so, not only experimental difficulties must be overcome but also new concepts for the correct analysis and interpretation of the measured data are necessary. Especially for nanoindentation and scratch analysis the well known classical concepts do not suffice. The authors will present the necessary extensions of such classical models and how they have to be applied.

TSP-11 Interfacial Structure and Electrical Properties of Epitaxial $NiSi_2$/Si Contacts Formed by a Solid-Phase Reaction in Ni-P/Si(100) System, ***H.-F. Hsu*** *(hfhsu@dragon.nchu.edu.tw), C.-L. Wu, T.-H. Chen, H.-Y. Wu*, National Chung Hsing University, Taiwan

As metal-oxide-semiconductor field-effect transistor (MOSFET) devices are shrunk to the nanometer scale, flat shallow metal/Si electrical contacts must be formed in the source/drain region. This work demonstrates a method for the formation of epitaxial $NiSi_2$ layers by a solid-phase reaction in Ni-P/Si(100) samples. The results show that the sheet resistance remained low when the samples were annealed at temperatures from 400 to 700°C for 30 s. Furthermore, annealing at 700°C, an epitaxial $NiSi_2$ layer with an atomically flat $NiSi_2$/Si interface was formed. The cross-sectional TEM images of epitaxial NiSi2/Si contacts formed by annealing at various periods show that both (100) and {111} interfaces were formed in the initial stage, and only the (100) interface remained at an annealing period ≥ 20s. This phenomenon results by reducing the interface energy. Additionally, a strong dependence of the Schottky barrier height on the interfacial structure was found. Schottky barrier height decreased as a mount of (100) interface increased.

TSP-12 GDOES for Accurate and Well Resolved Thin Film and Coating Analysis, ***P. Schaaf*** *(peter.schaaf@tu-ilmenau.de), M. Wilke, L. Spieß, G. Teichert, H. Romanus*, TU Ilmenau, Institut für Werkstofftechnik, Germany

In the last years, glow discharge optical emission spectrometry (GDOES) gained more and more importance in the analysis of functional coatings. GDOES thereby represents an interesting alternative to common depth profiling techniques like AES and SIMS, based on its unique combination of high erosion rates and erosion depths, sensitivity, analysis of nonconductive layers and easy quantification even for light elements such as C, N, O and H. Starting with the fundamentals of GDOES, a short overview on new developments in instrument design for accurate and well resolved thin film analyses is presented.

The article focuses on the analytical capabilities of glow discharge optical emission spectrometry in the analysis of metallic coatings and thin films. Results illustrating the high depth resolution, confirmation of stoichiometry, the detection of light elements in coatings as well as contaminations on the surface or in interfaces will be demonstrated by measurements of: a multilayer system Cr/Ti on silicon, interface contaminations on silicon during deposition of aluminum, Al_2O_3-nanoparticle containing conversion coatings on zinc for corrosion resistance, Ti_3SiC_2 MAX-phase coatings by pulsed laser deposition and hydrogen detection in a V/Fe multilayer system. The selected examples illustrate that GDOES can be successfully adopted as analytical tool in the development of new materials and coatings. A discussion of the results as well as of the limitations of GDOES are presented.

TSP-14 Characterization and Properties of Multilayered BN/SiO_2 Thin Films for Tailoring Thermal and Mechanical Contact Interfaces, ***J. Hu*** *(jianjun.hu@wpafb.af.mil), J.E. Bultman,* Air Force Research Laboratory/UDRI, *J.J. Gengler,* Air Force Research Laboratory/Spectral Energies, *C. Muratore, A.A. Voevodin*, Air Force Research Laboratory

In order to develop thermal and mechanical contact interfaces, multilayered BN/SiO_2 thin films were deposited on Inconel and silicon substrates using a magnetron sputtering (MS) assisted pulsed laser deposition (PLD) system. The SiO_2 layers were grown by magnetron sputtering of a silicon target with reactive oxygen gas added in the chamber, and the BN layers were homogeneously grown by pulsed laser ablation of a BN target. The SiO_2 and BN layers were deposited alternatively on the substrates, and each layer was grown at a thickness of approximately 100 nm that was monitored with a calibrated quartz oscillator. There are some fundamental scientific motivations promoting this study on the BN/SiO_2 multilayer films, e.g., the

BN materials possess high thermal conductivity, low friction coefficient, high thermal shock resistance, chemical inertness and good thermal stability at high temperatures. In particular, the alternative SiO_2 layers between BN layers were introduced to increase the through-thickness thermal resistance by phonon scattering at BN/SiO_2 interfaces, as well as thermal protection by highly dissipating heat along BN surfaces so as to reduce local hot spots with less thermal stress. The microstructure and chemistry of the films were studied using X-ray diffraction, micro Raman spectroscopy, a focused ion beam, and transmission electron microscope associated with EDS and EELS spectrometers (which provided the information on both surface and in-depth film properties). A high-temperature tribometer was used to measure the friction coefficient of the films. The thermal conductivity was characterized with a time-domain thermoreflectance (TDTR) technique . Further thermal and mechanical measurements are sought to evaluate the films. Here the multilayer architecture of thin films can provide an effective approach to tailor the thermal and mechanical contact interfaces with a highly anisotropic thermal conductivity .

TSP-15 Atom Probe Reconstruction Limitations in the Quantification of Interfacial Intermixing in Multilayered Thin Films, *J.G. Brons,* University of Alabama*, A.A. Herzing, I.M. Anderson,* NIST*, **G.B. Thompson** (gthompson@eng.ua.edu)*, University of Alabama

Intermixing between thin film layers can alter mechanical and thermal transport properties, phase stability and growth textures. Quantification of the degree of intermixing is crucial to elucidate the mechanisms of intermixing and their scaling effect on properties as listed previously. Atom probe tomography has received considerable attention for this characterization because of its ability to identify and provide reconstructions of atoms with near atomic spatial 3D resolution. In general, these atom probe reconstruction algorithms assume a constant evaporation field across the surface of the specimen. In reality, chemical inhomogeneity (i.e. discrete interfaces) modulates the evaporation field at the specimen surface. This introduces reconstruction artifacts and degrades the spatial resolution of the atom probe tomography technique. Multilayer thin films provide ideal specimen geometries to measure and quantify these artifacts. Thin films can be deposited with near atomic layer precision and can exhibit large planar surfaces with various degrees of intermixing across the interfaces. A series of Fe/Ni and Ti/Nb multilayers with bilayer repeat distances of 4 nm and 10 nm have been sputter-deposited onto n-doped Si [001] substrates. The multilayers were annular focus ion beam milled into the required needle-shaped geometry for the atom probe analysis with the film interfaces oriented with the bilayer chemical modulations parallel and perpendicular to the specimen apex. This was done to compare field evaporation behavior at these limiting geometries. The atom probe compositional profiles were then compared to Electron Energy Loss Spectroscopy (EELS) compositional profiles to determine the fidelity of the reconstructions through cross-comparison microscopy. The best agreement between the profiles was seen for Fe/Ni (similar field strengths) in a perpendicular-to-the-apex orientation.

TSP-16 Wear Properties of Thick TiSiCN Coatings, *J.-F. Su, Y. Chen, X. Nie (xnie@uwindsor.ca),* University of Windsor, Canada*, R. Wei,* Southwest Research Institute*, **S. Cui***, University of Windsor, Canada

Hard coatings with large coating thicknesses have been increasingly considered as protective surface layers for improved wear resistance of key mechanical components. With plasma-enhanced magnetron sputtering (PEMS) technology, a series of thick carbonitride TiSiCN coatings were deposited on H13 steels. Using enhancement of ion bombardment prior to and during deposition to increase the coating adhesion and limit columnar growth, single-layered TiSiCN coatings with the coating thickness of 30-490 microns have been successfully prepared. Morphology and microstructure were analyzed using optical and scanning electron microscopes and X-ray diffraction. While nanoindentation was performed to determine the hardness and Young's modulus with mapping, pin-on-disk and impact-sliding tests were conducted to evaluate the wear resistance of the coatings. The relationship between thickness and wear properties were particularly discussed.

TSP-17 Pressure Cell for Thermal Conductivity Measurement of Thin Films under Applied Stress with the Time Domain Thermoreflectance Technique, ***J.E. Bultman**, A.J. Safriet,* Air Force Research Laboratory/UDRI*, J.J. Gengler (jjgengler@gmail.com),* Air Force Research Laboratory/Spectral Energies*, A.R. Waite,* Air Force Research Laboratory/UTC*, C. Muratore, J.G. Jones,* Air Force Research Laboratory*, B.M. Howe, I. Petrov*, University of Illinois at Urbana-Champaign

Recently the time domain thermoreflectance (TDTR) technique has received much attention as a reliable method for measuring thermal conductivity of thin films. The technique relies on the change in surface reflectance measured with a laser probe beam under the temperature change induced with a laser pump beam. The technique is very versatile and was shown to be operated at different temperature regimes. Thermal conductivity of thin films can be also influenced by surface stress conditions, which for some of the film interfaces can be on the order of 1 GPa due to either mechanical or thermal expansion induced loads. It is then necessary to have a method of thin film thermal conductivity measurements under stressed conditions. This abstract discusses the design of a pressure cell, where thin films are subjected to a regulated pressure (up to 175 MPa), while allowing for the entrance and precise alignment of both pump and probe laser beams needed for the TDTR technique. The design incorporates a custom made piezo-element which can allow for either in-situ stress measurements or be used as an additional actuator of steady and oscillating stress fields. Femtosecond laser pump pulses are then applied to the stressed thin film surfaces and probe beam reflectivity data is fit with models for thermal diffusivity to extract the data on thin film thermal conductivity and interface thermal resistance. The cell was used for Al, SiO_2, MoS_2, composite, and polymer films to derive thermal conductivity at different thin film stress conditions.

TSP-20 Thermal Properties of Metal/Carbon Interfaces, ***C. Muratore** (Chris.Muratore@wpafb.af.mil),* Air Force Research Laboratory*, S. Shenogin,* UES/Air Force Research Laboratory*, J.J. Gengler,* Air Force Research Laboratory/Spectral Energies*, J. Hu,* Air Force Research Laboratory/UDRI*, A. Roy, A.A. Voevodin*, Air Force Research Laboratory

Most applications of carbon nanotubes require contact with more ordinary materials, such as metals or polymers. Unfortunately, the extraordinary thermo-electro-mechanical properties of nanotubes are often negated at the interface between the nanotubes and whatever they touch, resulting in a major shortfall between the measured and predicted performance of nanotube-based materials. One of the most troubling discrepancies in projected versus measured properties is found in thermal conductivity measurements of nanotube-containing composite materials. For example, a continuous network of thermally conductive nanotubes (or about 1 percent, by volume) within an organic matrix (k = 0.3 W m^{-1} K^{-1}) should yield a 30-fold increase in thermal conductivity over the pure matrix phase alone, based on simple effective medium theory. Despite this potential increase, experimental results typically show an increase of only a factor of 2 at best in composites with nanotube additives. To better understand the nature of interfacial resistance in carbon nanotubes, modeling and experimental studies investigating engineered interfaces on highly oriented pyrolytic graphite (HOPG) samples were conducted. This substrate was selected as a practical 2-dimensioinal analog for nanotube sidewalls to facilitate modeling and experimentation. Molecular dynamics simulations of heat transfer through metal carbon interfaces were conducted, and measurements of thermal conductance at these interfaces were made by analysis of the time-domain thermoreflectance data from the samples. Metal films were selected to identify effects of atomic mass, chemical interactions with graphite and mechanical properties. For example, metals known to exhibit in situ formation of an interfacial carbide layer when in contact with a carbon source and heated, such as titanium and boron, were investigated, and the effect of this carbide layer formation on interfacial conductance was examined. Graded and sharp interfaces were also considered with computational and experimental efforts.

