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	Carbon and Nitride Materials: Synthesis-Structure-Property Relationships
E	Tribology and Mechanical Behavior of Coatings and Thin Films
F	Characterization: Linking Synthesis Properties and Microstructure
G	Applications, Manufacturing, and Equipment
H	New Horizons in Coatings and Thin Films
TS1	Experimental and Computational Studies of Molecular materials and Thin Films
TS2	Coatings for Fuel Cells and Batteries
TS3	Bioactive Coatings and Surface Biofunctionalization
TS4	Surface Engineering for Thermal Transport, Storage, and Harvesting

Monday Morning, April 26, 2010

	Hard Coatings and Vapor Deposition Technology **Room: Pacific Salon 3 - Session B1-1** **Sputtering Coatings and Technologies** **Moderators:** P. Eklund, Linköping University, M.-S. Wong, National Dong Hwa University	**Hard Coatings and Vapor Deposition Technology** **Room: Town & Country - Session B4** **Laser and Ion Beam Surface and Coating Engineering** **Moderators:** K. Sarakinos, RWTH Aachen University, W. Waldhauser, Joanneum Research Forschungsgesellschaft GmbH
10:00 am	**B1-1-1** Structure and Properties of AlCrSiON Oxynitrides Prepared Using Pulsed DC Magnetron Sputtering, H. NAJAFI, **A. KARIMI**, EPFL, Switzerland, M. MORSTEIN, Platit AG, Switzerland	**B4-1 Invited** An Oveerview of Laser Ablation: Thin Films and Nano-Particles, **J. MAZUMDER**, University of Michigan
10:20 am	**B1-1-2** Plasma-Enhanced Cylindrical Magnetron Deposition of Tantalum Coatings on Interior Surfaces of Steel Cylinders, **S. LEE**, US Army ARDEC-Benet Labs, M. CIPOLLO, F. YEE, US Army RDECOM, R. WEI, E. LANGA, K. COULTER, Southwest Research Institute	Invited talk continued.
10:40 am	**B1-1-3 Invited** Industrial Scale Sputter Deposition of Photocatalytic and Solid Electrolyte Oxide Coatings, **L.P. NIELSEN**, S. SØNDERBY, K.P. ALMTOFT, I.H. ANDERSEN, B.H. CHRISTENSEN, M.B. SØRENSEN, Danish Technological Institute, Denmark, A.J. NIELSEN, J. BØTTIGER, University of Aarhus, Denmark	**B4-3** Deposition of Nanolaminate Films by Pulsed Laser Deposition from Pre-Synthesized MAX-Phase Targets, **P. SCHAAF**, C. LANGE, Ilmenau University of Technology, Germany, M. WILKE, MFPA Weimar, Germany, M. HOPFELD, Ilmenau University of Technology, Germany
11:00 am	Invited talk continued.	**B4-4** Laser Assisted Deposition of Industrial CAE-PVD TiN Thin Films, **J. ESPARZA**, Asociación de la Industria Navarra, Spain, X. DE LA FUENTE, ICMA-CSIC, Spain
11:20 am	**B1-1-5** Modelling and Experimental Characterization of Serial Co-Sputtering, **T. KUBART**, T. NYBERG, Uppsala University, Sweden, A. PFLUG, Fraunhofer IST, Germany, M. AUSTGEN, D. KOEHL, M. WUTTIG, RWTH Aachen, Germany, S. BERG, Uppsala university, Sweden	**B4-5 Invited** Surface Nanostructures Induced by Low Energy Ion Sputtering, **S. FACSKO**, A. KELLER, M. RANJAN, W. MÖLLER, Forschungszentrum Dresden Rossendorf e.V., Germany
11:40 am	**B1-1-6** Significant Reduction of Arc Caused Sputtering Losses, P. LACH, P. OZIMEK, **M. ZELECH0WSKI**, HUETTINGER Electronic Sp Z.o.o., Poland, G. HINTZ, Hüttinger Elektronik GmbH, Germany	Invited talk continued.
12:00 pm		**B4-7** Pulsed Laser Deposition of Low Work Function coatings for Field Emission cathodes, **S. FAIRCHILD**, Air Force Research Laboratory, T. MURRAY, University of Dayton, B. TOWNE, Air Force Research Laboratory, M. CAHAY, University of Cincinnati, T. BACK, University of Dayton
12:20 pm		

Monday Morning, April 26, 2010

	Tribology & Mechanical Behavior of Coatings & Thin Films **Room: Pacific Salon 1 - Session E3-1** **Tribology of Nanostructured and Amorphous Films** **Moderators:** J. Fontaine, Ecole Centrale de Lyon, R.D. Evans, Timken Company	**Characterization: Linking Synthesis Properties and Microstructure** **Room: Royal Palm 1-3 - Session F2** **In Situ Characterization** **Moderators:** D. Depla, Ghent University, F. Giuliani, Imperial College London
10:00 am	**E3-1-1** Tribological and Mechanical Properties of Nanostructured Hydrogenated Amorphous Carbon and Titanium Diboride Films, **B. ZHAO**, Y.W. CHUNG, Northwestern University	**F2-1 Invited** Plasticity and Debonding of Thin Metallic Films Studied by in Situ Tensile Testing, **G. DEHM**, M.J. CORDILL, Montanuniversität Leoben, Austria, C. KIRCHLECHNER, Austrian Academy of Sciences, Austria, J. KECKES, Montanuniversität Leoben, Austria, M. SMOLKA, Kompetenzzentrum Automobil- und Industrie-Elektronik GmbH, Austria, F. FISCHER, Montanuniversität Leoben, Austria
10:20 am	**E3-1-3** Tribology of Nanocrystalline Diamond Coatings, **N.D. THEODORE**, US Naval Research Laboratory, M. WIORA, Ulm University, K.J. WAHL, US Naval Resarch Laboratory	Invited talk continued.
10:40 am	**E3-1-4** Influence of Ultraviolet Ray Irradiation on CN_x Coating's Tribological Characteristics, **T. TOKOROYAMA**, N. UMEHARA, Nagoya University, Japan, Y. FUWA, Toyota Motors Co., Ltd., Japan	**F2-3** Stress and Microstructure Evolution During Polycrystalline Metallic Film Growth : Influence of the Nucleation Conditions, **A. FILLON**, G. ABADIAS, A. MICHEL, C. JAOUEN, University of Poitiers, France
11:00 am	**E3-1-5 Invited** Tribology of Nanocrystalline Diamond and Amorphous Carbon Films: Achieving Ultralow Friction and Wear, **R.W. CARPICK**, University of Pennsylvania	**F2-4** *In Situ* Tribology of Hard, Protective Coatings, **H.W. STRAUSS**, McGill University, CANADA, S. HASSANI, J.-E. KLEMBERG-SAPIEHA, L. MARTINU, Ecole Polytechnique de Montreal, Canada, R. CHROMIK, McGill University, Canada
11:20 am	Invited talk continued.	**F2-5** Growth Process of Zirconium Diboride Thin Films Prepared by Ultrahigh-Vacuum CVD, **Y. YAMADA-TAKAMURA**, S. BERA, JAIST, Japan
11:40 am		
12:00 pm		
12:20 pm		

Monday Morning, April 26, 2010

	Applications, Manufacturing, and Equipment **Room: Sunset - Session G1-1** **Innovations in Surface Coatings and Treatments** **Moderators:** M. Rodmar, Sandvik Tooling, A. Leyland, University of Sheffield	**Applications, Manufacturing, and Equipment** **Room: Royal Palm 4-6 - Session G5/H5** **Coatings for Renewable Energy Harvesting Systems** **Moderators:** L. Bardos, Uppsala University, S. Roy, Newcastle University
10:00 am	**G1-1-1 Invited** Commercialization of Filtered Cathodic Arc Technology - Progress and Prospects, **R.P. WELTY**, Magplas Technik LLC	**G5/H5-1 Invited** Evaluation of the Anti-Fouling Properties of Atmospheric Plasma Deposited Siloxane Coatings, **D.P. DOWLING**, C.E. NWANKIRE, University College Dublin, Ireland
10:20 am	Invited talk continued.	Invited talk continued.
10:40 am	**G1-1-3** Plasmaphysical Characterization and Technological Application of a Hollow Cathode Plasma Source with an Axial Magnetic Field, **F. FIETZKE**, B. ZIMMERMANN, Fraunhofer Institute for Electron Beam and Plasma Technology FEP, Germany	**G5/H5-3** Cold Atmospheric Plasma Treatment of Energy System Components, **H. BARANKOVA**, L. BARDOS, Uppsala University, Sweden
11:00 am	**G1-1-4** Internal Plasma Processing of Narrow Halls and Tubes with Microwave Propagation Along Plasma-Sheath Interfaces, **H. KOUSAKA**, K. MORI, N. UMEHARA, Nagoya University, Japan, N. TAMURA, T. SHINDO, Contamination Control Services Inc., Japan	
11:20 am	**G1-1-5** Theoretical Investigation of Plasma Ion Implantation into Cylindrical Bore Based on Internal Inductively-Coupled Radio-Frequency Discharge, **X.B. TIAN**, Z.J. WANG, B.Y. GUAN, C.Z. GONG, S.Q. YANG, Harbin Institute of Technology, China, R.K.Y. FU, P.K. CHU, City University of Hong Kong, China	
11:40 am	**G1-1-6** EnFACE – a Maskless MicroScale Pattern Transfer Technique, **S. ROY**, Newcastle University, United Kingdom	
12:00 pm	**G1-1-7** Alumina-Graphite Coating by a Novel Technique: Friction Oxidation Deposition (FOD) Applied on Ti6Al4V Alloy, **J. DIABB**, M.A.L. HERNANDEZ-RODRIGUEZ, Universidad Autonoma de Nuevo Leon, FIME, Mexico	
12:20 pm		

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Monday Afternoon, April 26, 2010