TSP-21 Pressure Dependence on Thermal Conductivity and Interface Conductance of Interface Materials for Thermal Switching, ***A.R. Waite** (adam.waite@wpafb.af.mil),* Air Force Research Laboratory/UTC*, J.J. Gengler,* Air Force Research Laboratory/Spectral Energies*, J.G. Jones, C. Muratore, A.A. Voevodin*, Air Force Research Laboratory

A cross-linked fluoropolymer/Ag nanocomposite for use as a thermal interface material in thermal switching applications was developed in a dual chamber Plasma Enhanced Chemical Vapor Deposition (PECVD) and magnetron sputtering system. The cross-linked fluoropolymer matrix material is an polymer thin film with low hardness (0.2 GPa), high Young's modulus (5.3 GPa), and ultra low thermal conductivity (~0.08 W/m*K). Processing conditions to control the size and volume fraction of metallic nanoparticles, determined by electron microscopy, within the polymer matrix were identified. Thermal conductivity of composites containing different volume fractions of metallic nanoparticle inclusions were measured with the time domain thermal reflectance (TDTR) technique to identify the percolation threshold (approximately 25 volume percent) by an increase in thermal conductivity beyond that expected from effective medium theory. Composite materials of different compositions above and below the percolation threshold were investigated in a pressure cell that allowed application of over 10 MPa during TDTR experiments, and also allowed microscopic observation of the interface. The effects of pressure on thermal conductivity were examined to evaluate performance of the composite as a pressure-actuated thermal switch, and compared to other standard and novel thermal interface materials. Mechanical properties of composites before and after application of pressure were also investigated to determine potential for repeated use as a switch.

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

Thermal and Environmental Barrier Coatings
Moderator: R. Wellman, Cranfield University, B.T. Hazel, Pratt & Whitney, R. Trice, Purdue University

8:00am **A2-2-1 Synchrotron Studies of Environmental Barrier Coatings**, ***K.T. Faber*** *(k-faber@northwestern.edu)*, Northwestern University **INVITED**

Silicon-based ceramics are promising candidates for structural components in gas turbine engines. However, the passivating oxide (SiO_2) that forms on their surface reacts with water vapor present in the combustion atmosphere, causing coating recession and necessitating the use of environmental barrier coatings (EBCs). EBC lifetime depends upon the phase stability of the coating, its chemical compatibility with and coefficient of thermal expansion relative to the Si-based substrate, and its mechanical and chemical robustness in the combustion environment. We report the use of synchrotron-derived high-energy X-rays to examine residual stresses, phase transformations, and reactivity with calcium-magnesium-aluminosilicate glass deposits in two EBC systems. In situ and ex situ X-ray studies of barium-strontium-aluminosilicate (BSAS) and ytterbium silicate coatings, both on SiC/SiC substrates, will be described.

8:40am **A2-2-3 Low Thermal Conductivity Multi-Phase Thermal Barrier Coatings**, ***V. Tolpygo*** *(Vladimir.Tolpygo@Honeywell.com), W. Baker,* Honeywell, *R. Leckie, C.G. Levi,* University of California, Santa Barbara, *A. Limarga, D. Clarke,* Harvard University, *K. Murphy*, Alcoa Howmet

Thermal barrier coatings used in modern gas turbines typically consist of a single-phase compound, such as tetragonal or cubic yttria-stabilized zirconia or various rare earth zirconates. In addition, the state-of-the-art coatings applied by EB-PVD have specific columnar structure in which each column is essentially a single crystal grown normally to the substrate surface. In this work, a different type of TBC architecture is explored. Using a proprietary multi-source PVD method, a set of multi-phase coatings based on the ternary yttria-zirconia-tantala system has been deposited. The new coatings also develop columnar morphology, which provides thermal strain compliance, but unlike the conventional TBC, the multi-phase columns have distinct nano-crystalline structure. This paper presents microstructural characterization and thermal conductivity measurements of such multi-phase nano-crystalline coatings. For comparison, several bulk ceramic specimens with similar chemistries, prepared from liquid precursors, have been evaluated. The issues of microstructural stability during high temperature aging, as well as the role of phase and grain boundaries are discussed. It is argued that the concept of multi-phase TBC provides a wide choice of compounds and various combinations of oxide phases that may be used for new and advanced thermal barrier coatings.

9:00am **A2-2-4 Deposition of Thick and 50 % Porous YpSZ Layer by Spraying Nitrate Solution in a Low Pressure Plasma Reactor**, *C. Fourmond,* ***F. Rousseau*** *(frederic-rousseau@chimie-paristech.fr), D. Morvan, F. Prima,* Chimie ParisTech, France, *M.H. Vidal-Setif, O. Lavigne*, ONERA, France

The deposition of Yttria partially Stabilized Zirconia (YpSZ) for Thermal Barrier Coating application (TBC) is a current topic of interest. The TBC must exhibit high thickness (100-300 µm), vertical cracks in order to be a strain tolerant layer, and high porosity to decrease the thermal conductivity. Deposition technique such as Electron Beam Physical Vapor Deposition (EBPVD) or Atmospheric Plasma Spray (APS) are usual techniques to obtain 10-20 % porous YpSZ layers. New plasma processes using a suspension of YpSZ as raw material are used to deposit layers containing nano-pores. In this paper, a solution of nitrate salt is introduced into a low pressure plasma discharge (600 Pa, 120 W) to obtain YpSZ layers. Recent works have shown that the plasma process permits to synthesize YpSZ layer exhibiting a very low thermal diffusivity (0.85×10^{-7} $m^2 . s^{-1}$ / 1100°C) compared to coatings obtained by APS (3×10^{-7} $m^2 . s^{-1}$ / 1100°C). Observations of the layers by SEM showed that YpSZ was highly porous : a high number of pores with a micro and a nano-metric size was revealed.

Several analyses were used to study the characteristics and the stability of the YpSZ layers obtained in the low pressure plasma reactor. Optical emission spectroscopy proved that the oxidant chemistry in the plasma is responsible for the formation of the oxide and the elimination of the nitrates at low temperature (T< 300°C onto the layer). SEM, water porosimetry and XRD analyses were performed on the deposit to study the effect of the parameters (composition, power, post-treatment, concentration of the solution, heat treatment) on the structure, the morphology and the stability of YpSZ coatings. For example, it was observed that YpSZ is 50 % porous and that the nanostructures of the coating resist at high temperature conditions (1100°C / 50 h).

9:20am **A2-2-5 Foreign Object Damage Phenomena of Various Thermal and Environmental Barrier Coatings**, ***S.R. Choi*** *(sung.choi1@navy.mil)*, Naval Air Systems Commands **INVITED**

Brittle ceramic coatings such as thermal barrier coatings (TBCs) and environmental barrier coatings (EBCs) are highly susceptible to damage by impacting particles when the impacting kinetic energy exceeds certain limits. This damage, termed foreign object damage (FOD), results in various problems to coatings as well as to substrates from delamination to cracking to catastrophic failure depending on the severity of impact. FOD tests have been conducted using a ballistic impact gun for various materials including TBCs (both EB-PVD and APS) and EBCs with metallic or ceramic substrates. A range of impact velocities from 50 to 340 m/s was applied in conjunction with 1.6 mm-diameter steel or ceramic ball projectiles. FOD was characterized in terms of impact variables such as impact velocity, projectile material and its shape, impact angle, and target materials. The severity of subsurface damage was also assessed between metallic and ceramic substrates. Phenomenological model to describe the impact behavior of various coatings will be also discussed.

10:00am **A2-2-7 Effect of Composition on the Growth and Microstructure of Hafnia-Zirconia Based Thermal Barrier Coatings**, ***M. Noor-A-Alam***, *A. Choudhuri, C. Ramana (rvchintalapalle@utep.edu)*, University of Texas at El Paso

Nanostructured hafnia(HfO_2)-zirconia(ZrO_2) based thermal barrier coatings (TBCs) were grown and studied their growth and microstructure. Composition variations of hafnia-zirconia TBCs were produced by varying the ratio of HfO_2 and ZrO_2 while maintaining the stabilizer yttria(Y_2O_3) constant at 7.5%. Coatings were fabricated using magnetron sputtering onto different substrate materials. The ratio of hafnia to zirconia was varied from 1:4 to 4:1. The crystal structure analysis performed by X-ray diffraction (XRD) indicates the stabilization of cubic phase in all the coatings. Morphology and interface characterization using scanning electron microscope (SEM) indicates the columnar growth of the coatings with a dense porous structure. Thermal stability evaluation performed using high temperature XRD indicates the enhanced stability of these coatings to elevated temperatures. No changes were found in crystal structure and morphology after the final thermal treatment at 1300°C. The result will be presented and discussed.

10:20am **A2-2-8 Characterization of Microstructure, Thermal and Electric Properties of $RE_2Zr_2O_7$ of the TBC Thermal Barrier Coatings Obtained by the APS Method**, ***A. Rozmyslowska-Grund***, *G. Moskal (grzegorz.moskal@polsl.pl)*, Silesian University of Technology, Poland

A range of presented investigations will concern characteristics of the TBC layers type $RE_2Zr_2O_7$ (RE = Gd, La, Sm, Nd). The layers were placed on a nickel superalloys type AMS5599 with an bond-coat type NiCrAlY, obtained by the VPS (vacuum plasma spraying) method. Thickness of the bond-coat is approx. 125µm in all cases. A ceramic layer was obtained in a result of plasma spraying by the APS method with powders of a general formula $RE_2Zr_2O_7$, obtained by a spray drying method. Thickness of obtained layers was comprised within a range 250-300µm. Rectangular samples were obtained of dimensions 40x20x2 mm.

A range of investigations, presented in the paper will comprise:

· evaluation of microstructure of a ceramic layer from a point of view of thickness, quality of a layer and quantity characteristics of cracks and pores architecture;

· evaluation of thermal diffusivity of a ceramic layer within a range of temperature 25-1100°C;

· determination of thermal conductivity of the TBC layers type $RE_2Zr_2O_7$;

· evaluation of electric properties by an impedance spectroscopy method – dependence of impedance and electric permittivity as a function of frequency of electric field within a range 10^1-10^6Hz and temperature within a range 20-1000°C;

· obtained results in investigations on electric properties of these materials will be correlated with investigations on thermal diffusivity and investigations of electron scanning microscopy and optical spectroscopy within a range of waves from 0.2-1.1 µm;

· basing on obtained impedance spectra for these materials and knowledge of dimensions and shapes of ceramic grains, which form these materials, a complex character of their electric conductivity was defined;

· analysis of obtained results of effective conductivity of these materials, basing on the Maxwell- Wagner multi-phase model.

Results, presented in the paper, are effects of long-running investigations, carried out by the Department of Materials Science in the Silesian University of Technology, and these investigations concerned heat-resisting coatings and layers type TBC.

Financial support of Structural Funds in the Operational Programme – Innovative Economy (IE OP) financed from the European Regional Development Fund -Project No POIG.01.01.02-00-015/09 is gratefully acknowledged.

10:40am **A2-2-9 Strain Localisation in Thermal Barrier Coatings Mechanical Compressive Test**, ***V. Maurel*** *(vincent.maurel@mat.ensmp.fr)*, Centre des Materiaux - Mines ParisTech, France, *P. de Bodman,* SNECMA Safran Group, France, *L. Rémy*, Centre des Materiaux - Mines ParisTech, France

Thermal Barrier Coatings (TBC) systems have been introduced in turbine blade technology to reduce surface temperature and oxidation damage. Recent studies have brought information about degradation kinetics and mechanisms under cyclic oxidation, but little data is available for coupled thermal and mechanical loads, closer to in-service conditions. During high temperature stage, oxide growth, diffusion and creep are involved in lowering the ceramic top-coat (TC) adherence to the aluminide bond-coat (BC) [1]. Furthermore, TC spallation is driven by thermal mismatch when TC undergoes maximum compressive strain in the low temperature range [2]. Compressive mechanical testing was successfully used to ascertain a critical strain at failure and thus the remaining life of an aged TBC system. This critical strain at failure is used in a new industrial lifetime model applied on real blade geometry [3-4].

To analyse experimental set-up, surface strain field measurement is achieved using Digital Image Correlation (DIC) technique. This study shows that very high level of strain localisation is obtained due to crystal plasticity along {111} plane of the FCC single crystal used for the substrate. A Finite Element Analysis (FEA) is performed taking into account crystal plasticity to simulate the substrate single crystal behaviour. Thus, we clarify the physics of the onset of spallation events: both strain fields, experimental and numerical, allow to infer that substrate strain localisation triggers TC breakaway at low temperatures. Moreover, this study allows to estimate the dispersion level in TBC lifetime due to industrial tolerance range for single crystal orientation.

This study was supported by turbine manufacturer SNECMA (SAFRAN).

[1] L. Rémy, A. Alam, and A. Bickard. Thermo-mechanical creep-fatigue of coated systems. ASTM, STP 1428:98–111, 2003.

[2] M. Harvey, C. Courcier, V. Maurel, and L. Rémy. Oxide and TBC spallation in beta-nial coated systems under mechanical loading. Surface and Coatings Technology, 203(5-7):432–436, 12/25 2008.

[3] C. Courcier, V. Maurel, L. Rémy, and A. Phelippeau. Damage based life prediction model for ebpvd thermal barrier coatings under thermal fatigue. LCF6 - Sixth International Conference on Low Cycle Fatigue, Berlin, Germany September 8 - 12, 2008.

[4] C. Courcier, V. Maurel, L. Rémy, and S. Quilici, Interfacial damage based life model for EB-PVD thermal barrier coating, Surface and Coatings Technology, in submission.

11:00am **A2-2-11 Analysis of Thermoelastic Characteristics for Vertical-Cracked Thermal Barrier Coatings Through Mathematical Approaches**, ***J. Go***, *Y.-G. Jung (jungyg@changwon.ac.kr), S. Kim,* Changwon National University, Korea, *U. Paik*, Hanyang University, Korea

Various defects, such as pores, cracks, and splat boundaries, are unavoidably formed in thermal barrier coatings (TBCs) during a plasma spray coating, which exert critical impact on the thermomechanical properties of TBCs, such as elastic modulus, thermal conductivity, and coefficient of thermal expansion [1]. TBC samples were prepared by TriplexPro^{TM}-200 system using different commercialized powders and the microstructure of TBC was controlled by the reheating the surface of TBC. The relatively porous TBC was prepared with METECO 204 C-NS and the relatively dense TBC with METECO 204 NS. The microstructure of the top coat in TBCs was just controlled, and the bond coat with about 300 mm thickness in the both top coats was prepared with AMDRY 962. The top coats were coated onto the bond coat, and then the surface of each TBC was reheated by plasma without powder feeding in same equipment. The rapid cooling process of the reheated top coat created vertical type cracks on the top coat. The microstructural characterizations of the relatively porous and dense TBCs with the vertical cracks were analyzed through mathematical approaches and compared to each other. A couple of governing partial differential equations was derived based on the thermoelastic theory [2], and a finite volume model was developed to evaluate the thermoelastic characteristics like temperature distribution profiles, displacement, and stresses, induced by a thermal fatigue for the governing equations. The radial stress of the vertical-cracked TBCs displayed the reverse undulation in the dense model and larger extension was developed in the porous model compared with the dense model.

Hard Coatings and Vapor Deposition Technology
Room: Golden West - Session B7

Thermodynamics and Kinetic Considerations for Coating Growth

Moderator: V. Gorokhovsky, Southwest Research Institute, San Antonio Texas, P. Patsalas, University of Ioannina

8:00am **B7-1 Suppression of Intermixing in Strain-Relaxed Epitaxial Layers**, *T.L. Leontiou,* Cyprus University of Technology, Cyprus, *J.D. Tersoff,* IBM, ***P.C. Kelires*** *(pantelis.kelires@cut.ac.cy)*, Cyprus University of Technology, Cyprus **INVITED**

Misfit strain plays a crucial role in heteroepitaxy, driving alloy intermixing or the introduction of dislocations. Initially, the focus was on avoiding the relaxation of misfit strain by dislocations. More recently, strain-relaxed layers have shown great promise as templates with variable lattice spacing, enabling structures with dramatically strain-enhanced electron mobilities for high-performance transistors.

On the other hand, intermixing of two different-sized components blurs the heterointerface and thus is highly detrimental for heterostructures. Intriguingly, these two modes of strain relaxation may couple. This has been widely discussed in the context of "strain-enhanced diffusion".

In this talk, we present our latest work which shows that these two modes can couple in an entirely different way, with important implications for the thermal stability of strain-relaxed template layers. Specifically, strain relaxation by dislocations can suppress intermixing between the heterolayer and the substrate. Intermixing is suppressed because, once the strain is fully relaxed by dislocations, intermixing would actually increase the strain.

We demonstrate this effect by carrying out Monte Carlo (MC) atomistic simulations for the thermodynamic equilibrium of heterolayer films. Continuum modeling for the thermodynamics and the kinetics of these systems reproduces the MC results. In this way, we can predict the extent and rate of intermixing in thin films as a function of temperature, degree of relaxation and other parameters. Our MC equilibrium results for Ge on effectively thin substrates like silicon-on-insulator (SOI) show a significant suppression of alloying in the film. The effect is even stronger for InAs on GaAs, due to the larger misfit. Continuum modeling allows us to extend these results to very thick (effectively semi-infinite) substrates, where we find a dramatic slowing-down of intermixing over long times.

The effect, which is of interest not only for planar films, but also for any structure relaxed by dislocations, including islands and other nanostructures, opens new possibilities for the control of stress and property optimization in semiconductor devices.

8:40am **B7-3 Theoretical Investigation of Atomistic Surface Processes in Multinary Nitrides Materials**, ***B. Alling*** *(bjoal@ifm.liu.se), L. Hultman*, Linköping University, Sweden

Theoretical studies based on first-principles calculations have provided increased understanding of mixing and decomposition thermodynamics in $Ti_{1-x}Al_xN$ and related refractory metastable solid solutions. In this work we move on from studies of the bulk towards investigation of surfaces and growth processes. We present results from calculations of the effects of Al-addition on the atomistic processes on TiN and $Ti_{1-x}Al_xN$ surfaces. These have impact on texture evolution and short range clustering tendencies during thin film growth.

9:00am **B7-5 Fundamental Aspects of Mixed Oxide Thin Film Growth**, ***M. Saraiva*** *(marta.saraiva@ugent.be)*, Ghent University, Belgium, *V. Georgieva, N. Jehanathan,* University of Antwerp, Belgium, *S. Mahieu, W.P. Leroy,* Ghent University, Belgium, *R. Persoons,* Flemish Institute for Technological Research (VITO), Belgium, *G. Van Tendeloo, A. Bogaerts,* University of Antwerp, Belgium, *D. Depla*, Ghent University, Belgium

The thin film growth mechanism of materials with a NaCl (B1) structure such as TiN and MgO is well understood. Therefore, MgO was chosen as a model material to investigate the compositional effect when Mg is replaced by other elements (M= Al, Cr, Y, Ti and Zr) to form a mixed oxide Mg(M)O thin film.

Kinetic arguments related to the mobility of the adparticles [1] explain the growth mechanism of the pure MgO thin films. The kinetic conditions also explain other observations on increasing the M content, namely the change in the preferential orientation of the MgO crystallites and the formation of a solid solution between MgO and the oxide of the metal M. However, when the M content in the thin films increases, XRD pole figures reveal a clear transition from a highly crystalline to a fully amorphous structure. These transitions were noticed for all systems studied, and its origin can not be explained from the same kinetic arguments.

The analogy between this transition and the crystalline to liquid transition noticed in the packing of hard spheres suggests a thermodynamic basis. The good correspondence between MD simulations and the experimental observations allows to check this idea. The transition can be understood from a lowering of the packing density of the filled octahedral positions in the MgO structure, similar to the hard sphere system. As the transition is a first order transition, the model predicts a mixture of crystalline and amorphous material at the phase boundary. This prediction is confirmed by TEM analysis which shows the presence of nanocrystals in an amorphous matrix.

This fundamental research can assist in tailoring the physical properties of materials as the latter depend strongly on the crystallographic properties of the thin films as indicated by hardness, surface energy and optical measurements.

[1] S. Mahieu, P. Ghekiere, D. Depla, and R. De Gryse, Thin Solid Films 515, 1229-1249 (2006).

9:20am **B7-6 Modelling Reactive Sputter Deposition of Titanium Nitride in a Triode Magnetron Sputtering System**, *J.C. Sagás (juliocesarsagas@gmail.com), D.A. Duarte,* Technological Institute of Aeronautics, Brazil, *L.C. Fontana,* Universidade do Estado de Santa Catarina - Brazil, ***T.R. Rosa**, D.R. Irala*, Technological Institute of Aeronautics, Brazil

In deposition of compounds by reactive sputtering is difficult to associate high deposition rates with a precise control of the film stoichiometry due to the formation of compound over the target surface, which leads to target poisoning and, as consequence, problems of stability. A typical feature of reactive sputtering is the hysteresis phenomenon observed from the partial pressure of the reactive gas (p) as function of the reactive gas flow rate (Q_{total}). In order to describe this process, a reliable model was developed, called Berg's model, which allows the understanding of relations between the experimental parameters and the hysteresis loop. From Berg's model is possible to predict a decrease in the hysteresis loop using small target areas, small collecting areas (small target-to-substrate distances) or non-realistic pumping speeds. On the other hand, an alternative configuration, based in conventional magnetron devices, presents itself as a way to suppress the hysteresis loop in, for example, TiN deposition. This system, called triode magnetron sputtering (TMS), consists of a grid inserted between the target and the substrate. This grid works as the discharge anode and the variation of the grid-to-target distance modifies the plasma impedance. This arrangement allows that all enclosed parameters can operate in a wider range than those used in conventional magnetron devices. In this work, an adaptation from Berg's model was done to the TMS in order to describe the reactive sputter deposition of TiN at different effective grid areas. In the adapted model, in addition to the balance equations for the target and collecting area (substrate and chamber walls), another equation was written to the grid. As the grid is inserted between the target and collecting area, only the sputtered material, which is not collected by the grid, can be deposited over the collecting area. The results shown that increasing the effective grid area decreases the hysteresis loop until completely suppress it, which means that the role of the collecting area decreases.