	Hard Coatings and Vapor Deposition Technology **Room: Pacific Salon 3 - Session B1-2** **Sputtering Coatings and Technologies** **Moderators:** P. Eklund, Linköping University, M.-S. Wong, National Dong Hwa University	**Hard Coatings and Vapor Deposition Technology** **Room: Town & Country - Session B6-1** **Hard and Multifunctional Nano-Structured Coatings** **Moderators:** C.P. Mulligan, U.S. Army ARDEC, Benét Laboratories, R. Sanjines, EPFL, P. Zeman, University of West Bohemia
1:30 pm	**B1-2-1 Invited** Measurement of Residual Stress and Elastic Constants of Transition Metal Nitride Thin Films, **J.-H. HUANG**, National Tsing Hua University, Taiwan	**B6-1-1** Morphological and Structural Development of AlTiN Coatings Deposited by Cathodic Vacuum Arc, **J. VETTER**, J. MUELLER, Sulzer Metaplas GmbH, Germany, J. ANDERSSON, J. JOLEN, L. KARLSSON, Seco Tools AB, Germany, J. ALAMI, G. ERKENS, Sulzer Metaplas GmbH, Germany
1:50 pm	Invited talk continued.	**B6-1-2** Mechanical and Tribological Properties of TiN/CrN Superlattices by MPP and Pulsed DC Sputtering, **J. WANG**, HeFei University of Technology, J. LIN, J.J. MOORE, B. MISHRA, C. MARINGER, Colorado School of Mines
2:10 pm	**B1-2-3** Thermal Stability and Oxidation Resistance of Magnetron Sputtered Ti-Zr-N and Ti-Ta-N Thin Films, **G. ABADIAS**, University of Poitiers, France, L.E. KOUTSOKERAS, University of Poitiers, France University of Ioannina, Greece, P.A. PATSALAS, University of Ioannina, Greece	**B6-1-3 Invited** New Generation Nanscale Multilayer Coatings to Serve High Temperature, Corrosion and Tribological Applications Deposited by HIPIMS, **P.EH. HOVSEPIAN**, A.P. EHIASARIAN, Sheffield Hallam University, United Kingdom, R.I. BRAUN, DLR-German Aerospace Centre, Germany
2:30 pm	**B1-2-4** Modified TiAlN Coatings for Cutting Tools Prepared by Magnetron Sputtering, **M. KEUNECKE**, C. STEIN, K. BEWILOGUA, Fraunhofer IST, Germany, W. KOELKER, Cemecon AG, Germany, D. KASSEL, H. VAN DEN BERG, Kennametal Technologies GmbH, Germany	Invited talk continued.
2:50 pm	**B1-2-5** Structure, Wear, and High Temperature Oxidation of SiAlON and SiZrON Films Grown by RF Reactive Magnetron Co-Sputtering, M.S. BYRNE, B.J. NUGENT, G.P. BERNHARDT, **R.J. LAD**, University of Maine	**B6-1-5** Application Oriented Characterization of Nitride Coatings for Cutting Tools, **M. LECHTHALER**, D. DE GREGORIO, M. RASCHKE, OC Oerlikon Balzers AG, Liechtenstein
3:10 pm	**B1-2-6** TiCN/TiNbCN Multilayer System with Enhanced Tribological Properties, **J. CAICEDO**, C. AMAYA, M. GOMEZ, Universidad del Valle, Colombia, L. YATE, A. LOUSA, J. ESTEVE, Universitat de Barcelona, Spain, P. PRIETO, Centro de Excelencia en Nuevos Materiales, Colombia	**B6-1-6** Theoretical Thermodynamics of Hard Coatings Materials - Beyond the Mean Field Approximation, **B. ALLING**, Linkoping University, Sweden
3:30 pm	**B1-2-7** Tribological Properties of Cr- and Ti-Doped MoS$_2$ Composite Coatings under Different Humidity Atmosphere, **X.-Z. DING**, X.T. ZENG, Singapore Institute of Manufacturing Technology, Singapore, X.Y. HE, Z. CHEN, Nanyang Technological University, Taiwan	**B6-1-7 *Graduate Student Award Finalist -** Controllably Manipulating AlN Incorporation in Hf$_x$Al$_{1-x}$N(001) Single-Crystal Thin Films During Magnetically–Unbalanced Reactive Magnetron Sputter Deposition by Low-Energy (10 to 80 eV) Ion-Bombardment, **B. HOWE**, E. SAMMANN, J.-G. WEN, M.R. SARDELA, T. SPILA, J.E. GREENE, I. PETROV, Univ of Illinois, A.A. VOEVODIN, AFRL, L. HULTMAN, Linköping Univ, Sweden
3:50 pm	**B1-2-8** Growth Behavior of Magnetron Sputtered Nanocomposite Films: Experimental Observation and Simulation, **T. PEI**, K.P. SHAHA, C. CHEN, Univ. of Groningen, The Netherlands, A. TURKIN, Kharkov Institute of Physics & Technology, Ukraine, I. VAINSHTEIN, J.T.M. DE HOSSON, Univ. of Groningen, The Netherlands	**B6-1-8 Invited** Design Concepts for Superhard Nitride Thin Films; Superlattices, Solid Solutions, and Nanocomposites, **L. HULTMAN**, Linköping University, Sweden
4:10 pm	**B1-2-9** Amorphous Metal Carbides: Magnetron Sputtering of Glassy Zr-Si-C Films, **M. HANSON**, S. URBONAITE, E. LEWIN, U. JANSSON, Uppsala University, Sweden	Invited talk continued.
4:30 pm	**B1-2-10** Characterizing an Inverted Cylindrical Magnetron During Aluminum and Alumina Depositions: Ion Energy Distribution and Langmuir Probe Studies, **S.L. MENSAH**, M. GORDON, University of Arkansas	**B6-1-10** Epitaxial Growth of ZrAlN Alloy and Superlattice Thin Films: Mechanical Properties and Structural Characterization, **N. GHAFOOR**, J. BIRCH, J. JENSEN, L. HULTMAN, M. ODÉN, Linköping University, Sweden
4:50 pm		**B6-1-11** Effect of the Aluminium Contents and the Bias Voltage on the Microstructure Formation in the Ti$_{1-x}$Al$_x$N Protective Coatings, **CH. WÜSTEFELD**, D. RAFAJA, V. KLEMM, TU Bergakademie Freiberg, Germany, M. KATHREIN, CERATIZIT Austria GmbH, Austria, C. MICHOTTE, CERATIZIT Luxembourt S.a.r.l., Austria, C. BAEHTZ, Forschungszentrum Rossendorf, Germany
5:10 pm		**B6-1-12** Microstructure and Characterization of Ni-Alloy/CrN Nanolayered Coatings with Various Bilayer Periods, **H.-H. HUANG**, F.-B. WU, National United University, Taiwan, J.-W. LEE, Tungnan University, Taiwan
5:30 pm		

Monday Afternoon, April 26, 2010

	Tribology & Mechanical Behavior of Coatings & Thin Films **Room: Pacific Salon 1 - Session E3-2** **Tribology of Nanostructured and Amorphous Films** **Moderators:** J. Fontaine, Ecole Centrale de Lyon, R.D. Evans, Timken Company	**Surface Engineering for Thermal Transport, Storage, and Harvesting** **Room: Sunrise - Session TS4** **Moderators:** A.A. Voevodin, Air Force Research Laboratory, T. Fischer, Purdue University
1:30 pm	**E3-2-1** Friction, Wear and Solid Lubrication Mechanisms of MoS_2/Sb_2O_3/Au Composite Coatings, **T.W. SCHARF**, The University of North Texas, P.G. KOTULA, S.V. PRASAD, Sandia National Laboratories	**TS4-1 Invited** Thermoelectric Energy Conversion in Multilayers and Embedded Nanoparticle Materials, **A. SHAKOURI**, University of California at Santa Cruz
1:50 pm	**E3-2-2** Friction Behaviour of Fullerene-Like WS_2 Nanoparticles in Ni-Matrix Coating Compared to PVD WS_2 and MoS_2 Coatings, **F. GUSTAVSSON**, S. JACOBSON, Uppsala University, Sweden	Invited talk continued.
2:10 pm	**E3-2-3** High-Power Ion Beam Deposition of Nanocomposite and Nanolaminate Multilayer Coatings: Synthesis and Characterization*, **T.J. RENK**, T.E. BUCHHEIT, P.G. KOTULA, S.V. PRASAD, Sandia National Laboratories	**TS4-3** Thermal Conductivity in Anisotropic Thin Film Materials, **C. MURATORE**, AFRL, J.J. HU, UDRI/AFRL, J. GENGLER, Spectral Energies/AFRL, R.C. MCLAREN, University of Illinois Urbana-Champaign, S.A. PUTNAM, AFRL/Universal Technology Corp., W.P. KING, D.G. CAHILL, University of Illinois Urbana-Champaign, A.A. VOEVODIN, AFRL
2:30 pm	**E3-2-4** Mapping Tribocorrosion Behaviour of ZrN_xO_y Nano-Structured Thin for Decorative Applications, **M.T. MATHEW**, Rush University Medical Center, E. ARIZA, L.A. ROCHA, P. CARVALHO, F. VAZ, Universidade do Minho, Portugal	**TS4-4** Time Domain Thermoreflectance and 3-Omega Comparison Studies of Polymer-Metallic-Ceramic Nanolaminate Coatings, **A.R. WAITE**, AFRL/Universal Technology Corp., J. GENGLER, Spectral Energies, LLC, J. JONES, AFRL, C. MURATORE, A.A. VOEVODIN, AFRL
2:50 pm	**E3-2-5** Microstructures and Mechanical Properties Evaluation of TiAlN/CrSiN Multilayered Thin Films with Different Bilayer Thickness, **J.-M. KAO**, J.-W. LEE, Tungnan University, Taiwan, L.-C. CHANG, Ming Chi University of Technology, Taiwan	**TS4-5** Effects of Combined Macro- and Nano-Scale Surface Structuring on Pool Boiling, **C.N. HUNTER**, Air Force Research Laboratory, S.A. PUTNAM, A.R. WAITE, Air Force Research Labs/Universal Technology Corp., C. MURATORE, J. JONES, L.J. GSCHWENDER, Air Force Research Laboratory
3:10 pm	**E3-2-6 Invited** Nanostructured Hard Coatings Deposited by Cathodic Arc Evaporation: from Concepts to Applications, **F. SANCHETTE**, C. DUCROS, CEA, France, T. SCHMITT, Ecole Centrale de Lyon, France, P. STEYER, INSA de Lyon, France	**TS4-6** Chromium-Containing Amorphous Hydrogenated Carbon Thin Films as Solar Selective Absorber Coatings: Effects of Hydrogen Content and Metal-Concentration, **H.-H. CHENG**, J.-M. TING, National Cheng Kung University, Taiwan
3:30 pm	Invited talk continued.	
3:50 pm	**E3-2-8** High-Temperature Sliding-Wear Performance of Nanomultilayer PVD Coatings, **F. KUSTAS**, D. FALSONE, Engineered Coatings, Inc., R. WEI, Southwest Research Institute, A. KUSTAS, J. WILLIAMS, Colorado State University	
4:10 pm	**E3-2-9 Invited** Application of Thick and Thin Film Coatings in Oil & Gas Drilling, **C. LIN**, Baker Hughes	
4:30 pm	Invited talk continued.	
4:50 pm	**E3-2-11** Comparative Analysis on Structure and Tribo-Mechanical Properties of Ti-B-C Nanocomposite Coatings Prepared by Magnetron Sputtering, **J.C. SÁNCHEZ-LOPÉZ**, M.D. ABAD, A. JUSTO, Instituto de Ciencia de Materiales de Sevilla (CSIC-US), Spain, M. BRIZUELA, A. GARCÍA-LUIS, Fundación Inasmet-Tecnalia, Spain	
5:10 pm	**E3-2-12** Particle Erosion Characteristics of Super-Elastic Hard Ti-Si-C Films Prepared by PECVD, **S. HASSANI**, J.-E. KLEMBERG-SAPIEHA, L. MARTINU, Ecole Polytechnique de Montreal, Canada	
5:30 pm	**E3-2-13** Tribological Properties of Nanoporous Anodic Aluminum Oxide Film, H.S. KIM, **H.S. AHN**, D.H. KIM, Seoul National University of Technology, Korea, J.H. HAHN, Korea Research Institute of Standards and Science, South Korea, W. LEE, S.J. CHO, Korea Research Institute of Standards and Science, Korea	