9:40am **B7-7 Thermodynamics of Small Systems Applied to Fluid Mixtures of Condensing Films at Critical Consulate Points**, ***M.A. Miller** (mmiller@swri.org)*, Southwest Research Institute **INVITED**

There is a pressing need for a far better scientific understanding of the thermodynamics and transport properties of fluid mixtures in small systems. Small systems exist at the interfaces between solids and fluids, fluids and fluids, pores, and at critical points. In engineering, one such small system might be the multiphase formation of mixtures of polymers or monomers condensing on the surface of a substrate which lead to unpredictable morphologies. The transport properties of these complex mixtures over very long periods of time cannot be predicted using elementary approaches, for which no adequate theoretical treatment has been developed

The gas-liquid critical point, or consolute point in a fluid mixture, provides a convenient physical model whereby the size of the system (in terms of the correlation length) may be adjusted to be of macroscopic proportions and the physics may be probed using the scattering of optical photons. It is in the interplay between "smallness" and non-linearity that even very weak symmetry-breaking fields, such as gravity or the surface potential, may have enormous influence on the structure and transport properties of a condensing film.

This work explores the theoretical framework with which structure and morphology may be predicted in condensing polymeric films by considering the effects of diverging correlation lengths ξ at or near critical consulate points. Experimental methods based on elastic and inelastic light scattering technique are further presented as a means of validating the theory of small systems.

10:20am **B7-9 Understanding the Catalytic Effect of H_2S on CVD-Growth of α-Al_2O_3:Thermodynamic Gas Phase Simulations and ab Initio Theory**, *A. Blomqvist,* Uppsala University, Sweden, ***C. Århammar** (cecilia.arhammar@sandvik.com),* Sandvik Tooling Stockholm SE, Sweden, *S. Norgren,* Sandvik Mining & Construction AB, Sweden, *F. Silvearv,* Uppsala University, Sweden, *M. Rodmar,* Sandvik Tooling Stockholm SE, Sweden, *R. Ahuja*, Uppsala University, Sweden

For many years, Al_2O_3 has been one of the most important materials in CVD-coatings, used in tools for metal machining applications. The first Al_2O_3 coated tungsten carbide cutting insert from Sandvik Coromant was introduced already in 1975 [1]. The room-temperature stable α-phase is the most commonly used Al_2O_3 polymorph. More than one decade ago it was found that the addition of a small amount of H_2S to the gas vastly enhanced the growth rate of α-Al_2O_3 and eliminated the *dog-bone effect* such that a uniform deposition of the edges and flat surfaces of the insert could be achieved [1].

There have been studies of the effect of H_2S on the macroscopic growth and gas phase reactions [1-4], but although there are indications that the H_2S interaction with the Al_2O_3 surface is strong [5, 6], there are no published results where the influence of H_2S on growth of α-Al_2O_3 has been proved on an atomic scale.

In this Paper we investigate the effect of H_2S on CVD-growth of α-Al_2O_3 on an atomistic level. We have applied a multiscale approach, where we use thermodynamic modeling (THERMOCALC and the Scientific Group Thermodata Europe (SGTE) database SSUB3) for gas phase reactions, and Density Functional Theory (DFT) [7] for surface reactions.

We use the ThermoCalc equilibrium calculations and data from non-equilibrium kinetic modeling [8], to obtain the relevant molecules used as input for our first principles calculations. The heat of formation of a number of possible relevant reactions of these molecules at three different surfaces and with different surface terminations of α-Al_2O_3 were calculated. The internal energy of the reaction was calculated using DFT, whereas the remaining part of the free energy was added from the SSUB3 database. Reaction barriers were calculated using the Nudge Elastic Band (NEB) approach. The effect of H2S compared to H_2O on the surface of Al_2O_3 was studied in detail. From our study we are able to present a possible scenario, supported by our theory, where H_2S acts as a catalyst in the CVD -growth of α-Al_2O_3.

[1] P. Mårtensson, Surface & Coatings Technology 200 (2006) 3626.

[2] K.H. Smith, J.N. Lindström, US Patent, #4 619 866 (1986).

[3] T. Oshika, A. Nishiyama, K. Nakaso, M. Shimada, K. Okuyama, J. Phys., IV France 9 (1999) 877.

[4] T. Oshika, M. Sato, A. Nishiyama, J. Phys., IV France 12, 113 (2002).

[5] O. Saur, T. Chevrau, J. Lamotte, j. Travert, J-C. Lavalley, J. Chem. Soc 77 (1981) 427.

[6] C.R. Apesteguia, J.F. Plasa de los Reyes, T.F. Garetto, J. M. Parera, Applied Catalysis 4 (1982) 5.

[7] G. Kresse and J. Furthmüller, Phys. Rev. B 54 11169 (1996).

[8] P. Tan, J. Muller, D. Neushutz, J. of Electrochemical Soc. 152 288 (2005).

10:40am **B7-10 Study of Structural Properties of PVD Coatings on Inclined Substrates**, *K. Kumar,* ***S. Mukherjee** (mukherji@ipr.res.in)*, Institute for Plasma Research, India

In general, the substrates which require surface modification using overlay coatings are three dimensional in nature, and consequently, normal incidence of the depositing flux cannot be ensured over the entire substrate area. This off – normal incidence can affect the columnar structure development and orientation of the coatings. The column orientation subsequently becomes the function of the angle of incidence of the sputtered flux resulting in anisotropies in macroscopic properties of the functional coatings. The present study aims to understand the structure development of coatings deposited on planar substrates kept at various inclinations with respect to the depositing flux using characterising tools like scanning electron microscopy and X – ray diffraction. The following aspects were focused on,

i. to identify the columnar microstructure and relate the column orientation with the angle of incident flux

ii. to study the effect of various deposition parameters like deposition time and duration on the column orientation

iii. the structure evolution of elemental coatings at the atomistic level is also simulated based on non – lattice, ballistic growth models

iv. to simulate the effect of deposition geometry on the column orientation

Coatings of copper and titanium nitride were deposited by magnetron sputter deposition method on silicon wafers of size 1 cm x 1 cm. The former is important in micro electronics industry and the later has wide tribological applications. The substrates were mounted symmetrically below the target race – track on holders which could align them in different inclinations (0 to 90 degrees). The planar magnetron used had a target diameter of 75 mm. Elemental targets of copper and titanium were used with argon as the sputtering gas. Stoichiometric TiN was deposited in a mixture of argon and nitrogen gas introduced at suitable flow rates using flow controllers. The deposition of TiN was done for different durations and that of Cu was done for different magnetron bias conditions so as to control the sputter yield and hence the deposition rate.

Well defined columnar microstructure of the coatings was revealed in the cross sectional micrographs of both types of coatings studied. The XRD analysis also revealed strong dependence of the substrate inclination angle on the crystallite size and preferred orientation of the diffraction planes.

Details of the characterisation and simulation results regarding the effect of the various deposition parameters considered will be presented.

11:00am **B7-11 Structural Analysis of Alumina Thin Films Deposited by Dual Magnetron Sputtering**, ***W. Engelhart*** *(wolfgang.engelhart@walter-tools.com), V. Schier,* Walter AG, Tübingen, Germany*, W. Dreher,* NMI Naturwissenschaftliches und Medizinisches Institut, Germany*, O. Eibl*, Universität Tübingen, Germany

Alumina thin films deposited by PVD are of high interest due to their outstanding mechanical and thermal properties. The crystal structure of these films is usually referred to as γ-Al_2O_3, however the crystal structure of γ-Al_2O_3 is not well defined even not for bulk materials. Alumina thin films were deposited by reactive dual magnetron sputtering (dms) at 550 °C on cemented carbide substrates. The alumina grain size is smaller than 50 nm measured by dark field imaging in the transmission electron microscope (TEM). The crystal structure was analyzed by energy-filtered electron diffraction showing a characteristic background due to a disordered structure different from γ-Al_2O_3 and any other known alumina phase. Indicating this we call the structure of the thin films pseudo γ-Al_2O_3. Reflections belonging to γ-Al_2O_3 with d lattice spacings between 0.2 nm and 0.4 nm were not visible but an intensity distribution corresponding to an amorphous structure was detected. Texture as origin for the missing reflections could be ruled out. Diffraction analysis was performed at room temperature and -145 °C and showed the static character of the disorder. Radial intensity distribution functions were determined from diffraction patterns and were compared to x-ray diffraction data published for γ-Al_2O_3. Differences between the two crystal structures were highlighted and discussed with respect to lattice spacings and intensities of the various reflections. For analyzing the crystal structure of these materials, energy filtering is absolutely necessary to identify reflections with small intensity on top of a large background. The films contained Ar with a mole fraction of about 5.6 at% as shown by energy dispersive x-ray (EDX) spectroscopy in the TEM. The plasmon energy of the disordered phase was found to be 26.1 eV as determined by electron energy-loss spectroscopy (EELS). This value corresponds to that of bulk alpha alumina [15]. A model is presented showing Ar and Al atoms as being primari ly responsible for the disorder. Mechanical properties of the films were investigated by nanoindenting. A Young modulus of 315±8 GPa was found. For bulk sapphire the Young modulus is 381±2 GPa and for the CVD deposited α-Al_2O_3 the Young modulus is 315.8±2 GPa.

Tribology and Mechanical Behavior of Coatings and Thin Films
Room: California - Session E2-3

Mechanical Properties and Adhesion
Moderator: M.-T. Lin, National Chung Hsing University & Chaoyang University of Technology, J. Michler, Empa

8:00am **E2-3-1 Optimization of the Scratch Test for Specific Coating Designs***,* ***G. Favaro*** *(gregory.favaro@csm-instruments.com),* CSM Instruments SA, Switzerland*, N. Bierwisch,* Saxonian Institute of Surface Mechanics, Germany*, Q.-H. Duong, P. Kempe,* CSM Instruments SA, Switzerland*, J. Ramm1,* Oerlikon Balzers AG, Switzerland*, N. Schwarzer,* Saxonian Institute of Surface Mechanics, Germany*, B. Widrig*, OC Oerlikon Balzers AG, Germany

The proper design of wear resistant coatings applied to cutting tools comprises the optimization of the mechanical properties (Young's modulus, yield strength, adhesion, intrinsic stresses, fracture, fretting and wear resistance etc.) of the coating-tool system.

The goal is to find material and structural solutions which keep the resulting stress strain field under typical application conditions below the stability limits of the system.

Based on nanoindentation measurements obtained from the coating-tool system which should be optimized, a scratch test is dimensioned with respect to load range and indenter geometry. The measured data from this "Physical Scratch Test" are used to simulate spatial stress profiles and to calculate the von Mises stress characteristics and the maximum tensile stresses in the scratch direction. In a further step, the simulations are used to suggest scratch parameters ("Fine Tuned Scratch Test") which increase the sensitivity of the test for specific depth regions in the coating-tool architecture and allow improved and more sensitive investigations of critical interfaces, transition layers and surface-near substrate regions.

The tests were performed at PVD coated inserts (nitrides and oxides) and compared with the results obtained from cutting tests.

8:20am **E2-3-2 A Modified Scratch Test for the Mechanical Characterization of Scratch Resistance and Adhesion of Thin Hard Coatings on Soft Substrates**, ***T. Sander*** *(sander@mfk.uni-erlangen.de), S. Tremmel, S. Wartzack*, University Erlangen-Nuremberg, Germany

The scratch resistance of coatings and the adhesion between coating and substrate is usually determined in model experiments preceded with sharp diamond indenters. These common methods as described for example in EN 1071-3 often fail for the combination of hard coatings on soft substrates due to very small critical loads. Hence in the industry are used a lot of highly subjective and provisional test methods. On the one hand quantitative comparability is difficult with common methods since defects already occur at very small loads for ductile and relative soft substrate materials like plastics. On the other hand wear of the indenter in contact with hard coatings like pure diamond-coatings requires its cost-intensive replacement.

In this article a macroscopic tribological-mechanical test method is suggested which uses balls of hardened steel as indenters. A wide scope can be applied for both soft and hard coatings and different substrate materials. By variation of the ball-diameter, the normal contact force and the sliding speed different levels of stress and wear can be created to analyse the tribological and mechanical behaviour between body and counterpart as well as the interface of coating and substrate. The method is also suitable for timesaving pilot tests to find out the proper ball size and load for following ball-on-disk-tests on a tribometer. To determine scratch resistance close to reality as usual scratch conditions on consumer products are better represented by a small ball than a sharp diamond indenter. Another benefit of the presented test method is the cost saving acquisition of the balls for indentation in very high quality as they are standard parts in the ball bearing industry. For every test on very hard coatings a new ball can be used with the possibility to detect the wear both on the base object and the counterpart. The occurring failure modes of coating and substrate can be compared also with comparatively easy numerical models to verify the results. Additional to the test concept first results of different coatings will be presented in this paper and compared with the results of common scratch tests.

8:40am **E2-3-3 The Plastic Deformation of Metallic Thin Films on Substrate Seen Through In Situ TEM Experiments**, ***M. Legros*** *(legros@cemes.fr)*, CEMES-CNRS, France **INVITED**

Thin metallic films on substrates exhibit a large resistance to deformation, and in the micron range, this dependence scales linearly with the inverse of the thickness. Such a linear increase of the films strength has been rationalized in term of confined dislocation motion (Nix, [1]). In this fairly simple, and thus popular model, the yield stress of a metallic film on a rigid substrate is attained when threading dislocations start to shear the film, increasing simultaneously the length of interfacial dislocations in their wake. This model leads to correct stress values for pseudo epitaxial metallic films (such as Al or Cu on sapphire) but falls short when it comes to metallic films that possess an amorphous interface with the substrate (Al on oxidized Si for instance) [2]. Considering the image forces seen by the interfacial dislocations in both systems, the opposite effect should be observed.

In films thinner than about 200 nm, yield stress plateaus or even decreases, clearly calling for an alternate relaxation mechanism. Parallel glide of dislocations, a potential symptom of enhanced grain boundary diffusion, is one of the possible substitution process, but so far, it has never been observed elsewhere than in Cu films [3].

Here, we will show that in situ TEM can display the dislocation mechanisms while they operate in thin films and thus directly corroborate or contradict existing theories. Examples will be taken from Al and Cu films on rigid substrates. The stress is induced by the difference of CTE between the film and the substrate, as in wafer curvature experiments. We found that, for thicker films, amorphous interfaces play the role of dislocations sinks, similarly to free surfaces [4]. The increased strength of metallic films with amorphous interfaces is thus dictated by the nucleation of fresh dislocations. In thinner films, scarce dislocation activity is clearly replaced by other processes. Diffusion processes are harder to observe and quantify [5], but plasticity can also be carried out by grain boundary migration[6], similarly to what has been recently observed in nanocrystalline metals [7, 8], and despite the presence of the substrate.

[1] Nix WD. Metall. Trans. A 1989;20A:2217.

[2] Dehm G, Balk TJ, Edongue H, Arzt E. Microelectronic Engineering 2003;70:412.

[3] Balk TJ, Dehm G, Arzt E. Acta Mat 2003;51:4471.

[4] Legros M, Hemker KJ, Gouldstone A, Suresh S, Keller-Flaig RM, Arzt E. Acta Mat 2002;50:3435.

[5] Legros M, Dehm G, Balk TJ, Arzt E. Science 2008;319:1646.

[6] Mompiou F, Caillard D, Legros M. Acta Mat 2009;57:2198.

[7] Rupert TJ, Gianola DS, Gan Y, Hemker KJ. Science 2009;326:1686.

[8] Gianola DS et al. Acta Materialia 2006;54:2253.

9:20am **E2-3-5 Correlation between Adhesion Strength and Coating/Substrate Mechanical Properties using the Scratch Test Technique**, ***B. Zhou***, *N. Randall (nra@csm-instruments.com)*, CSM Instruments

Scratch testing, as a mature technique for coating adhesion quantification, has been widely adopted by both industrial and academic fields over recent years. Following the urgent needs of very small materials characterization, nano-scratch testing has gradually replaced the traditional pull-off test for the study of ultra-thin film properties. In this research, the relationship between the adhesion strength and film/substrate mechanical properties was investigated to provide fundamental but crucial knowledge of the scratch mechanism. Five thin films were deposited using sputtering onto different polished substrate materials which span from soft silicon dioxide to hard sapphire. The surface roughness of the bare substrates was measured using Scanning Force Microscopy. Scratch tests were performed using a Nano Scratch Tester with a sphero-conical diamond indenter. A progressive load mode was employed to cause coating failure during scratch on the film surface. The critical values of different failure mechanisms, such as cracking, spallation, and delamination were accurately determined according to the scratch panorama image, penetration and residual depth data. In addition, the Hardness (H) and Modulus (E) values of the thin films and substrates were measured with an Ultra Nanoindentation Tester. The scratch critical failure loads were then plotted versus film/substrate H and E ratios. The relationship developed between these parameters was described in terms of the true mechanism behind scratch adhesion of such hard coatings.

9:40am **E2-3-6 Numerical and Experimental Analyses of Scratch Tests Conducted on Coated Systems with Residual Stress Gradients**, *N.K. Fukumasu (newton.fukumasu@gmail.com)*, ***R.M. Souza***, University of Sao Paulo, Brazil, *A.A.C. Recco*, University of Santa Catarina, Brazil, *A.P. Tschiptschin*, University of Sao Paulo, Brazil

In this work, finite element (FEM) and experimental studies were conducted to understand adhesive and cohesive failures in coated systems with thin film residual stress gradients. The FEM analyses considered a rigid indenter applying normal and tangential loads on the coated systems. Three different cases of variation of film compressive stresses were considered. Stresses: (i) increased from the surface to the film/substrate interface; (ii) decreased from the surface to the film/substrate interface or (iii) were uniform along film thickness. In the numerical studies, the mechanical behavior of both coating and substrate was considered elastic-perfectly plastic. In the experimental portion of this work, a set of depositions of titanium nitride thin films was conducted varying the value of substrate bias during deposition, as an attempt to experimentally prepare specimens with the same trend of residual stress gradient as those analyzed numerically. These specimens were later submitted to scratch tests in order to analyze the critical loads obtained in each case. Numerical results provided a comparison of the distribution of stresses obtained in each simulation, indicating a trend of easier film debonding for the conditions where the stress values were more compressive at the interface and decreased towards the surface. This result is in qualitative agreement with the experimental study, in which lower critical loads were observed for the films where deposition started with high values of substrate bias and the bias was reduced as the deposition proceeded.

10:00am **E2-3-7 Mechanical and Wear Characterization of Electroless Nickel-Boron Coatings**, *V. Vitry (veronique.vitry@umons.ac.be)*, *A.-F. Kanta*, ***F. Delaunois***, Université de Mons, Belgium

Nanocrystalline electroless nickel-boron deposits were synthesized on steel substrates and submitted to heat treatment under non-reactive atmosphere to enhance their properties. Their mechanical and tribological properties were investigated by various methods including nanoindentation, Taber wear testing and scratch tests. Their structural properties were also studied.

The hardness of the deposits increased from 900 to 1250 hv_{100} due to optimal crystallization of the nanocrystalline coating while the Taber wear index was halved after heat treatement.

The scratch tests resistance of the coatings was good in both as-deposited and heat treated conditions.

The mechanisms inducing the modification of the mechanical and tribological properties were discussed and they were linked to the structural state of the material.

10:20am **E2-3-12 Micro-Scratch Testing for Interface Characterizations of Diamond-Coated Tools**, ***P. Lu***, University of Alabama, *X. Xiao*, *M.J. Lukitsch*, General Motors Research and Development Center, *K. Chou (kchou@eng.ua.edu)*, The University of Alabama

Interface adhesion is one of the foremost important properties of diamond-coated tools, critically linked to their machining performance. Despite of significant advances in diamond deposition technologies that can produce superior diamond properties, coating-substrate adhesion remains the major challenge to extend tool life and understanding the adhesion characteristics are of primary interests to coated-tool makers and users.

In this study, a micro-scratch tester was applied to evaluate the adhesion of diamond coated carbide tools, about 4 µm thickness, at the room temperature. A diamond indenter with a tip radius of 50 µm was employed. The scratch speed was 2 mm/min with the progressive loading method. The scratch length for each test was 5 mm. The maximum normal forces applied were 30 N. During the testing, tangential force, acoustic emission (AE) signals, and depth of the scratch were acquired. Scratch marks and delamination areas were examined by digital microscopy, white-light interferometery and scanning electron microscopy.

The results indicate that the onset of delamination can be clearly captured from the force and AE signals. Though scratch testing may provide information such as critical loads, the interface characteristics cannot be directly utilized when evaluating interface behaviors of a diamond-coated tool subject to tribological loading. Therefore, a finite element analysis (FEA) model was developed to simulate the scratch process with the interface modeled by a cohesive zone. The results indicate that it is feasible to use FEA combined with scratch tests to evaluate the interface properties, i.e., the cohesive zone strength and characteristic length.

10:40am **E2-3-8 Investigation of the Mechanical Properties of Hierarchically Structured Gold Nanoparticles**, ***A.J. Smith***, *Y.W. Hao*, *E.I. Meletis (meletis@uta.edu)*, University of Texas at Arlington

Due to the superior properties of nanoparticles over their bulk counterparts, the development of new, novel nanoparticles remains an area of intense investigation. Recent research in our laboratory has resulted in the synthesis of spherical hollow gold nanoparticles (HGNPs) showing three degrees of hierarchy (particle diameter ~100 nm, wall thickness ~20 nm and grain size ~5 nm). Such HGNPs can display very unique mechanical properties. Recent characterization of hierarchically structured CdS hollow nanoparticles has shown them to have a shear strength approaching the theoretical strength of the material. [1] Synthesis of HGNPs in our laboratory provides a golden opportunity to further investigate the mechanical response of such hierarchically structured nanomaterils and develop a broader understanding of their behavior. In the present study, we report results from nanoindentation experiments that were conducted on a series of HGNPs to explore their mechanical response.

[1] Shan, Z. W. et al. Ultra high stress and strain in hierarchically structured hollow nanoparticles. Nature Materials 7, 947-952 (2008).

11:00am **E2-3-10 Influence of the Nitriding and TiAlN/TiN Coating Thickness on the Mechanical Properties and Adhesion of Duplex Treated AISI H13 Steel**, ***R. Torres*** *(ricardo.torres@pucpr.br), P.C. Soares,* Pontifícia Universidade Católica do Parana, Brazil*, C.M. Lepienski,* Universidade Federal do Parana, Brazil*, R.M. Souza, M. Faria, A.P. Tschiptschin*, University of Sao Paulo, Brazil

AISI H13 die steel substrates were low pressure gas nitrided to different thickness and hardness value. Nitrided and non nitrided samples were subsequently coated with bi-layer TiAlN/TiN to two different thicknesses: 3 and 8 µm. The hardness was measured across the sample thickness and observed to be higher when a thinner coating was deposited over nitrided substrates. The hardness behavior across relatively thin coating was not affected by the nitrided surface hardness or thickness of the nitrided layer in the range of values examined here (80-150 µm). On the other hand, the hardness behavior of thicker coating was affected by the nitrided layer. Moreover, the adhesion of the coating system over nitrided and non nitrided substrates was tested through scratch tests. The adhesion of a thinner coating is better than the adhesion of a thicker coating at given nitrided substrate condition. The adhesion of a thicker coating is influenced by the nitrided case features. A harder and thicker nitrided case improves the adhesion of a thicker coating system. Spallation is the failure mode a thinner coating system while chipping was observed to be the failure mode of a thicker coating system.