Monday Afternoon, April 26, 2010

	Characterization: Linking Synthesis Properties and Microstructure **Room: Royal Palm 1-3 - Session F3** **Application of Ion and Electron Microscopy** **Moderator:** M. Watanabe, Lehigh University	**Applications, Manufacturing, and Equipment** **Room: Sunset - Session G1-2** **Innovations in Surface Coatings and Treatments** **Moderators:** M. Rodmar, Sandvik Tooling, A. Leyland, University of Sheffield
1:30 pm	**F3-1 Invited** Nano-Scale Characterization of Interfaces by Scanning Transmission Electron Microscopy, **V. SROT**, Max Planck Inst for Metals Res., Germany, C.. SCHEU, Ludwig-Maximilians-Univ. of Munich, Germany, M. WATANABE, Lehigh Univ., U. WEGST, Drexel Univ., M. RÜHLE, P.A. VAN AKEN, Max Planck Inst . for Metals Res., Germany	**G1-2-1 Invited** Nano-Structured Multi-Functional Composite Coatings and their Applications, **X.T. ZENG**, Singapore Institute of Manufacturing Technology, Singapore
1:50 pm	Invited talk continued.	Invited talk continued.
2:10 pm	**F3-3** Application of Electron Microscopy and Spectroscopy Techniques to the Characterization of Nanostructured TiAlSiN Coatings, V. GODINHO, D. PHILIPPON, T.C. ROJAS, Instituto de Ciencia de Materiales de Sevilla, Spain, M.-P. DELPLANCKE-OGLETREE, Université Libre de Bruxelles, Belgium, **A. FERNANDEZ**, nstituto de Ciencia de Materiales de Sevilla, Spain	**G1-2-3** Influence of Interface and Multi Layer Structure on Corrosion and Erosion Resistance of Thin Films (PVD), **J. ELLERMEIER**, O. DURST, U. DEPNER, T. TROSSMANN, H. SCHEERER, C. BERGER, TU Darmstadt, Zentrum für Konstruktionswerkstoffe, Germany
2:30 pm	**F3-4** A TEM Study on the Thermal Stability of Sputtered Al_2O_3 Coatings, **V. EDLMAYR**, Montanuniversität Leoben, Austria, D. KIENER, C.. SCHEU, Ludwig-Maximilians-University of Munich, Germany, C. MITTERER, Montanuniversität Leoben, Austria	**G1-2-4** Novel Materials for Thermal Compensated Strain Gauges, **R. BANDORF**, U. HECKMANN, M. LUEBKE, M. PETERS, G. BRAEUER, Fraunhofer IST, Germany
2:50 pm	**F3-5** Atomic Structure Characterization of Cu/MgO(001) Interfaces by C_S-Corrected HRTEM, **S. CAZOTTES**, Z.L. ZHANG, Erich Schmid Institute of Material Science, Austria, R. DANIEL, Montanuniversität Leoben, Austria, D.G. GALL, Rensselaer Polytechnic Institute, G. DEHM, Montanuniversität Leoben, Austria	**G1-2-5** SiBNCO PVD Coatings for High Performance Applications, J. VETTER, Sulzer Metaplas GmbH, Germany, **M. ISAKA**, T. ISHIKAWA, K. KUBOTA, Hitachi Tool Engineering, Japan, G. ERKENS, J. MUELLER, J. ALAMI, Sulzer Metaplas GmbH, Germany
3:10 pm	**F3-6 Invited** On Overview of the TEAM Microscope and its Applications to Interface Problems, **U. DAHMEN**, National Center for Electron Microscopy, LBNL	**G1-2-6** Ultra-Fast and Thick Boriding as a Novel Surface Treatment for Demanding Tribological Applications, **A. ERDEMIR**, Argonne National Laboratory, G. KARTAL, Istanbul Technical University, Turkey, O.L. ERYILMAZ, V. SISTA, G. KRUMDICK, Argonne National Laboratory, S. TIMUR, Istanbul Technical University, Turkey
3:30 pm	Invited talk continued.	**G1-2-7** Using Electroless Plating Cu Technology for TFT-LCD Application, **Y.-T. CHOU**, P.-T. LIU, C.-Y. SU, National Chiao Tung University, Taiwan, H.-M. CHEN, Liquide Laboratories, Japan
3:50 pm	**B5-2-4 **Graduate Student Award Finalist** 3D-Atom Probe Investigations of Ti-Al-N Thin Films, **R. RACHBAUER**, S. MASSL, E. STERGAR, Montanuniversität Leoben, Austria, P. FELFER, University of Sydney, Australia, P.H. MAYRHOFER, Montanuniversität Leoben, Austria	**G1-2-8** Etching Properties of Si and HfO_2 in an Inductively Coupled Plasma Etcher, **S.H. LEE**, B. O'SHAUGHNESSY, University of Texas at Dallas, K.J. PARK, Y.H. JOH, DMS, Korea, K.J. CHUNG, Hanyang University, Korea, G.S. LEE, J.Y. KIM, M.J. KIM, University of Texas at Dallas
4:10 pm		
4:30 pm		
4:50 pm		
5:10 pm		
5:30 pm		

Monday Afternoon, April 26, 2010

Coatings for Fuel Cells and Batteries
Room: Royal Palm 4-6 - Session TS2

Moderators: T. Soczka-Guth, Daimler AG, E. Yu, Newcastle University, B.A. Bude, Mercedes Benz Research and Development North America

1:30 pm	**TS2-3** Recent Progress in Development of Protective Coatings for SOFC Interconnect at PNNL, **G.X. XIA**, J.D. TEMPLETON, Z.M. NIE, Z.G. YANG, J.W. STEVENSON, Pacific Northwest National Laboratory	
1:50 pm	**TS2-4** Effect of Substrate Alloy Composition on Oxidation and Electrical Conductivity Behavior of Co-plated Interconnect Steels, **J.H. ZHU**, Z.H. BI, Tennessee Technological University	
2:10 pm	**TS2-5** Properties of YSZ Electrolyte Deposited by RF Magnetron Sputtering for SOFC Applications, **J. YOON**, N.M. SAMMES, C.M. AN, Y.W. SIN, Colorado School of Mines	
2:30 pm	**TS2-6** Constitution, Microstructure, and Battery Performance of Magnetron Sputtered Li-Co-O Thin Film Cathodes for Lithium-Ion Batteries as a Function of the Working Gas Pressure, **C. ZIEBERT**, B. KETTERER, M. RINKE, C. ADELHELM, S. ULRICH, K.-H. ZUM GAHR, S. INDRIS, TH. SCHIMMEL, Karlsruhe Institute of Technology, Germany	
2:50 pm	**TS2-7 Invited** Anode Coatings for a Direct Glucose Fuel Cell Application, **T. VIDAKOVIC**, Otto-von-Guericke-Unversity, Germany, I. IVANOV, Max-Planck-Insittue, Germany, K. SUNDMACHER, Otto-von-Guericke-Unversity & Max-Planck-Institute, Germany	
3:10 pm	Invited talk continued.	
3:30 pm	**TS2-9** Pseudocapacitive Performance of Hybrid Manganese Oxide Films with Multiwalled-CNTs Additions, **C.-K. LIN**, C.-Y. TSAY, C.-H. WU, C.-Y. CHEN, Feng Chia University, Taiwan, S.-C. WANG, Southern Taiwan University, Taiwan	
3:50 pm	**TS2-10** Conductive Coatings for Stainless Steel Bipolar Plates for PEM Fuel Cells, **G.V. DADHEECH**, M. ABD ELHAMID, General Motors	
4:10 pm	**TS2-11** Nanostructured Titania Materials for PEM Fuel Cell Water Management, **M. ABD ELHAMID**, G.V. DADHEECH, General Motors	
4:30 pm	**TS2-12** Deposition of Hydrothermally Synthesized Pt on Carbon Nanofibers for Use as Direct Methanol Fuel Cell Electrodes, **C.Y. HUANG**, C.M. CHUNG, J.-M. TING, National Cheng Kung University, Taiwan	
4:50 pm	**TS2-1 Invited** To be Announced, **D. REPENNING**, O.Mt GmbH, Germany	
5:10 pm	Invited talk continued.	
5:30 pm		

Tuesday Morning, April 27, 2010

	Coatings for Use at High Temperature **Room: Sunrise - Session A1-1** **Coatings to Resist High Temperature Oxidation** **Moderators:** Y. Zhang, Tennessee Technological University, D. Naumenko, Forschungszentrum Jülich GmbH	**Hard Coatings and Vapor Deposition Technology** **Room: Pacific Salon 3 - Session B1-3** **Sputtering Coatings and Technologies** **Moderators:** P. Eklund, Linköping University, M.-S. Wong, National Dong Hwa University
8:00 am	**A1-1-1 Invited** Oxidation and Hot Corrosion of MCrAlY Alloys, **G.H. MEIER**, F.S. PETTIT, University of Pittsburgh	**B1-3-1 Invited** Sputter-Deposited Thin-Film AlN-Based Electro-Acoustic Devices for Biosensor Applications, **G. WINGQVIST**, Linköping University, Sweden
8:20 am	Invited talk continued.	Invited talk continued.
8:40 am	**A1-1-3** Characterization of the Alumina Scale Formed on a Commercial MCrAlY Coating, **K.A. UNOCIC**, B.A. PINT, Oak Ridge National Laboratory	**B1-3-3** Enhancement of Bottom Electrode on Ferroelectric Properties and Fatigue Properties of BFO/STO Symmetrical Structure, **S.J. CHIU**, National Tsing Hua University, Taiwan, H.-Y. LEE, National Synchrotron Radiation Research Center, Taiwan, G.-P. YU, J.-H. HUANG, National Tsing Hua University, Taiwan
9:00 am	**A1-1-4** Thermodynamic Investigation into the Equilibrium Phase Fractions, Phase Compositions and Phase Transformation in the NiCoCrAl System at Elevated Temperatures, **K. MA**, J.M. SCHOENUNG, University of California, Davis	**B1-3-4** Role of Electrode Materials on Resistive Switching Behaviors of Al_2O_3-Based Memory Devices, **S.-Y. WANG**, D.-Y. LEE, T.-Y. TSENG, National Chiao Tung University, Taiwan
9:20 am	**A1-1-5** Modeling Aluminum Depletion Kinetics in MCrAlY Coatings, **M. RUDOLPHI**, D. RENUSCH, M. SCHÜTZE, Karl-Winnacker-Institut der DECHEMA e.V., Germany	**B1-3-5** Optical Emission Spectroscopy of Radio Frequency PVD Process Related to the AlN Film Stechiometry and Deposition Rate, **J. ACOSTA**, ITESM-CEM, Mexico, E. BAUER-GROSSE, V. BRIEN, P. PIGEAT, R. HUGON
9:40 am	**A1-1-6** Reactivity and Microstructure Evolution of SPS Prepared CoNiCrAlY/Talc Cermet, N. RATEL, D. MONCEAU, **D. OQUAB**, C. ESTOURNÈS, CIRIMAT, France	
10:00 am	**A1-1-7** Effect of Rare Earth (CeO_2) Addition on Oxidation Behavior of Detonation-Gun Sprayed NiCrAlY Coating on Ni-Based Superalloy, **S. KAMAL**, R. JAYAGANTHAN, S. PRAKASH, I.I.T -Roorkee, INDIA	
10:20 am	**A1-1-8 Invited** The Effects of Chemical Composition on the Oxidation Behavior of Platinum-Modified Aluminide Coatings, **K. TOLPYGO**, Honeywell Aerospace	
10:40 am	Invited talk continued.	
11:00 am	**A1-1-10** Early Stages of Oxidation of NiPtAl Coatings in Low and High pO_2 Gases, **P. SONG**, D. NAUMENKO, Forschungszentrum Jülich GmbH, Germany, W. BRAUE, German Aerospace Center (DLR), Germany, L. SINGHEISER, Forschungszentrum Jülich GmbH, Germany, W. QUADAKKERS, Forschungszentrum Jülich GmbH, Institute of Energy Research, D-52425, Jülich, Germany	
11:20 am		
11:40 am		
12:00 pm		