11:20am **E2-3-11 Microstructure and Characterization of Ternary Sputtering Ni-Ru-P Coatings**, ***Y.-C. Hsiao****, F.-B. Wu (fbwu@nuu.edu.tw)*, National United University, Taiwan

In the study, the ternary Ni-Ru-P alloy coatings were fabricated by magnetron dual-gun co-sputtering technique. The chemical composition variation of the coatings in terms of sputtering input power was investigated. The Ni-Ru-P coatings exhibited a Ru content ranged from 3.3 to 64.6 at.% as the Ru deposition input power was controlled at 15 to 100W. The phase transformation of the Ni-Ru-P coatings with respect to annealing treatment was analyzed by X-ray diffraction technique. The Ni-Ru-P coatings exhibited an amorphous/nanocrystalline feature under a vacuum annealing temperature up to 450^{o}C. Ni(Ru) and Ni-P precipitation phases under annealing temperature above 500^{o}C were observed. The influence of Ru on the thermal stability of Ni-P-based alloy coating was discussed. The variation in roughness of the alloy coatings attributed by the Ru contents was also analyzed. The sputtered Ni-Ru-P coatings exhibited superior mechanical and anti-oxidation characteristics as compared to the Ni-P coating. The introduction of Ru significantly strengthened the Ni-P-based coating. The Ni-Ru-P coating systems were also compared with Ni-Ru binary coating in order to understand the effect of P in Ni-based coatings.

11:40am **E2-3-13 Adhesive Interlayers' Effect on the Entire Structure Strength of Glass Molding Tools" Pt-Ir Coatings by Nanotests Determined***, F. Klocke,* RWTH Aachen University, Germany, CERTH, Greece & IPT, Germany*, K.-D. Bouzakis (bouzakis@eng.auth.gr),* Aristoteles University of Thessaloniki, Greece, CERTH, Greece & IPT, Germany, ***K. Georgiadis,*** IPT, Germany*, S. Gerardis, G. Skordaris, M. Pappa*, Aristoteles University of Thessaloniki, Greece, CERTH, Greece & IPT, Germany

Precision glass molding is a medium to large scale production technology of complex optical components with high surface quality and form accuracy. However, the process is only economically viable if a long lifetime of the molding tools can be guaranteed. This can be achieved by using protective coatings on the optical surfaces of the molding tools. The most commonly used coatings for this application are based on noble metals, as they show reduced interaction with the glass during molding. The coatings must have excellent mechanical and chemical properties at high temperatures to withstand the stresses during molding and simultaneously extreme low surface roughness and defects density. The form accuracy of the molding tools is in the nm range and must be maintained even after the coating deposition. Therefore, very thin films of approximately 300 nm thickness are used. High film adhesion and strength properties are necessary for preventing surface defects and coating delamination.

In the described investigations, platinum (Pt)- iridium (Ir) coatings were deposited directly on cemented carbide samples by Physical Vapour Deposition (PVD) process. Moreover, for improving the adhesion, different materials such as of Ni and Cr were employed as adhesive interlayers at various thicknesses. These interlayers were deposited on the substrate before the Pt-Ir film, during the same PVD process. Appropriate experimental procedures were conducted for characterizing the coatings' mechanical and adhesion properties such as nanoindentations, nano-impact and nano-scratch tests. FEM calculations simulating the films' loadings during nano-impact test explain the effect of the adhesive interlayer on the entire coating substrate structure strength.

12:00pm **E2-3-9 A Study on the Microstructures and Mechanical Properties of Ti-Al-Cr-Si-N Nanocomposite Thin Films Prepared by Pulsed DC Reactive Magnetron Sputtering System**, ***P.-C. Huang,*** Tungnan University*, J.-W. Lee (jefflee@mail.mcut.edu.tw),* Mingchi University of Technology, Taiwan*, H.-P. Chen,* Tungnan University, Taiwan*, Y.-C. Chan, H.-W. Chen, J.-G. Duh*, National Tsing Hua University, Taiwan

Surface modification technology can be used to deposit a foreign hard coating material onto the surface of interest to achieve specific properties, such as high strength, adequate adhesion, wear and corrosion resistance. In this study, the Ti-Al and Cr-Si targets were used to fabricate the Ti-Al-Cr-Si-N nanocomposite thin films with various Cr and Si contents by a pulsed DC magnetron sputtering system. The crystalline structure of coatings was determined by a glancing angle X-ray diffractometer. The surface roughness of thin films was explored by an atomic force microscopy (AFM). The surface and cross-sectional morphologies of thin films were examined by a scanning electron microscopy (SEM) and transmission electron microscopy (TEM), respectively. The adhesion, hardness and nanotribological properties of thin films were evaluated by a nanoindenter and scratch tester respectively. It was observed that the hardness and nanotribological properties was strongly influenced by the Cr and Si contents of Ti-Al-Cr-Si-N nanocomposite thin films in this work.

New Horizons in Coatings and Thin Films
Room: Royal Palm 1-3 - Session F2-2

High Power Impulse Magnetron Sputtering
Moderator: R. Bandorf, Fraunhofer IST, J. Sapieha, Ecole Polytechnique de Montreal

8:00am **F2-2-1 The influence of High Power Impulse Magnetron Sputtering (HIPIMS) Pulse Parameters on Plasma, Target and Substrate Interactions for Chromium**, ***F. Papa*** *(fpapa@hauzer.nl),* Hauzer Techno Coating, BV, Netherlands*, H. Gerdes, R. Bandorf,* Fraunhofer IST, Germany*, A.P. Ehiasarian,* Sheffield Hallam University, UK*, I. Kolev, R. Tietema,* Hauzer Techno Coating, BV, Netherlands*, G. Braeuer,* Fraunhofer IST, Germany*, T. Krug*, Hauzer Techno Coating, BV, Netherlands **INVITED**

High Power Impulse Magnetron Sputtering (HIPIMS) has been of great interest over the past decade. It's main benefit being that at least some of the sputtered target material can be ionized. Due to this ionization, it is possible to modify and tailor coating properties in ways which are not easily possible with DC magnetron sputtering. There still exist, however, many questions concerning the relationships between peak pulse energy and the resulting degree of ionization and the ion/deposited particle ratio at the substrate. Since the main mechanism for ionization is electron impact ionization, it is expected that the degree of ionization will increase linearly with peak cathode current. This is though, only one side of the equation. Magnetic field strength greatly influences the discharge characteristics and deposition rate. In turn, this changes the nature of the ion/deposited particle interaction at the substrate. In this study, peak cathode current has been held as the control variable. Around this control, the magnetic field strength, pulse length and degree of pre-ionization have been varied. Pulses of 500-1000µs were characterized with a peak cathode current density between 0.1-1 A/cm^2 for chromium. Time resolved optical emission spectroscopy was used to examine the evolution of ionized species during the pulse. Density corrected deposition rate measurements were made in order to determine the deposition rate per pulse segment as related to pulse energy. A biased probe was used to collect the ion flux at the substrate position. From these measurements, the ion/deposited particle ratio has been calculated. The microstructure of the coatings deposited under the various conditions is also examined. It has been found that there is a strong relationship between the pulse shape and the resulting plasma composition and deposition rate due to the spatial evolution of HIPIMS plasmas.

8:40am **F2-2-3 A Comparison of PET Plasma Pre-Treatment Using Medium Frequency and Low Frequency-High Power Pulse Oxygen-Containing Discharges**, *M. Audronis (martynas.audronis@gencoa.com), V. Bellido-Gonzalez,* Gencoa Ltd, UK, *S. Hinder, **M. Baker**,* University of Surrey, UK, *A. Matthews*, University of Sheffield, UK

Vacuum web coating is an important manufacturing process that is used to produce technological thin films for a wide variety of applications, such as solar cells, displays and solid state lighting. Thin film adhesion to the polymer web is one of most important quality characteristics of a coated product. It can be improved significantly by web plasma pre-treatment methods, which are now used routinely in roll-to-roll coating systems. Magnetically enhanced plasma treatments are established processes to enhance quality and performance of plasma processed and/or vacuum coated web products.

In this paper we present results on flexible polymeric substrate (PET) pre-treatment using a method comprising a magnetically enhanced plasma powered by either a) medium frequency (50-250 kHz) or b) low frequency (50-300 Hz) high power (HIPIMS) sources. Plasma pre-treatment processes are carried out in Ar – O_2 atmosphere. The effects of different pre-treatments on the surface properties are investigated by XPS, ToF-SIMS and AFM and compared.

9:00am **F2-2-4 Growth of HfO_2-Based High-k Dielectric Films by High Power Impulse Magnetron Sputtering**, ***K. Sarakinos** (Kostas@ifm.liu.se), B. Lü, H. Arwin,* Linköping University, Sweden, *K. Konstantinidis,* CIRMAP, University of Mons, Belgium, *M. to Baben, D. Music, J.M. Schneider,* RWTH Aachen University, Germany, *U. Helmersson*, Linköping University, Sweden

Hafnium dioxide (HfO_2) films are widely used as dielectric layers in microelectronic devices. Among the various polymorphs of HfO_2 the high temperature cubic (c) and tetragonal (t) phases are of importance since they exhibit significantly larger dielectric constant (k) as compared to the low temperature monoclinic (m) HfO_2 configuration. In the present study we grow films at room temperature by sputtering a metallic hafnium target in a reactive Ar-O_2-N_2 atmosphere employing high power impulse magnetron sputtering (HiPIMS). The deposition process exhibits a stable transition zone between the metallic and the compound sputtering mode which enables to tune the composition of the target surface (target coverage) by varying the partial pressures of the sputtering gases. The well defined target coverage conditions, in turn, facilitate control over the non-metal sublattice configuration of the growing hafnium oxynitride (Hf-O-N) films in terms of N and O incorporation. Structural characterization tools are employed to define deposition conditions that lead to the growth of films with the HfO_2 crystal structure. Experimental data and first principle calculations suggest that N incorporation and O vacancies favor the formation of the c- and the t-HfO_2 crystal structure at the expense of the m-HfO_2 one [1]. Optical analysis employing spectroscopic ellipsometry in the near-infrared to ultra-violet spectral range indicates that Hf-O-N films with the crystal structure of c- and t-HfO_2 exhibit larger dielectric constants as compared to films with the m-HfO_2 structure.

[1] K. Sarakinos *et al.*, J. Appl. Phys. 108 (2010) 014904

9:20am **F2-2-5 Growth of V-Al-C Thin Films by HPPMS and DC Magnetron Sputtering Using a Multi-Component Target**, ***Y. Jiang** (yan.jiang@mch.rwth-aachen.de), S. Mraz, T. Takahashi*, RWTH Aachen University, Germany

V-Al-C thin films were deposited onto Al_2O_3 (11-20) substrates by HPPMS and DC magnetron sputtering using a hot-sintered multi-component target with 2:1:1 MAX phase-like composition. The film composition was found to be a strong function of the deposition pressure and target-to-substrate distance. The formation of crystalline phases with the close-to-MAX-phase-like composition was investigated as a function of the substrate temperature, from room temperature up to 500°C, and duty cycle, from 1.7 % to 20 %, respectively. Al-containing hexagonal vanadium carbide was formed during both DC and HPPMS at 500°C, where the lattice parameter of the hexagonal solid solution was dependent on the duty cycle employed during HPPMS. The change in c lattice parameter comparing DC sputtering with HPPMS at a duty cycle of 5 % is with 2.6 % rather extensive and appears to be primarily affected by the ion bombardment by film forming species. Plasma composition analysis data supports this notion. The here presented data are of relevance for understanding the mechanisms that govern the growth of MAX phase thin films at low substrate temperatures.

9:40am **F2-2-7 Rotatable Magnetron Sputtering of Aluminium in Continuous and Pulse Modes Using Different Strength Magnetic Arrays**, ***M. Audronis** (martynas.audronis@gencoa.com), V. Bellido-Gonzalez, R. Brown*, Gencoa Ltd, UK

Sputter target utilisation and film deposition rate are the two characteristics that affect the productivity of a sputter-based vacuum coating manufacturing processes most significantly. Hence, these characteristics are important when selecting a deposition method. Sputter cathode manufacturers are constantly striving to improve the target utilisation and maximise the deposition rate. On the other hand efforts are made to improve properties of existing coatings and develop new. Power supply technologies have played a major role in aiding film property improvements (e.g. arc free operation in medium frequency AC power mode for fabrication of insulating oxide films). High Power Impulse Magnetron Sputtering (HIPIMS) is one such recently developed power supply technology that holds a promise to enhance many thin film material systems. In general, it is known that HIPIMS exhibits relatively low deposition rates as compared to Direct Current (DC) sputtering processes.

In this paper we present preliminary results of industrial size (150 mm target O.D.) rotatable magnetron sputtering of aluminium target in continuous and pulse (HIPIMS) modes using standard commercially available magnetic arrays, such as a normal strength array (e.g. as used for DC and AC processing) and an 'RF' array (i.e. as commonly used for RF rotatable magnetron sputtering). A comparison is made in terms of magnetic field distribution, process characteristics and deposition rates. It is shown that deposition rates using HIPIMS and one of the commercially available magnetic arrays can be as high as those obtained when operating in DC mode.

Applications, Manufacturing, and Equipment
Room: Royal Palm 4-6 - Session G5

Coatings, Pre-Treatment, Post-Treatment and Duplex Technology
Moderator: N. Bagcivan, RWTH Aachen University, E. Kusano, Kanazawa Institute of Technology

8:00am **G5-1 The Growth of Single Fe_2B Phase on Low Carbon Steel via Phase Homogenization in Electrochemical Boriding (PHEB)**, ***G. Kartal** (kartalgu@itu.edu.tr), S. Timur,* Istanbul Technical University, Turkey, *O.L. Eryilmaz, A. Erdemir*, Argonne National Laboratory

In this study, we introduce a new process which results in the formation of a single phase Fe_2B layer on low carbon steel substrates. Although, FeB phase is much harder and more common than Fe_2B in all of the boriding operations, it has very poor fracture toughness, hence can fracture or delaminate easily from the surface under high normal or tangential loading. We call the new process "phase homogenization in electrochemical boriding" (PHEB) in which we perform electrochemical boriding for about 15 min at 950°C in an electrolyte consisting of 90% borax and 10% sodium carbonate then we turn of power and leave samples in the bath for additional 45 min without any polarization. The typical current density during the electrochemical boriding is about 200 A/m^2. The total thickness of the resultant boride layer was about 65 micrometer (i.e., 30 micrometer thick FeB and 35 micrometer Fe_2B layers) after 15 min of electrochemical boriding. However, during the additional holding time of 45 min, the thickness of the boride layer increased to 80 micrometer and consisted of only Fe_2B phase as confirmed by glancing angle x - ray diffraction and scanning electron microscope in backscattering mode. The microscopic characterization of boride layers revealed a very dense and homogenously thick boride layer whose microhardness was about 16 GPa. The fracture behavior and adhesion of the boride layer was evaluated using the Daimler-Benz Rockwell C test and found to be excellent, i.e., consistent with an HF1 rating.

8:20am **G5-2 Duplex Treatment for Forming Tools**, ***A. Reiter** (Andreas.Reiter@oerlikon.com)*, Oerlikon Balzers, Germany **INVITED**

PVD coatings are widely used in various Forming tools applications. In several specific cases like sheet metal forming of high strength steel sheets or cold extrusion the tool surface is exposed to severe surface load. Here PVD coatings sometimes cannot show their excellent performance if the substrate material underneath does not supply enough support due to low hardness and strength. In Al-pressure die casting the process related thermocycles induce heat cracks in the substrate material propagating into the PVD coating. The combination of Nitriding with PVD processes is a suitable and industrialized solution for creating a kind of multilayer structure. Nitriding layers stand out for high surface hardness and thermal stable compressive stresses. This yields in an increased resistance against plastic deformation and fatigue. Thus it is possible to reduce property differences between hard layers and substrate, to increase the support function of soft substrate materials and the resistance against thermal fatigue. Concerning the PVD layer properties like coating adhesion, abrasive wear resistance, improved resistance against crack propagation and impact resistance can substantially be improved. In several application cases the positive impact of the Duplex technology on the tool performance will be shown.

9:00am **G5-4 Development of rf/dc Plasma Systems for Nitriding of Aluminum Alloys**, ***T. Aizawa*** *(taizawa@sic.shibaura-it.ac.jp), Y. Sugita*, Shibaura Institute of Technology, Japan

DC-based plasma systems have been widely utilized for plasma nitriding in commercial. In addition, pulse bias technique is combined with this DC-based plasma technology for efficient nitriding. In the present study, rf/dc-combined plasma systems are proposed for plasma nitriding. Different from the conventional rf-system, it works around 2 MHz with frequency control for matching. Owing to prompt response in mili-second to varying plasma conditions, nitrogen plasma is easily ignited and controlled at wider range of pressure. Since the sample temperature is controlled independently from plasmas, processing conditions for nitriding are optimized in the broad feasible combinations. Due to this combination of rf-plasma with dc-plasma, sputtering effect by dc bias is reduced in the present system.

Aluminum alloys with A2017 and A2024 are employed to demonstrate the practical feasibility of this system. After pretreatment of samples, they are subjected to pre-sputtering for removal of surface oxide layers; then, they are plasma-nitrided at T = 673 K for various pressure conditions. Their microstructure is characterized by XRD, SEM and XPS to quantitatively identify the formation of AlN and to describe the formation rate of nitrided layer. The effect of pressure or plasma density on the formation rate is also discussed to find an optimum condition for efficient plasma nitriding. Micro-hardness test is performed to evaluate on the mechanical properties of nitrided aluminum alloys.

9:20am **G5-5 Adherent Nanocrystalline Diamond Thin Films Grown on Surface-Modified Ti and Ti Alloys at Moderate Temperatures**, ***Y.-S. Li*** *(yul088@mail.usask.ca)*, University of Saskatchewan, Canada

Metallic Ti and its alloys are widely used in aerospace, bio-medical and chemical industries because of their low density, high specific strength and high corrosion resistance. However, their extended applications are limited by their poor tribological properties. Chemical vapor deposition of wear/corrosion resistant diamond coatings on such substrates will significantly enhance the durability and service performances of these materials. High quality diamond coatings are difficult to deposit on the Ti metal and alloys due to low coating adhesion strength and severe chemical reaction between the gas reactants and the substrate which deteriorates the mechanical properties of the substrate. In this study, a series of plasma surface modification strategies have been carried out to enhance nucleation, growth and adhesion of diamond as well as the prevention of the substrate chemical reaction. The diamond film quality, chemical and structural natures of the interfacial layers and the substrate near-surfaces are characterized.

9:40am **G5-7 Alumina Coatings Obtained by Thermal Spraying and Plasma-Anodizing - a Comparison**, ***T. Lampke***, *D. Meyer (daniel.meyer@mb.tu-chemnitz.de), G. Alisch, D. Nickel, I. Scharf*, Chemnitz University of Technology, Germany **INVITED**

Thermally sprayed alumina coatings are widely used in a range of industrial applications to improve wear and erosion resistance, corrosion protection and thermal insulation of metallic surfaces. These properties are required for many components for production processes in the paper and printing industry. By means of efficient and adjustable coating processes, long-term use of the refined surfaces is obtained. It can be seen that cost-efficient arc-sprayed Al_2O_3 coatings post-treated by plasma-electrolytic oxidation (PEO) form layers with outstanding hardness, bonding strength, abrasion and corrosion resistance as well as extended service time. The generated layers (arc-sprayed and PEO-converted) show a thickness of up to 250 µm and a microhardness of up to 1600 HV0.1. These coatings are designed to partially replace hard chromium.

The oxide nucleation begins at energetically preferred sites at the surface and forms a non-porous barrier layer. Then the formed oxide layers are partly melted and additional high-temperature phases at the oxide/electrolyte interface, like spinel or mixed oxides, are formed. This rapid oxide formation process stops when the electric field strength falls under a critical value self-induced by the growing layer thickness. In general, the achieved composition and properties depend on the substrate phase composition, the electrolyte composition, and the treatment regimes (temperature, processing time, voltages, current densities, current forms AC/DC etc.).

In conclusion, different substrates coated by thermal spraying of aluminium and other valve metals can be converted by PEO to fully or partially oxidized surfaces with outstanding properties. In the presented article, these coatings will be mechanically and chemically evaluated and compared to standard APS-Al_2O_3 coatings.

10:20am **G5-8 Repair of Thermal Damage in Gate Dielectric for Germanium-Based Metal-Oxide-Semiconductor Device by Supercritical Fluid Technology**, ***C.-S. Huang***, *P.-T. Liu (ptliu@mail.nctu.edu.tw)*, National Chiao Tung University, Taiwan

Supercritical fluid (SCF) technology is employed at 150°C as a post-gate dielectric treatment to restore the germanium-based metal-oxide-semiconductor (Ge-MOS) device characteristics after thermal annealing. Ge diffusion into gate dielectric insulators could cause the electrical degradation during high-temperature post-dielectric annealing (PDA) and thermal cycles in fabrication processes. These issues cause it to be difficult to implement the gate-first process in Ge-MOS technology. Therefore, low-temperature process and the method for recovering from electrical degradation are critical for the Ge-MOS technology development. In this work, after a typical post-gate dielectric annealing the implementation of SCF treatment can restore the Ge-MOS degradation from the high-temperature thermal annealing. These improvements are achieved since the SCF with high permeability passivates the traps in the gate dielectric film through oxidation with carried oxidant (H_2O).