Tuesday Morning, April 27, 2010

	Hard Coatings and Vapor Deposition Technology **Room: Town & Country - Session B6-2** **Hard and Multifunctional Nano-Structured Coatings** **Moderators:** C.P. Mulligan, U.S. Army ARDEC, Benét Laboratories, R. Sanjines, EPFL, P. Zeman, University of West Bohemia	**Tribology & Mechanical Behavior of Coatings & Thin Films** **Room: Pacific Salon 1 - Session E2-1** **Mechanical Properties and Adhesion** **Moderators:** R. Chromik, McGill University, L. Davies, Caterpillar, J. Michler, Empa
8:00 am	**B6-2-1** The Role of Interfaces in the Strengthening and Stability of Superhard Nanocomposites, **S. VEPREK**, R.F. ZHANG, S.H. SHENG, Technical University Munich, Germany, A.S. ARGON, Massachusetts Institute of Technology, M. JILEK, SHM s.r.o, A. BERGMAIER, Universität der Bundeswehr, Germany	**E2-1-1 Invited** Strength: Size Matters in 1, 2 and 3 D, **W.W. GERBERICH**, BEABER, L.M. HALE, D.D. STAUFFER, University of Minnesota
8:20 am	**B6-2-2** Durability of CrSiN Nanocomposite Coatings: Key-Role of Grain Boundaries and Interfaces, **T. SCHMITT**, Ecole Centrale de Lyon, France, P. STEYER, INSA de Lyon, France, J. FONTAINE, Ecole Centrale de Lyon, France, N. MARY, INSA Lyon, France, F. SANCHETTE, CEA, France, C. ESNOUF, INSA Lyon, France	Invited talk continued.
8:40 am	**B6-2-3 Invited** Advanced Modelling of Structures and Properties of Crystalline, Nanocrystalline and Amorphous Nitrogen-Based Materials, **J. HOUSKA**, University of West Bohemia, Czech Republic	**E2-1-3** Some Unpleasant Truth About Dynamic/Oscillatory Indentation Measurement Procedures, **N. SCHWARZER**, Saxonian Institute of Surface Mechanics, Germany
9:00 am	Invited talk continued.	**E2-1-4** On Hall-Petch Strengthening Below 10 nm Grain Size, **A.F. JANKOWSKI**, Texas Tech University
9:20 am	**B6-2-5** Electrical Conductivity in Si-Based Transition Metal Nanocomposite Nitrides, **R. SANJINES**, D. OEZER, C. SANDU, EPFL, Switzerland, J. PATSCHEIDER, Empa, Switzerland	**E2-1-5** The Effect of Microstructure on the Mechanical Properties of Submicron Thin Films and Nanostructured Devices, **S.J. BULL**, Newcastle University, United Kingdom
9:40 am	**B6-2-6** Microstructure and Mechanical Properties of Nanocomposite Ti-B-C, Ti-B-C-N, and Ti-B-C-N-Si Films Deposited by Unbalanced Magnetron Sputtering, **I.-W. PARK**, J.J. MOORE, B. MISHRA, Colorado School of Mines, A.A. VOEVODIN, Air Force Research Laboratory, K.H. KIM, NCRC-HyMAS, Korea, E.A. LEVASHOV, Moscow State Institute for Steels and Alloys,, Russia	**E2-1-6** The Effect of Surface Roughness on Nanoindentation of Hard Coatings: Simulation and Experiment, **C. WALTER**, C. MITTERER, Montanuniversität Leoben, Austria
10:00 am	**B6-2-7** Combinatorial Approach to the Growth of Al-Cr-O-N Thin Films by Reactive r.f. Magnetron Sputtering, **D. DIECHLE**, M. STÜBER, H. LEISTE, S. ULRICH, Forschungszentrum Karlsruhe, Germany	**E2-1-7** Size Effects in Ceramics - The influence of Yield Stress on the Effect of Size, **S. KORTE**, R.J. STEARN, W.J. CLEGG, University of Cambridge, United Kingdom
10:20 am	**B6-2-8 Invited** Design of hard Ti-Based Nitride Coatings and Multilayer Structuring, **T. SUZUKI**, N. FUKUMOTO, Keio University, Japan, H. HASEGAWA, Okayama University, Japan, T. WATANABE, Kanagawa Academy of Science and Technology, Japan, S. KINOSHITA, Tungaloy Corporation, Japan	**E2-1-8** Numerical Simulation of Nanoindentation and Comparisons with Experimental Results for hard Metal and TiN Film, **J.D. BRESSAN**, State University of Santa Catarina, Brazil, C.M. LEPIENSKI, Federal University of Parana, Brazil
10:40 am	Invited talk continued.	**E2-1-9 Invited** Dimensionality of Plasticity Size Effects- the ‘Thinness’ Effect, **N.M. JENNETT**, X.D. HOU, National Physical Laboratory, United Kingdom, R. GHISLENI, J. MICHLER, Empa, Switzerland, A.J. BUSHBY, Queen Mary University of London, United Kingdom
11:00 am	**B6-2-11** Multifunctional NbC-Based Nanocomposite Thin Films, **N. NEDFORS**, Uppsala University, Sweden, O. TENGSTRAND, Linköping University, Sweden, E. LEWIN, A. FURLAN, Uppsala University, Sweden, P. EKLUND, L. HULTMAN, Linköping University, Sweden, U. JANSSON, Uppsala University, Sweden	Invited talk continued.
11:20 am		**E2-1-11** Mechanical Properties Extraction of Bulk Materials and Thin Films Based on Vickers Instrumented Indentation Tests, **S.A. RODRIGUEZ**, M.C.M. FARIAS, R.M. SOUZA, University of São Paulo, Brazil
11:40 am		**E2-1-12** Effects of Mechanical Properties, Residual Stress and Indenter Tip Geometry on Instrumented Indentation Data in Thin Films, **C.E.K. MADY**, S.A. RODRIGUEZ, A.G. GÓMEZ, R.M. SOUZA, University of São Paulo, Brazil
12:00 pm		

Tuesday Morning, April 27, 2010

	Characterization: Linking Synthesis Properties and Microstructure **Room: Royal Palm 1-3 - Session F1-1** **Advances in Characterization of Coatings and Thin Films** **Moderators:** P. Schaaf, Ilmenau University of Technology, M. Baker, University of Surrey	**New Horizons in Coatings and Thin Films** **Room: Royal Palm 4-6 - Session H1-1** **Nanoparticle, Nanowiere, Nanotube, and Graphene Thin-Films and Coatings** **Moderators:** S. Kodambaka, University of California Los Angeles, D. Frankel, Newcastle University
8:00 am	**F1-1-1 Invited** GDOES for Accurate Well Resolved Coatings and Thin Film Analysis, **M. WILKE**, G. TEICHERT, Bauhaus-University Weimar, Germany, P. SCHAAF, Ilmenau University of Technology, Germany	**H1-1-1** Preparation of Ni-P/Al_2O_3 Core-shell Structure Nanoparticles by Electroless Deposition with Pd-free Surface Activation, **H.T. HSU**, W.S. CHANG, Feng Chia University, Taiwan, C.H. LIN, Industrial Technology Research Institute, Taiwan, T.J. YANG, Feng Chia University, Taiwan
8:20 am	Invited talk continued.	**H1-1-2** Gadolinium-Doped Ceria Particle Films for Intermediate-Temperature Gas Sensing Applications, **C.-Y. CHEN**, C.-L. LIU, P.-L. SUN, C.-J. CHANG, C.-K. LIN, Feng Chia University, Taiwan
8:40 am	**F1-1-3** Effect of Process Conditions on Microscopic Structure and Macroscopic Properties of Zinc-Based Coatings, **J. BAIER**, U. BECK, T. LANGE, BAM, Germany, G. MOLLATH, Fraunhofer-Institute IPK, Germany, M. SAHRE, BAM, Germany, A. SPILLE-KOHOFF, CFX Berlin Software GmbH, Germany	**H1-1-3 Invited** Carbon Onions, Some Methods of Preparation and Possible Applications, **L. SILLER**, Newcastle University, United Kingdom
9:00 am	**F1-1-4** Thorough XPS Analyses to Investigate Thin Films Components and Improve Performances of All-Solid-State Thin Films Batteries, **B. FLEUTOT**, ICMCB & STMicroelectronics, B. PECQUENARD, ICMCB, France, H. MARTINEZ, IPREM, France, A. LEVASSEUR, ICMCB, France	Invited talk continued.
9:20 am	**F1-1-5** Chemical States in Al-Si-N Nanocomposite Thin Films as Evidenced by XPS, A. PÉLISSON-SCHECKER, H.J. HUG, **J. PATSCHEIDER**, Empa, Switzerland	**H1-1-5** Fabrication of Gold and Aluminum Nanodot Assisted Growth of Nanoroots for Application in Amorphous/Crystalline Silicon Composite Thin Film Solar Cells, **B. NEWTON**, H. MOHAMMED, University of Arkansas, H. ABU-SAFE, Lebanese American University, Lebanon, H. NASEEM, University of Arkansas
9:40 am	**F1-1-6 Invited** Recent Advanced in XPS for Thin Film Analys, **C. BLOMFIELD**, Kratos Analytical Ltd., Manchester, UK, D. Suman, Kratos Analytical Inc., New York	**H1-1-6** Formation and Nonvolatile memory characteristics of W nanocrystals by In-Situ Steam Generation Oxidation, **S.-C. CHEN**, National Tsing Hua University, Taiwan, T.-C. CHANG, National Sun Yat-Sen University, Taiwan, C.-M. HSIEH, S.M. SZE, National Chiao Tung University, Taiwan, W.-P. NIEN, C.-W. CHAN, ProMOS Technologies, Taiwan, F.-S. HUANG, National Tsing Hua University, Taiwan
10:00 am	Invited talk continued.	**H1-1-7** Fabrication and Memory Effect of Nickel Nanocrystals Formed by Co-Evaporating with Dielectric Pallets, **C.-W. HU**, Natl Chiao-Tung Univ, Taiwan, T.-C. CHANG, Natl Sun Yat-Sen Univ, C.-H. TU, Natl Chiao-Tung Univ, Y.-H. HUANG, Natl Tsing Hua Univ, C.-C. LIN, Natl Chiao-Tung Univ, M.-C. CHEN, Natl Sun Yat-Sen Univ, F.-S. HUANG, Natl Tsing Hua Univ, S.M. SZE, T.-Y. TSENG, Natl Chiao-Tung Univ
10:20 am	**F1-1-8** Formation of $CoSi_2/CoSi_xN_y$ Nanocrystals for Nonvolatile Memory Application, **J.-J. HUANG**, T.-C. CHANG, National Sun Yat-sen University, Taiwan	**H1-1-8 Invited** Observation of Single Colloidal Platinum Nanocrystal Growth Trajectories, **H. ZHENG**, R. SMITH, Lawrence Berkeley National Lab, J.-W. JUN, University of California at Berkeley, C. KISIELOWSKI, U. DAHMEN, Lawrence Berkeley National Lab, P. ALIVISATOS, University of California at Berkeley
10:40 am	**F1-1-9** Microstructure of Cr/ta-C Multilayers as Studied by SAXS, TEM and EELS, **U. RATAYSKI**, D. RAFAJA, V. KLEMM, U. MÜHLE, TU Bergakademie Freiberg, Germany, H.-J. SCHEIBE, M. LEONHARDT, Fraunhofer Institute for Materials and Beam Technology IWS, Germany	Invited talk continued.
11:00 am	**F1-1-10** Hydrogen Incorporation on the Improvement of Electrical Characteristics for IGZO TFT, **S.-Y. HUANG**, T.-C. CHANG, M.-C. CHEN, S.-C. CHEN, S.-W. TSAO, National Sun Yat-sen University, Taiwan	**H1-1-10** Substrate-Induced Semiconducting Graphene on Palladium, **S.-Y. KWON**, (UNIST), Korea, C.V. CIOBANU, Colorado School of Mines, V. PETROVA, University of Illinois, V.B. SHENOY, Brown University, J.B. BARENO, University of Illinois, V.G. GAMBIN, Northrop Grumman Space and Technology, I. PETROV, University of Illinois, S. KODAMBAKA, University of California Los Angeles
11:20 am	**F1-1-11** Resistance Switching of MnO_2 Thin Film of Nonvolatile Memory Application, **Y.-T. TSAI**, National Chiao-Tung University, Taiwan, T.-C. CHANG, National Sun Yat-Sen University, Taiwan, C.-C. LIN, L.-S. CHIANG, S.M. SZE, T.-Y. TSENG, National Chiao-Tung University, Taiwan	**H1-1-11** Synthesis of Graphene Oxide (GO): Effects of Processing Steps and Parameters on the Resulting GO Thin Film, **T.T. WU**, J.-M. TING, National Cheng Kung University, Taiwan
11:40 am		
12:00 pm		

Bioactive Coatings and Surface Biofunctionalization
Room: Sunset - Session TS3-1

Moderators: S. Kumar, University of South Australia,
E. Saiz, Lawrence Berkeley National Laboratory

8:00 am	**TS3-1-1 Invited** Functionalization of Implant Surfaces, **J. JANSEN**, Radboud University Nijmegen Medical Center, The Netherlands	
8:20 am	Invited talk continued.	
8:40 am	**TS3-1-3** Corrosion and Tribological Properties of PVD and CVD Coatings in a Simulated Biomedical Environment, **L. WANG**, X. NIE, University of Windsor, Canada	
9:00 am	**TS3-1-4** Comparison of Tribological and Anti-Microbial Properties of CrN/Ag, ZrN/Ag, TiN/Ag, and CrN/Cu Nanocomposite Coatings, **P. KELLY**, H. LI, K.A. WHITEHEAD, J. VERRAN, Manchester Metropolitan University, United Kingdom, R.D. ARNELL, University of Central Lancashire, United Kingdom, I. IORDANOVA, University of Sofia, Bulgaria	
9:20 am	**TS3-1-5** Development of Si_xO_y Surface Modifications for Improved Bonding in Biomedical Implants, **J PIASCIK**, RTI International, S WOLTER, Duke University, S GREGO, B. STONER, RTI International	
9:40 am	**TS3-1-6** Study of Bactericidal Efficiency of Magnetron Sputtered TiO_2 Films Deposited at Varying Oxygen Partial Pressure, **I. BANERJEE**, A. BIHARI PANDA, P. LAHA, H K, B. SARKAR, P.K. BARHAI, Birla Institute of Technology, India, A. DAS, Bhabha Atomic Research Center, India, MAHAPATRA, Birla Institute of Technology, India	
10:00 am		
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10:40 am		
11:00 am		
11:20 am		
11:40 am		
12:00 pm		

Tuesday Afternoon, April 27, 2010

	Coatings for Use at High Temperature **Room: Sunrise - Session A1-2** **Coatings to Resist High Temperature Oxidation** **Moderators:** Y. Zhang, Tennessee Technological University, D. Naumenko, Forschungszentrum Jülich GmbH	**Hard Coatings and Vapor Deposition Technology** **Room: Town & Country - Session B6-3** **Hard and Multifunctional Nano-Structured Coatings** **Moderators:** C.P. Mulligan, U.S. Army ARDEC, Benét Laboratories, R. Sanjines, EPFL, P. Zeman, University of West Bohemia
1:30 pm	**A1-2-1** Electrodeposition from Ionic Liquids - A New Future for Bond Coat Technology, **M. CRAIG**, M. ROBINSON, Cranfield University, United Kingdom, S. CAPORALI, U. BARDI, Universita di Firenza, Italy, J.R. NICHOLLS, Cranfield University, United Kingdom	**B6-3-2 Invited** Hard and Decorative Coatings Based on Nanocomposites Consisting of Dielectric Matrixes Embedded with Metal Nanoparticles, **A. CAVALEIRO**, University of Coimbra, Portugal
1:50 pm	**A1-2-2** NiAl(CrZrHfSi) High Temperature Overlay Coating for Gas Turbine Engines, **B.T. HAZEL**, R. DAROLIA, M.H. RUCKER, General Electric	Invited talk continued.
2:10 pm	**A1-2-3** Effects of Substrate Surface Roughness and Microstructure on the Properties of dc Magnetron Sputter Deposited NiAl-Hf and NiAl-Cr-Hf Coatings, **M.L. WEAVER**, M.A. BESTOR, M.S. KIRSCH, J.P. ALFANO, The University of Alabama	**B6-3-4** Ag Solid Lubricant Transport in CrN-Ag Nanocomposite Coatings, **C.P. MULLIGAN**, U.S. Army ARDEC, Benét Laboratories, T.A. BLANCHET, D.G. GALL, Rensselaer Polytechnic Institute
2:30 pm	**A1-2-4** Formation of High Temperature Multifunction Coatings on the Basis of Spherical Al Particles, **V. KOLARIK**, M. JUEZ LORENZO, P. KODJAMANOVA, H. FIETZEK, Fraunhofer ICT, Germany	**B6-3-5** Adaptive VN/Ag Nanocomposite Coatings in the 25 to 1000° C Temperature Rante, **S.M. AOUADI**, D. STONE, D.P. SINGH, A. ABU-NADA, Southern Illinois University Carbondale, K. POLYCHRONOPOULOU, F. NAHIF, C.G. REBHOLZ, University of Cyprus, C. MURATORE, A.A. VOEVODIN, Air Force Research Laboratory
2:50 pm	**A1-2-5 Invited** Platinum Group Metal-Containing Bond Coats, **T. POLLOCK**, D. WIDREVITZ, R. ADHARAPURAPU, J. ZHU, University of Michigan, D.M. LIPKIN, GE Global Research Center	**B6-3-6** Ag -T i(C, N)-Based Coatings for Biomedical Applications: Influence of Composition and Structure on the Mechanical/Tribological and Biological Behaviour, S. RIBEIRO, Univ do Minho, Portugal, J.C. SÁNCHEZ-LOPÉZ, M.D. ABAD, Inst de Ciencia de Matls de Sevilla , R. ESCOBAR GALINDO, Inst de Ciencia de Matls de Madrid, M. HENRIQUES, **S. CARVALHO**, Univ do Minho
3:10 pm	Invited talk continued.	**B6-3-7** Plasma Spray Deposition of Optical NanoComposites Coatings and Preforms, **M. GELL**, E.H. JORDAN, C. MUOTO, J ROTH, University of Connecticut
3:30 pm	**A1-2-7** High-Temperature Behavior of Magnetron Sputtered Si-B-C-N Materials Far Above 1000° C, **P. ZEMAN**, S. PROKSOVA, R. CERSTVY, J. VLCEK, University of West Bohemia, Czech Republic	**B6-3-8 Invited**The Synthesis of Metal Oxides by Reactive Cathodic Arc Evaporation, **J. RAMM**, H. RUDIGIER, B. WIDRIG, OC Oerlikon Balzers AG, Liechtenstein, M. DÖBELI, Paul Scherrer Institute and ETH Zurich, Switzerland, L. DE ABREU VIEIRA, A. DOMMANN, A. NEELS, CSEM SA Neuchâtel, Switzerland, J. THOMAS, Leibniz-Institut für Festkörper- und Werkstoffforschung Dresden, Germany
3:50 pm	**A1-2-8** Oxidation Behavior of Si-Doped Nanocomposite CrAlSiN Coatings, **H.-W. CHEN**, J.-G. DUH, National Tsing Hua University, Taiwan	Invited talk continued.
4:10 pm	**A1-2-9** TaN_x Diffusion Barrier on Cobalt Cemented Tungsten Carbide, Y.-I. CHEN, B.-L. LIN, **Y.-C. KUO**, National Taiwan Ocean University, Taiwan	**B6-3-10** Mechanical and Tribological Behavior of TiCN Coatings Deposited by Large Area Filtered Cathodic Vacuum Arc, **Y.H. CHENG**, T. BROWNE, B. HECKERMAN, American Eagle Instruments, Inc.
4:30 pm	**A1-2-10** Advanced High Temperature Coatings for Turbine Blade Applications: *A REVIEW*, **F. GHADAMI**, University of Tehran, Iran	
4:50 pm		
5:10 pm		
5:30 pm		

Tuesday Afternoon, April 27, 2010

	Tribology & Mechanical Behavior of Coatings & Thin Films **Room: Pacific Salon 1 - Session E2-2** **Mechanical Properties and Adhesion** **Moderators:** R. Chromik, McGill University, L. Davies, Caterpillar, J. Michler, Empa	**Characterization: Linking Synthesis Properties and Microstructure** **Room: Royal Palm 1-3 - Session F1-2** **Advances in Characterization of Coatings and Thin Films** **Moderators:** P. Schaaf, Ilmenau University of Technology, M. Baker, University of Surrey
1:30 pm	**E2-2-1 Invited** Double-Brittle Transitions in Micropillar Compression, P.R. HOWIE, S. KORTE, University of Cambridge, United Kingdom, R. GHISLENI, J. MICHLER, Empa, Switzerland, **W.J. CLEGG**, University of Cambridge, United Kingdom	**F1-2-1 Invited** Femtosecond Laser Spectroscopy of Spins: Magnetization Dynamics in Thin Magnetic Films with Spatio-Temporal Resolution, **E. CARPENE**, ULTRAS, CNR-INFM, Dipartimento di Fisica, Politecnico di Milano, Italy, E. MANCINI, D. DAZZI, C. DALLERA, ULTRAS, CNR-INFM, Italy, E. PUPPIN, CNISM, Italy, S. DE SILVESTRI, ULTRAS, CNR-INFM, Italy
1:50 pm	Invited talk continued.	Invited talk continued.
2:10 pm	**E2-2-3** Yield Strength, Deformation, and Fracture of Coherently Strained InGaAs Superlattice by In-Situ Micropillar Compression, **R. GHISLENI**, Empa, Switzerland, B. EHRLER, Queen Mary University of London, United Kingdom, R. RAGHAVAN, Empa, Switzerland, K. P’ NG, A.J. BUSHBY, Queen Mary University of London, United Kingdom, J. MICHLER, Empa, Switzerland	**F1-2-3** In-Situ XRD Observations of Rapid Reactions in Nanoscale Ni-Al Multilayer Foils Using Synchrotron Radiation, C.G. REBHOLZ, **I.E. GUNDUZ**, K. FADENBERGER, C. TSOTSOS, University of Cyprus, B. SCHMITT, Paul Scherrer Institut, Cyprus, C. DOUMANIDIS, University of Cyprus
2:30 pm	**E2-2-4** Analysis of the Mechanical and Tribological Properties of the Multilayer Ultrathin Films for MEMS Applications, **K.A. RZEPIEJEWSKA-MALYSKA**, R. KOODAKAL, J. MICHLER, Empa, Switzerland	**F1-2-4** XRD In-Situ Study of Time and Thickness Dependence of Crystallization of Amorphous TiO_2 Thin Films and Powders, **R. KUZEL**, L. NICHTOVA, Z. MATEJ, Charles University in Prague, Czech Republic, J. MUSIL, University of West Bohemia, Czech Republic
2:50 pm	**E2-2-5** 3D Finite Element Study of Scratch Tests Conducted on Coated Systems with Orthotropic Elastic-Plastic Material Properties, **N. FUKUMASU**, R.M. SOUZA, A.P. TSCHIPTSCHIN, University of São Paulo, Brazil	**F1-2-5** Resistive Switching Characteristics of IGZO Thin Films for Nonvolatile Memory Applications, **M.-C. CHEN**, T.-C. CHANG, S.-Y. HUANG, S.-C. CHEN, National Sun Yat-Sen University, Taiwan, C.-W. HU, S.M. SZE, National Chiao Tung University, Taiwan
3:10 pm	**E2-2-6** Scratch Resistance of Platinum Coatings, M. TOPIĆ, iThemba LABS, South Africa, **G. FAVARO**, CSM Instruments, Switzerland, R. BUCHER, iThemba LABS, South Africa, C.I. LANG, University of Cape Town, South Africa	
3:30 pm	**E2-2-7** Fundamentals of Adhesion of Thermal Spray Coatings: Adhesion of Single Splats, **E. BALIĆ**, M. HADAD, Empa, Switzerland, P. BANDYOPADHYAY, IIT Kharagpur, India, J. MICHLER, Empa, Switzerland	
3:50 pm	**E2-2-8** Evaluation of Ti Cold Spray Splats by Indentation and Ball Shear Testing, **R. CHROMIK**, D. GOLDBAUM, J. AJAJA, S. YUE, J. SHOCKLEY, McGill University, Canada, E. IRISSOU, J.-G. LEGOUX, National Research Council Canada (NRC), Canada, N. RANDALL, CSM Instruments	
4:10 pm	**E2-2-9** Fatigue Behavior of a Structural Steel Coated with 50% WC-Co/50% Colmonoy Alloy Deposited by Means of HVOF Thermal Spray, **E.S. PUCHI-CABRERA**, Universidad Central de Venezuela	
4:30 pm	**E2-2-10** Adhesion of Composite Structured TiTaBN Coatings Deposited by Magnetron Sputtering, **I. EFEOGLU**, Atatürk University, Turkey, O. BARAN, Erzincan University, Turkey, B. PRAKASH, Luleå University of Technology, Turkey	
4:50 pm	**E2-2-11** High Temperature Testing of Transition Metal Nitride Materials, **F. GIULIANI**, Imperial College London, United Kingdom, P.H. MAYRHOFER, Montanuniversität Leoben, Austria	
5:10 pm	**E2-2-12** High-Precision Determination of Residual Stress of Polycrystalline Coatings Using the Optimised XRD-sin$^2\psi$ Technique, **Q. LUO**, Sheffield Hallam University, United Kingdom	
5:30 pm	**E2-2-13** Boron Containing Coating Systems for Hot Forming Tools, **H. PASCHKE**, Fraunhofer IST, Germany	