10:40am **G5-10 Improvements on the Cavitation Erosion Resistance of Austenitic Stainless Steels by Plasma Surface Alloying Processes with Carbon and Nitrogen Followed by PAPVD Cr-Al-N**, ***C. Godoy*** *(gcgodoy@uaigiga.com.br), R. Borges,* Universidade Federal de Minas Gerais, Brazil*, J.C. Avelar-Batista Wilson,* Tecvac Ltd, UK*, R.G. Melo*, Universidade Federal de Minas Gerais, Brazil

Two low temperature plasma surface alloying processes (low temperature plasma nitriding and low temperature plasma carburising) have been successfully developed for austenitic stainless steels. Both processes significantly enhance their wear resistance without compromising the corrosion resistance [1]. In a previous investigation into the cavitation erosion resistance of ferritic steels, C. Godoy et al. [2] concluded that plasma nitriding followed by PAPVD Cr-N coating was a very effective surface treatment combination to improve their cavitation erosion performance. Austenitic systems are usually preferred for cavitation erosion protection due to their structure with low stalking fault energy. In this work, plasma carburising and a sequential plasma carburising followed by plasma nitriding were carried out in an attempt to further enhance the cavitation erosion resistance of austenitic stainless steels. Five systems were investigated: Uncoated, untreated AISI 316 steel (S1); plasma carburised steel (S2); hybrid plasma treated (i.e. sequentially plasma carburised and plasma nitrided) steel (S3); plasma carburised and PAPVD Cr-Al-N-coated steel (duplex S4) and hybrid plasma treated (as in S3) and PAPVD Cr-Al-N-coated steel (duplex S5). Mass loss plots were obtained as a function of time so that cavitation erosion rates and incubation times could be determined. All duplex systems exhibited a significant increase in the incubation period compared to that of the uncoated steels. Both duplex (S4 e S5) yielded a 25-fold and 22-fold increase, respectively, in the incubation period of the AISI 316 steel. Although uncoated, plasma treated systems also displayed an increase in the incubation time compared to that of the uncoated, untreated AISI 316 steel, they were outperformed by duplex (i.e., plasma treated + coated) systems. The most effective plasma surface treatment without PAPVD Cr-Al-N coating was plasma carburising. Cavitation erosion rates were found to decrease as the depth of hardened layers increased. Plasma carburised systems (S2 and S4) exhibited the lowest erosion rates as a result of deeper hardened layers that were intrinsically produced by that process. Results strongly indicate that PAPVD coatings are of prime importance to increase incubation periods (and therefore delay the onset of cavitation erosion) whilst deep hardened layers are paramount to minimise erosion rates.

[1] Y. Sun, Materials Science and Engineering A 404 (2005) 124–129

[2] C. Godoy et al., Surf. Coat. Technol. 200 (2006) 5370-5378.

11:00am **G5-6 Microstructure and Properties Thermally Sprayed and Laser Remelted of the Fe-Cr-Mo-W-Mn-C-B Coating**, ***A. Iwaniak*** *(aleksander.iwaniak@polsl.pl), G. Moskal*, Silesian University of Technology, Poland

In the study, there have been shown the tests results concerning the microstructure and selected properties of the nanocomposite coating based on iron, which was thermally sprayed and then remelted by laser. In the process of wire-arc spraying with the use of a composite wire type Fe-Cr-Mo-W-Mn-C-B there was formed a coating of 3% porosity and hardness about 600 HV0,3. Next the coating was processed by 2 kW continuous power diode laser in order to remelt it. The complete remelting of the coating and its metallurgical joint to a steel base was obtained. Remelting of the coating caused the increase of its hardness and reduced porosity. The microstructure, thermal diffusivity and erosion coating were studied by scanning electron microscopy (SEM, EPMA), X-ray diffractometry, impulse method Laser Flash and erosion test before and after the remelting process.

Financial support of Structural Funds in the Operational Programme - Innovative Economy (IE OP) financed from the European Regional Development Fund - Project No POIG.01.01.02-00-015/09 is gratefully acknowledged.

Authors Index

Bold page numbers indicate the presenter

— C —

— D —

— E —

— L —

— M —

— N —

— O —

— P —

— Q —

— R —

Contents lists available at ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

ICMCTF 2011 EXECUTIVE COMMITTEE

GENERAL CHAIRMAN
Steve J. Bull
Newcastle University
Merz Court
Newcaste Upon Tyne NE1 7RU
United Kingdom
+44-191-222-7913, Fax: +44-191-222-5292
s.j.bull@ncl.ac.uk

PROCEEDINGS EDITORS
Gregory Abadias
University of Poitiers
Laboratoire de Physique des Materiaux, CNRS
SP2MI, Teleport 2
Bd. Marie et Pierre Curie
86982 Chasseneuil Futuroscope, France
+33-5-4949-6748, Fax: +33-5-4949-6692
gregory.abadias@univ-poitiers.fr

Christopher Muratore
Air Force Research Laboratory
Materials and Manufacturing Directorate
Thermal Sciences & Materials Branch
Wright-Patterson AFB, OH 45433, USA
+1-937-255-2568, Fax: +1-937-255-2176
chris.muratore@wpafb.af.mil

Claus Rebholz
University of Cyprus
Mechanical & Manufacturing Engineering
75 Kallipoleos Street
1678 Nicosia, Cyprus
+357-22-892-282, Fax: +357-22-892-254
claus@ucy.ac.cy

Ivan Petrov
University of Illinois
Frederick Seitz Materials Research Laboratory
104 S. Goodwin Avenue
Urbana, IL 61801, USA
+1-217-333-8396
petrov@illinois.edu

Michael Stüber
Karlsruhe Institute of Technology (KIT)
Institute for Applied Materials (IAM)
Hermann-von-Helmoltz-Platz 1
76344 Eggenstein-Leopoldshafen, Germany
+49-721-608-23889, Fax: +49-721-608-24567
michael.stueber@kit.edu

PROGRAM CHAIRMAN
Ali Erdemir
Argonne National Laboratory
Building 212, Room D-222
9700 South Cass Avenue
USA
+1-630-252-6571, Fax: +1-630-252-5568
erdemir@anl.gov

EXHIBITS CHAIRMAN
Jeannette De Gennaro
AVS
125 Maiden Lane, 15th Floor
New York, NY 10038, USA
+1-212-248-0200 ext 229, Fax: +1-212-248-0245
cell: +1-201-961-248-5268
jeannette@avs.org

TREASURER
Andrey Voevodin
Air Force Research Laboratory
2941 Hobson Way Room 106
Wright-Patterson AFB, OH 45433, USA
+1-937-255-4651, Fax: +1-877-350-9964
a.voevodin@woh.rr.com

PAST CHAIRMAN
Kathy Wahl
U.S. Naval Research Laboratory
4555 Overlook Avenue
Washington, DC 20375, USA
+1-202-767-5419
kathryn.wahl@nrl.navy.mil

CONFERENCE MANAGER
Phyllis Greene
3090 S. Bridle Drive; Rafter J
Jackson, WY 83001-9124, USA
+1-307-734-8009
pgreene@mrl.uiuc.edu

CONFERENCE ADMINISTRATOR
Mary S. Gray
Suite 136
14001-C Saint Germain Drive
Centreville, VA 20121, USA
+1-703-266-3287, Fax: +1-703-968-8877
icmctf@mindspring.com

Thin Solid Films 520 (2011) viii

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

ICMCTF 2011 EXECUTIVE COMMITTEE

GENERAL CHAIRMAN
Steve J. Bull
Newcastle University
Merz Court
Newcaste Upon Tyne NE1 7RU
United Kingdom
+44-191-222-7913, Fax : +44-191-222-5292
s.j.bull@ncl.ac.uk

PROCEEDINGS EDITORS
Gregory Abadias
University of Poitiers
Laboratoire de Physique des Materiaux, CNRS
SP2MI, Teleport 2
Bd. Marie et Pierre Curie
86982 Chasseneuil Futuroscope, France
+33-5-4949-6748, Fax : +33-5-4949-6692
gregory. abadias@univ-poitiers.fr

Christopher Muratore
Air Force Research Laboratory
Materials and Manufacturing Directorate
Thermal Sciences & Materials Branch
Wright-Patterson AFB, OH 45433, USA
+1-937-255-2568, Fax : +1-937-255-2176
chris.muratore@wpafb.af.mil

Claus Rebholz
University of Cyprus
Mechanical & Manufacturing Engineering
75 Kallipoleos Street
1678 Nicosia, Cyprus
+357-22-89-2282, Fax: +357-22-892-254
claus@ucy.ac.cy

Ivan Petrov
University of Illinois
Frederick Seitz Materials Research Laboratory
104 S. Goodwin Avenue
Urbana, IL 61801, USA
+1-217-333-8396
petrov@illinois.edu

Michael Stüber
Karlsruhe Institute of Technology (KIT)
Institute for Applied Materials (IAM)
Hermann-von-Helmoltz-Platz 1
76344 Eggenstein-Leopoldshafen, Germany
+49-721-608-23889, Fax: +49-721-608-24567
michael.stueber@kit.edu

PROGRAM CHAIRMAN
Ali Erdemir
Argonne National Laboratory
Building 212, Room D-222
9700 South Cass Avenue
USA
+1-630-252-6571, Fax : +1-630-252-5568
erdemir@anl.gov

EXHIBITS CHAIRMAN
Jeannette DeGennaro
AVS
125 Maiden Lane, 15th Floor
New York, NY 10038, USA
+1-212-248-0200 ext 229, Fax: +1-212-248-0245
cell: +1-201-961-248-5268
jeannette@avs.org

TREASURER
Andrey Voevodin
Air Force Research Laboratory
2941 Hobson Way Room 106
Wright-Patterson AFB, OH 45433, USA
+1-937-255-4651, Fax: +1-877-350-9964
a.voevodin@woh.rr.com

PAST CHAIR
Kathy Wahl
U.S. Naval Research Laboratory
4555 Overlook Avenue
Washington, DC 20375, USA
+1-202-767-5419
kathryn.wahl@nrl.navy.mil

CONFERENCE MANAGER
Phyllis Greene
3090 S. Bridle Drive; Rafter J
Jackson, WY 83001-9124, United States
+1-307-734-8009
pgreene@mrl.uiuc.edu

CONFERENCE ADMINISTRATOR
Mary S. Gray
Suite 136
14001-C Saint Germain Drive
Centreville, VA 20121, USA
+1-703-266-3287, Fax: +1-703-968-8877
icmctf@mindspring.com

ICMCTF 2011 EXHIBITORS

COMPANY	BOOTH #	COMPANY	BOOTH #
AEP Technology	208	Labtec Sales Partners LLC	413
Agilent Technologies	**206**	Maney Publishing	006
AJA International, Inc.	**210**	Mantis Deposition Ltd	309
AVS (American Vacuum Society)	214	MeiVac, Inc.	116
Brooks Automation	**310**	MELEC GmbH	409
CEMECON AG	308	Micro Materials, Ltd.	311
CETR	**001**	Nano-Master, Inc.	312
Compass Instruments, Inc.	211	NanoScience Instruments, Inc.	205
CSM Instruments	**303**	Oerlikon Leybold Vacuum USA, Inc.	109
Elsevier BV	**314**	Omicron Nanotechnology USA	404
Extrel CMS	306	Plansee SE	002
Falex Tribology NV	211	Plasmaterials, Inc.	203
Fischer Technology, Inc.	207	Process Materials Inc.	408
Gencoa	411	Refining Systems	004
Hauzer Techno Coating B.V.	**313**	Reynard Corporation	107
Helium Leak Testing, Inc.	108	**Saxonian Inst. of Surface Mechanics**	**305**
Hiden Analytical, Inc.	307	**Semicore Equipment, Inc.**	**403**
Horiba Scientific	412	SHINTO Scientific	410
Hysitron, Inc.	213	**Soleras Ltd**	**316**
Impact Coatings AB	**315**	South Bay Technology, Inc.	103
Impedans Ltd.	106	**Super Conductor Materials**	**003**
Intlvac	304	Surface Modification Systems, Inc.	105
IonBond LLC	114	Tetra GmbH	211
ION-TOF USA	204	Thermo Fisher Scientific	110
ISYS Inc.	407	TRIBOTECHNIC	415
J.A. Woollam Co., Inc.	405	**UC Components**	**406**
Julabo USA, Inc.	104	ULVAC, Inc.	209
Kratos Analytical	**215**	**Vacuum Research Corporation**	**005**
Kurt J Lesker Company	**216**	ZPulser LLC.	112

Bold Listings denote our generous sponsors