Tuesday Afternoon, April 27, 2010

	Applications, Manufacturing, and Equipment **Room: Pacific Salon 3 - Session G6** **Coatings, Pre-Treatment, Post-Treatment and Duplex Technology** **Moderators:** N. Bagcivan, RWTH Aachen University, E. Kusano, Kanazawa Institute of Technology	**New Horizons in Coatings and Thin Films** **Room: Royal Palm 4-6 - Session H1-2\Nanoparticle, Nanowiere, Nanotube, and Graphene Thin-Films and Coatings** **Moderators:** S. Kodambaka, University of California Los Angeles, D. Frankel, Newcastle University
1:30 pm	**G6-1** Characterization of Duplex Layer Structures Produced by Plasma-Assisted Low Temperature Nitrocarburizing Treatment of Austenic Stainless Steel 316L, **Y. GUO**, G. MARCOS, T. CZERWIEC, T. BELMONTE, Ecole des Mines de Nancy, France	**H1-2-1** Surface Energy of Carbon Fullerenes and Nanotubes, **D. HOLEC**, M.A. HARTMANN, Montanuniversität Leoben, Austria, F.G. RAMMERSTORFER, Vienna University of Technology, Austria, O. PARIS, F.D. FISCHER, P.H. MAYRHOFER, Montanuniversität Leoben, Austria
1:50 pm	**G6-2 Invited** Cemented Carbides Mechanical Treatments and Nanointerlayers for Improving the Adhesion of Hppms Pvd Films on Cutting Inserts, **K.-D. BOUZAKIS**, G. SKORDARIS, S. GERARDIS, G. KATIRTZOGLOU, S. MAKRIMALLAKIS, E. BOUZAKIS Aristoteles Univ of Thessaloniki, Greece / Fraunhofer, T. LEYENDECKER, S. BOLZ, W. KOELKER, CemeCon AG, Germany	**H1-2-2** Growth Mechanisms of Carbon Nanotubes (CNTs) by RF or DC PECVD at Low Temperature, **H.Y. WANG**, J.J. MOORE, M. BRAJENDRA, Colorado School of Mines
2:10 pm	Invited talk continued.	**H1-2-3** Silver Vanadate Nanorods: Synthesis, Characterization and Performance, **K. POLYCHRONOPOULOU**, University of Cyprus, D.P. SINGH, Southern Illinois University Carbondale, A. HADJIAFXENTI, C.G. REBHOLZ, University of Cyprus, S.M. AOUADI, Southern Illinois University Carbondale
2:30 pm	**G6-4** Effects of Post Deposition Annealing on Resistive Switching Characteristics of SrZrO$_3$ Thin Films, **M.-H. LIN**, M.-C. WU, S.W. JAN, Y.H. HUANG, National Chiao Tung University, Taiwan, C.-H. LIN, Windbond Electroncs Corporation, Taiwan, T.-Y. TSENG, National Chiao Tung University, Taiwan	**H1-2-4** Fabrication of Nanodevices from Horizontally Grown Silicon Nanowires Using a Thin Aluminum Film as a Catalyst, **H. MOHAMMED**, University of Arkansas, H. ABU-SAFE, Lebanese American University, Lebanon, B. NEWTON, S. EL-GHAZALY, H. NASEEM, University of Arkansas
2:50 pm	**G6-5** Improvement of Press Dies Used for the Production of Diamond Composites by Means of DUPLEX-PVD-Coatings, W. TILLMANN, E. VOGLI, **S. MOMENI**, TU Dortmund, Germany	**H1-2-5** Characterization and Optical Properties of Cu$_2$O Nanowire Arrays Growth by PAM Template, **Y.M. SHEN**, Y.-T. SHIN, National Cheng Kung University, Taiwan, S.-C. WANG, Southern Taiwan University, Taiwan, J.-L. HUANG, National Cheng Kung University, Taiwan
3:10 pm	**G6-6** Effect of Process Duration on Structure, Chemistry, and Mechanical Properties of Borided Low Carbon Steels, **G. KARTAL**, S. TIMUR, Istanbul Technical University, Turkey, O.L. ERYILMAZ, A. ERDEMIR, G. KRUMDICK, Argonne National Laboratory	**H1-2-6** Size Reduction of One-Dimensional ZnO Through the Addition of NaOH into Zn(NO$_3$)$_2$/(NH$_4$)$_2$CO$_3$ Mixture, **W.-Y. WU**, National University of Tainan, Taiwan, J.-M. TING, W.-Y. KUNG, National Cheng Kung University, Taiwan
3:30 pm	**G6-7** Plasma Modification of Al$_2$O$_3$ for Improved Adhesive Strength in Composite Materials, **A. BUJANDA**, D. PAPPAS, C. HO, B.E. STEIN, R.E. JENSEN, U.S. Army Research Laboratory	**H1-2-7** Controllable Synthesis of Well-Ordered ZnO Nanorod Arrays by Nanosphere Lithography and Their Field Emission Properties, **H. YAO**, T.-Y. TSENG, H. LIN, National Chiao Tung University, Taiwan
3:50 pm	**G6-8** Electrochemical Behaviour of HVOF Coatings Based on Cermet-Ni Based Alloys Mixture, **L.G. GIL**, UNEXPO, Venezuela, R. FRAGIEL, A. RODRIQUEZ, Universidad Central de Venezuela (UCV), Venezuela, J. SUBERO, Universidad Nacional Experimental Politecnica (UNEXPO), Venezuela, M.H. STAIA, Universidad Central de	**H1-2-8** Selective Growth of ZnO Nanorods for Gas Sensors Using Ink-Jet Printing and Hydrothermal Processes, C.-J. CHANG, **S.-T. HUNG**, C.-K. LIN, C.-Y. CHEN, E.-H. KUO, Feng Chia University, Taiwan
4:10 pm	**G6-9** Effect of Plasma Nitrocarburizing on Properties of AISI 4340 Steel Submitted to Different Heat Treatments, **V.H. BAGGIO-SCHEID**, J.A. ABDALLA, Institute of Advanced Studies, Brazil	
4:30 pm	**G6-10** Duplex Plasma Technology for Aluminum, **S. MEIER**, Fraunhofer IWM, Germany	
4:50 pm	**G6-11** Improvement of the Cavitation Erosion Resistance of UNS 31803 Stainless Steel by Duplex Treatment, D.H. MESA, Technological University of Pereira, Colombia, C.E. PINEDO, Heat Tech Ltd., Brazil, **A.P. TSCHIPTSCHIN**, University of São Paulo, Brazil	
5:10 pm	**G6-12** Low Temperature Plasma Carburizing of AISI F51 Duplex Stainless Steel, **C.E. PINEDO**, Heat Tech Ltd., Brazil, J.D. BRESSAN, State University of Santa Catarina, A.P. TSCHIPTSCHIN, University of São Paulo, Brazil	
5:30 pm	**G6-13** Mechanical and Corrosion Properties of Duplex Treated AISI301 Stainless Steel, **M. AZZI**, M.B. BENKAHOUL, J.-E. KLEMBERG-SAPIEHA, L. MARTINU, Ecole Polytechnique de Montreal, Canada	

Tuesday Afternoon, April 27, 2010

Bioactive Coatings and Surface Biofunctionalization
Room: Sunset - Session TS3-2

Moderators: S. Kumar, University of South Australia,
E. Saiz, Lawrence Berkeley National Laboratory

1:30 pm	**TS3-2-1 Invited** Engineering Nanostructured Devices for Bioadhesive Drug Delivery, **T. DESAI**, University of California	
1:50 pm	Invited talk continued.	
2:10 pm	**TS3-2-3** Freeform Plasma Generated Maskless Cell Patterning for Tissue Engineering Applications, **E. YILDIRIM-AYAN**, Drexel University, H. AYAN, Murray State University, D. PAPPAS, U.S. Army Research Laboratory, A. FRIDMAN, W. SUN, Drexel University	
2:30 pm	**TS3-2-4** Surface Modification of Polyurethane and Silicone for Therapeutic Medical Technics by Means of Electron Beam, **C. WETZEL**, J. SCHÖENFELDER , W. SCHWARZ, Fraunhofer Institute for Electron Beam and Plasma Technology, Germany, R.H.W. FUNK, University of Technology Dresden – Institute of Anatomy, Germay	
2:50 pm	**TS3-2-5** Modification of the Surface of Polymer Implants by Deposition of Multifunctional Bioactive Nanostructured Films (MuBiNaFs) With and Without Stem Cells, **D.V. SHTANSKY**, I.A. BASHKOVA, A.N. SHEVEIKO, National Univ of Sci & Tech "MISIS", Russia, M.C. JIMENEZ DE HARO, Instituto de Ciencia de Materiales de Sevilla, Spain, A.S. GRIGORYAN, Central Research Dental Institute, Russia	
3:10 pm	**TS3-2-6 Invited** Nanotechnology for Improving Regenerative Medicine, **T. WEBSTER**, Brown University	
3:30 pm	Invited talk continued.	
3:50 pm	**TS3-2-8** Osteoblast Growth Affected by Micro-arc Oxidized β -titanium Alloy, **H.-T. CHEN**, Feng Chia Univ; China Medical Univ Hospital, Taiwan, C.-J. CHUNG, Central Taiwan Univ of Sci & Tech, Taiwan, T.-C. YANG, Feng Chia Univ, Taiwan, I.-P. CHIANG, C.-H. TANG, China Medical Univ, Taiwan, K.-C. CHEN, J.-L. HE, Feng Chia Univ, Taiwan	
4:10 pm	**TS3-2-9** Development of Surface Modification Techniques for the Covalent Attachment of Insulin-Like Growth Factor-1 (IGF-1) on PECVD Silica-Coated Titanium, **S. KUMAR**, E. SZILI, University of South Australia, M. DENICHILO, TGR BioSciences, Australia, R. SMART, University of South Australia, N. VOELCKER, Flinders University of South Australia	
4:30 pm		
4:50 pm		
5:10 pm		
5:30 pm		

Wednesday Morning, April 28, 2010

	Coatings for Use at High Temperature **Room: Sunrise - Session A1-3** **Coatings to Resist High Temperature Oxidation** **Moderators:** Y. Zhang, Tennessee Technological University, D. Naumenko, Forschungszentrum Jülich GmbH	**Hard Coatings and Vapor Deposition Technology** **Room: Town & Country - Session B2** **Arc and E-Beam Coatings and Technologies** **Moderators:** I. Gorokhovsky, Southwest Research Institute, J. Vetter, Sulzer Metaplas GmbH
8:00 am	**A1-3-1** Determination of the DBTT of Aluminide Coatings and its Influence on the Mechanical Behavior of Coated Specimens, **S. DRYEPONDT**, Oak Ridge National Laboraotry, B.A. PINT, Oak Ridge National Laboratory	**B2-1** Arc Plasma Acceleration: A Method for Improving Coating Quality by Decreasing Macro Particle Inclusions, **W. BETH**, V. KHOMINICH, Phygen Coatings, Inc.
8:20 am	**A1-3-2** Oxidation Performance of Low-Temperature Pack Aluminide Coatings on Ferritic-Martensitic Steels, **B.L. BATES**, Y. ZHANG, Tennessee Technological University, B.A. PINT, Oak Ridge National Laboratory	**B2-2 Invited** The Electron Beam High Rate Deposition in Combination with Guided Arc Discharges - Present State and Actual Developments, **J.-P. HEINß**, FEP, Germany
8:40 am	**A1-3-3** The Dependence of High Temperature Resistance of Aluminized Steel Exposed to Water Vapour Oxidation, C.-J. WANG, **M. BADARUDDIN**, National Taiwan University of Science and Technology, Taiwan	Invited talk continued.
9:00 am	**A1-3-4 Invited** Thin Pure-Metal Films Allowing to Rapid Development of α-Al$_2$O$_3$ Scale on High-Temperature Alloys and Coatings, **S. HAYASHI**, Y. KITAJIMA, T. NARITA, S. UKAI, Hokkaido University, Japan	**B2-4** Structure and Mechanical Properties of Single- and Multilayer Hard TiAlN/TiAlYN-based Coatings, Produced by Reactive Cathodic-Arc Evaporation, **V. GOLTVYANYTSYA**, S. GOLTVYANYTSYA, Real Ltd., Ukraine, A. DEMCHYSHYN, L. KULAK, Institute of Problems in Material Science, NANU, Ukraine
9:20 am	Invited talk continued.	**B2-5** Microstructure Evolution of Ti$_3$SiC$_2$ MAX Phase Cathodes During Reactive Cathodic Arc Evaporation, **J.Q. ZHU**, A. ERIKSSON, N. GHAFOOR, Linköping University, Sweden, M. JOHANSSON, SECO Tools AB, Sweden, J. ROSEN, L. HULTMAN, M. ODÉN, Linköping University, Sweden
9:40 am	**A1-3-6** Development of Thermally Grown Oxide on β-NiAl During Initial Stages of Oxidation at 1100°C, **H. CHOI**, University of Central Florida, J. JEDLINSKI, AGH University of Science and Technology, Poland, Y. SOHN, University of Central Florida	**B2-6** Influence of Process Parameters on Structure of TiAlN Coating Prepared by a System With Rotary Arc Cathodes, P. VOGL, PIVOT a.s., Czech Republic, **M. JILEK JR.**, SHM, s.r.o., Czech Republic
10:00 am	**A1-3-7** Influence of Thermal Exposure on the Stability of Non-Equilibrium Microstructures of Sputter Deposited Nanocrystalline 304 and 310 SS Coatings, **N.S. CHERUVU**, R. WEI, Southwest Research Institute, D.W. GANDY, Electric Power Research Institute	**B2-7** Optimization of Micro Arc Oxidation Processes for Corrosion Resistance of Ti6Al4Valloys by Using Taguchi Method, **E. DEMIRCI**, E. ASLAN, Y. TOTIK, I. EFEOGLU, Atatürk University, Turkey
10:20 am	**A1-3-8** The High-Temperature Oxidation Behavior of Hot-Dipping Al/Al-Si Coating on High Silicon Ductile Iron, **M.B. LIN**, National Taiwan University of Science and Technology, Taiwan	**B2-8** Phase Formation of Alumina Thin Films Deposited by Ionized PVD, K. SARAKINOS, D. MUSIC, RWTH Aachen University, Germany, F. NAHIF, University of Cyprus, K. JIANG, A. BRAUN, C. ZILKENS, **J.M. SCHNEIDER**, RWTH Aachen University, Germany
10:40 am	**A1-3-10 Invited** A review of Sulphidation and Oxidation Processes in Gasturbines, their Simulation and Modelling via Laboratory Tests, **D.S. RICKERBY**, Rolls-Royce plc, United Kingdom	**B2-9 Invited** Processing With Pulsed Plasmas: A Comparison of Cathodic Arcs and High Power Impulse Magnetron Sputtering, **A. ANDERS**, Lawrence Berkeley National Laboratory
11:00 am	Invited talk continued.	Invited talk continued.
11:20 am		**B2-11** Evaluation of Residual Stress and Coating Composition on Rounded Surfaces and Edges by Measurements and Cutting Tests, **J. BOHLMARK**,H.I. BLOMQVIST, M.L. AHLGREN, Sandvik Tooling Sverige AB, Sweden
11:40 am		**B2-12** Highly Transparent and Conductive ZnO:Al Thin Films Prepared by Laser Induced High Current Pulsed Arc at Low Deposition Temperature, **J.-B. WU**, C.-Y. CHEN, J.-J. CHANG, C.-T. SHIH, M.-S. LEU, Industrial Technology Research Institute, Taiwan
12:00 pm		

Wednesday Morning, April 28, 2010

	Fundamentals and Technology of Multifunctional Thin Films: Towards Optoelectronic Device Applications **Room: Royal Palm 1-3 - Session C3** **Optical Characterization of Thin Films** **Moderators:** U. Beck, BAM, E. Schubert, University of Nebraska-Lincoln	**Tribology & Mechanical Behavior of Coatings & Thin Films** **Room: Pacific Salon 1 - Session E2-3** **Mechanical Properties and Adhesion** **Moderators:** R. Chromik, McGill University, L. Davies, Caterpillar, J. Michler, Empa
8:00 am	**C3-1** Photoluminescence, Photoacoustic and Raman Spectra of Zinc Oxide Films Grown by LP-MOCVD Using Diethylzinc and Water as Precursors, **T. TERASAKO**, T. YAMANAKA, S. YURA, Ehime University, Japan, M. YAGI, Kagawa National College of Technology, Japan, S. SHIRAKATA, Ehime University, Japan	**E2-3-1** Viscoelastic Properties of Thin Polymer Film on Rigid Substrate, **J.-L. LOUBET**, S. BEC, S. PAVAN, Ecole Centrale de Lyon, France
8:20 am	**C3-2** ZnO Preferred Orientation Control by Homo- and Hetro-Structure Buffer Layer Growth on Si (111) Using Atomic Layer Deposition with Flow-Rate Interruption Method, **C.-S. KU**, National Synchrotron Radiation Research Center, Taiwan, J.-M. HUANG, C.-M. LIN, National Hsinchu University of Education, Taiwan, H.-Y. LEE, National Synchrotron Radiation Research Center, Taiwan	**E2-3-2 Invited** Mechanical Properties Determined Via Probing of Freestanding Thin Films, **M.R. BEGLEY**, University of California, Santa Barbara
8:40 am	**C3-3 Invited** Study of Magnetic Interfaces with Polarized Soft X-Rays, **C.S.-H. SÁNCHEZ-HANKE**, Brookhaven National Laboratory	Invited talk continued.
9:00 am	Invited talk continued.	**E2-3-4** Numerical Study of Tensile Tests Conducted on Systems with Elastic-Plastic Films Deposited onto Elastic-Plastic Substrates, N. FUKUMASU, C.M. ANGELO, University of São Paulo, Brazil, M. IGNAT, Universidad de Chile, **R.M. SOUZA**, University of São Paulo, Brazil
9:20 am	**C3-5** Vectorial Scattering Spectroscopic Ellipsometry Analysis of Dielectric Thin Films on Textured Solar Cells, M.F. SAENGER, University of Nebraska-Lincoln, C.M. HERZINGER, J.A. Woollam Co., Inc., M. SCHADEL, Q-Cells A.G., Germany, **J. HILFIKER**, J. SUN, J.A. Woollam Co., Inc., T. HOFMANN, SCHUBERT, Univ of Nebraska-Lincoln, J.A. WOOLLAM, Univ of Nebraska-Lincoln and J.A. Woollam Co., Inc.	**E2-3-5** Thermal Fatigue of Ion Nitrided and Duplex-Treated Hot-Work Tool Steel, M.A. QUIÑONES-SALINAS, **R.D. MERCADO-SOLIS**, Universidad Autonoma de Nuevo Leon, Mexico, J. SMOLIK, A. MAZURKIEWICZ, Institute for Sustainable Technologies, Poland
9:40 am	**C3-6 Invited** *In-Situ* Studies on Thin Functional Polymer Films by Ellipsometry and Vibrational Spectroscopy, **K.-J. EICHHORN**, Leibniz-Institut für Polymerforschung Dresden e.V., Germany	**E2-3-6** Contact Resonance Force Microscopy Technique to Determine Local Elastic Properties, **J.H. HAHN**, Korea Research Institute of Standards and Science, South Korea, D.H. KIM, H.S. AHN, Seoul National University of Technology, South Korea
10:00 am	Invited talk continued.	**E2-3-7 Invited**Semiconductor Nanowires in Novel Device Concepts: the need for Structural and Mechanical Integrity and Ways to Reliably Characterize these Properties, **S. CHRISTIANSEN**, Max-Planck-Inst of Microstructure Physics, TH. STELZNER, V. SIVAKOV, Inst of Photonic Tech, Albert Einstein, BERGER, Max-Planck Inst , Albert Einsteinstr, S. HOFFMANN, J. MICHLER, Empa
10:20 am	**C3-8** Monitoring Protein Deposition of Self-Assembled Monolayers of Alkanethiols on Gold *In Situ* with Combined Quartz Crystal Microbalance and Spectroscopic Ellipsometry, **K.B. RODENHAUSEN**, B.A. DUENSING, A.K. PANNIER, SCHUBERT, University of Nebraska-Lincoln	Invited talk continued.
10:40 am	**C3-9** Evolution of Crystalline Phase Formation of Titanium Oxide Thin Films using Reactive Magnetron Sputtering and Annealing, C.-K. CHUNG, **M.-W. LIAO**, National Cheng Kung University, Taiwan	**E2-3-9** Development of a Biaxial Tensile Module at Synchrotron Beamline for the Study of Mechanical Properties of Supported Thin Films, **P.O. RENAULT**, S. DJAZIRI, E. LE BOURHIS, P. GOUDEAU, Univ of Poitiers-France, G. GEANDIER, D. THIAUDIÈRE, A. BOUAFFAD, Synchrotron Soleil, O. CASTELNAU, R. CHIRON, R. RANDRIAMAZAORO, LPMTM-CNRS, D. FAURIE, LPMTM-CNRS
11:00 am	**C3-10** Pulsed Laser Deposition of $(MoO_3)_{1-x}(V_2O_5)_x$ Thin Films: Preparation, Characterization and Gasochromic Studies, **C.-C. CHANG**, T.K. CHEN, J.-Y. LUO, T.-W. HUANG, K.-W. YEH, C.-T. KE, P.-C. HSU, M.-J. WANG, M.-K. WU, Academia Sinica, Taiwan	**E2-3-10** Determination of Residual Stresses and their Relaxation in Brush-Plated Gold and Silver Coatings Depending on Current Density, H. LILLE, J. KÕO, **A. RYABCHIKOV**, Estonian University of Life Sciences, Estonia, R. VEINTHAL, V. MIKLI, Tallinn University of Technology, Estonia
11:20 am	**C3-11** Numerical Ellipsometry: Advanced Analysis of Thin Absorbing Films in the n-k Plane, **F. URBAN**, D. BARTON, Florida International University	**E2-3-11** Nano Mechanical Characterization of Ultra Thin DLC Coatings by Nanoindentation and Nano Scratch Testing, **N. RANDALL**, CSM Instruments, USA, G. FAVARO, CSM Instruments, Switzerland
11:40 am		
12:00 pm		

Wednesday Morning, April 28, 2010

	Applications, Manufacturing, and Equipment **Room: Pacific Salon 3 - Session G2** **Coatings for Automotive and Aerospace Applications** **Moderators:** H. Rudigier, OC Oerlikon Balzers AG, G.V. Dadheech, General Motors	**New Horizons in Coatings and Thin Films** **Room: Royal Palm 4-6 - Session H3** **Surface Engineering of Coatings: Tribo, Bio and Nano-Corrosion Effects** **Moderators:** M. Stack, University of Strathclyde, M.T. Mathew, Rush University Medical Center
8:00 am	**G2-1** Plasma Coatings for High Efficient Power Train in Automobile, K. BOBZIN, N. BAGCIVAN, RWTH Aachen University, Germany, N. GOEBBELS, **K. YILMAZ**, Surface Engineering Institute RWTH Aachen, Germany	**H3-1 Invited** Nano-Scale Surface Engineering for Tribological and Biomedical Applications, **M. ZOU**, University of Arkansas
8:20 am	**G2-2** Wear and Corrosion Protection of AJ62 Mg Alloy by Plasma Electrolytic Oxidation (PEO) Process for Mg Engine Application, **P. ZHANG**, X. NIE, University of Windsor, Canada	Invited talk continued.
8:40 am	**G2-3** A Study on the Influence of Bond Material on Honing Engine Cylinder Bores with Diamond Coated Stones, **L. SABRI**, S. MEZGHANI, Arts et Métiers Paris Tech, France, M. EL MANSORI, Arts et Métiers ParisTech, France	**H3-3** Influence of Rare Earth Element Incorporation on the Behavior of Magnetron Sputtered Al Based Alloys, **J. CREUS**, C. REBERE, C. BERZIOU, A. PEREZ, S. TOUZAIN, Université de la Rochelle, France, A. BILLARD, Lermps, Utbm, France
9:00 am	**G2-4 Invited** Opportunities and Challenges to Coatings Applications in the Automotive Industry - Select Case Studies, **M.L. LUKITSCH**, GM Research & Development Center	**H3-4** Corrosion Resistance of Amorphous Niobium Oxide Thin Films, **S.E. RODIL**, G. RAMIREZ, D. TURCIO-ORTEGA, S. MUHL, Universidad Nacional Autónoma de México, Mexico, L. ESCOBAR-ALARCON, E. CAMPS, Instituto Nacional de Investigaciones Nucleares, Mexico
9:20 am	Invited talk continued.	**H3-5** Electrochemical Behavior of the TiN Coating for the Orthopedic Applications: Influence of Immersion Time and Protein Content, M.T. MATHEW, Rush Univ Medical Center, R. POURZAL, Univ of Duisburg-Essen, Germany, **M. MCFARLAND**, Acree Technologies Incorporated, N.J. HALLAB, Rush Univ, A. FISCHER, Univ of Duisburg-Essen, Germany, M.A. WIMMER, Rush Univ
9:40 am	**G2-6** Wear-Resistant HVOF- Coatings of Aluminum Steel Hybrid Structures, W. TILLMANN, E. VOGLI, **B. RUETHER**, TU Dortmund, Germany	**H3-6** Surface Nanocrystallization in a NiTi Alloy Subjected to Surface Mechanical Attrition Treatment, **T. HU**, City University of Hong Kong, China, C. CHU, Southeast University, China, R.K.Y. FU, P.K. CHU, City University of Hong Kong, China, J. LU, The Hong Kong Polytechnic University, China, K.W.K. YEUNG, The University of Hong Kong, China
10:00 am	**G2-7** Influence of Simulated Stamping Force on Coating Failure Behavior, **J.F. SU**, X. NIE, University of Windsor, Canada, T. MULHOLLAND, General Motors Company	**H3-7 Invited** Bio-Corrosion and Cell Culture: Implications in Dentistry and Orthopedics, **C. SUKOTJO**, University of Illinois, M.A. WIMMER, Rush University
10:20 am	**G2-8 Invited** From Coatings to Electrochemical Energy Storage for Automotive Applications, **Y.T. CHENG**, University of Kentucky	Invited talk continued.
10:40 am	Invited talk continued.	**H3-9** Identification of Tribo-Corrosion Regimes for Dental Materials and Coatings, **M. STACK**, C. HODGE, University of Strathclyde, United Kingdom
11:00 am		**H3-10** Comparison of the Properties of Al-Ti and Al-Mg EBPVD Coatings, **A. PEREZ**, Université de La Rochelle, France, F. SANCHETTE, CEA, France, A. BILLARD, Lermps, Utbm, France, C.R. RÉBÉRÉ, C. BERZIOU, S. TOUZAIN, J. CREUS, Université de La Rochelle, France
11:20 am		**H3-11 **Graduate Student Award Finalist** Influence of pH on the Tribocorrosion Nature of the CpTi in an Oral Environment: Mechanisms and Synergism, **S. ABEY**, University of Illinois, M.T. MATHEW, D.J. HALL, Rush University Medical Center, N.J. HALLAB, M.A. WIMMER, Rush University, C. SUKOTJO, University of Illinois
11:40 am		**H3-12** In-Situ Impedance Spectroscopy Characterisation of Plasma Electrolytic Oxidation Process for Deposition of Ca- and P-Containing Coatings on Ti, **A. ALEKSEY**, University of Sheffield, United Kingdom, E. PARFENOV, Ufa State Aviation Technological University, Russia, A. MATTHEWS, University of Sheffield, United Kingdom
12:00 pm		**H3-13** Tribological Behaivor and Corrosion Performance of Nanocomposite Coating Layer of nc-TiN/a-Si3N4Deposited by Sputtering on AISI 316L Stainless Steel Duplex for Biomedical Applications, **J. GARCIA**, M. FLORES, Universidad de Guadalajara, Mexico

Experimental and Computational Studies of Molecular materials and Thin Films
Room: Sunset - Session TS1

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

8:00 am	**TS1-1 Invited** Printed Electronic and Photonic Materials for Device Applications, **G. JABBOUR**, Arizona State University	
8:20 am	Invited talk continued.	
8:40 am	**TS1-3 Invited** Microscopic Characterization of Organic Thin Films for Appliactions in Organic Electronics, **G. WITTE**, Philipps-University Marburg, Germany	
9:00 am	Invited talk continued.	
9:20 am	**TS1-5** Controlling Organic Semiconductor Growth for High Performance Organic Transistors, **A. VIKAR**, S. MANSFELD, Y. ITO, Z. BAO, Stanford University	
9:40 am	**TS1-6** Controlling Organic Semiconductor Crystallization and Morphology using Solution Shearing, **G. GIRI**, Stanford University, H. BECERRIL, Brigham Young University, E. VERPLOEGEN, Z. BAO, Stanford University	
10:00 am	**TS1-7** Aligned Growth of Pentacene on Pre-Patterned Substrates, **V.A. POZDIN**, A. ZAKHIDOV, D.-M. SMILGIES, G.M. MALLIARAAS, Cornell University	
10:20 am	**TS1-8 Invited** Computational Insight Towards Understanding Design Rules for Functional II-Electron Systems, **P. CLANCY**, R.A. CANTRELL, Cornell University	
10:40 am	Invited talk continued.	
11:00 am	**TS1-10 Invited** Architectural Complexity and Tunable Chemical Function in Metal - Organic Coordination Networks at Surfaces, **S.L. TAIT**, Indiana University	
11:20 am	Invited talk continued.	
11:40 am	**TS1-12** A Family of High Strength Ternary Titanium and Vanadium Nitride Thin Films, D. SANGIOVANNI, **V. CHIRITA**, L. HULTMAN, Linkoping University, Sweden	
12:00 pm		

Wednesday Afternoon, April 28, 2010

	Coatings for Use at High Temperature **Room: Sunrise - Session A2** **Coatings for Use in Harsh Thermochemical Environments** **Moderator:** J.R. Nicholls, Cranfield University	**Fundamentals and Technology of Multifunctional Thin Films: Towards Optoelectronic Device Applications** **Room: Royal Palm 1-3 - Session C1** **Recent Advances in Optical Thin Films** **Moderators:** J. Bellum, Sandia National Laboratories, R. Sczupak, Reynard Corporation
1:30 pm	**A2-1** Hot Corrosion of New HIPIMS Nanostructured and Microstructured Coatings on Gamma-TiAl, LASANTA, M. TEJERO, A. REY, S. MATO, M.P. HIERRO, **F.J. PERÉZ**, Universidad Complutense de Madrid, Spain, P.EH. HOVSEPIAN, A.P. EHIASARIAN, Sheffield Hallam University, United Kingdom	**C1-1** Colloidal Monolayer and Patterned Films Made of Titania Sub-Micron Particles Prepared by Sol-Gel Process, **S. PORTAL**, C. CORBELLA, R. AMADE, O. ARTEAGA, M.A. VALLVÉ, J. IGNÉS-MULLOL, E. BERTRAN, University of Barcelona, Spain
1:50 pm	**A2-2 Invited** The Role of Alkali Compounds in the Corrosion of High Temperature Steels, **L.-G. JOHANSSON**, J.-E. SVENSSON, M. HALVARSSON, J. PETTERSSON, N. FOLKESON, Chalmers Univ of Technology, Sweden, C. PETTERSSON, Volvo Powertrain, Sweden, T. JONSSON, S. KARLSSON, Chalmers Univ of Technology, Sweden	**C1-2** Centrifuge Technology: A Breakthrough in Quantitative Adhesion Testing of Optical Coatings, **U. BECK**, G. REINERS, BAM, Germany, D. LERCHE, U. RIETZ, LUM GmbH, Germany, H. NIEDERWALD, Carl Zeiss Jena GmbH, Germany
2:10 pm	Invited talk continued.	**C1-3 Invited** Mechanisms of Sub-Picosecond Pulse Laser-Induced Damage to Optical Thin Films, **W. RUDOLPH**, L. EMMERT, D. NGUYEN, University of New Mexico, C.S. MENONI, E. KROUS, D. PATEL, Colorado State University
2:30 pm	**A2-4** Effect of Coating Composition on the Protective Behavior of Cr/Cr Oxide Coatings Against Metal Dusting, L. MELO, **D. MELO**, Instituto Politécnico Nacional, Mexico, O. SALAS, ITESM, Mexico, V.M. LOPEZ-HIRATA, Instituto Politécnico Nacional, Mexico, J. OSEGUERA, ITESM, Mexico	Invited talk continued.
2:50 pm	**A2-5** Development of Residual Stresses During Deposition of Protective Coatings Against Metal Dusting, **L.M. LÓPEZ**, ITESM, Mexico, D. MELO, Instituto Politécnico Nacional, Mexico, O. SALAS, ITESM, Mexico, R. REICHELT, University of Muenster, Germany, J. OSEGUERA, ITESM, Mexico, J. MUÑOZ, CINVESTAV-Qro., Mexico	**C1-5** Synthesis, Structure, and Optical Properties of Au-TiO_2 and Cu-TiO_2 Nanocomposite Thin Films, **A.N. RANADE**, M.E. GRAHAM, Y.W. CHUNG, Northwestern University
3:10 pm	**A2-6** Evaluation of the Protective Behavior of Al/Al Oxide Coatings Under Carburizing Atmospheres, **J.D. ALVAREZ**, O. SALAS, J. OSEGUERA, ITESM, Mexico, D. MELO, Instituto Politécnico Nacional, Mexico	**C1-6** Persistent Conductivity in Post-Growth Doped ZnO Films Following Pulsed UV Laser Irradiation, **G.J.. EXARHOS**, Pacific Northwest National Laboratory, L.J. WANG, Carleton College
3:30 pm	**A2-7** Modelling Hot Corrosion Processes for Alloys and Coating Systems in Industrial Gas Turbines Burning Bio-Mass Derived Fuels, J.R. NICHOLLS, **N.J. SIMMS**, A. ENCINAS-OROPESA, L. NALIN, Cranfield University, United Kingdom	
3:50 pm	**A2-8** Microstructure Evolution and Surface Characteristics of Ni-Based Coatings Under Phosphate Glasses Molding Process, **K.-C. CHANG**, Y.-C. HSIAO, C.-C. CHANG, F.-B. WU, National United University, Taiwan	
4:10 pm	**A2-9** High Temperature Properties of Multilayer CrAlSiN Coatings Deposited on Hot Work Tool Steel AISI H11, E. TORRES, **D. UGUES**, Z. BRYTAN, Politecnico di Torino, Italy	
4:30 pm		
4:50 pm		
5:10 pm		
5:30 pm		
5:50 pm		

Wednesday Afternoon, April 28, 2010

	Carbon & Nitride Matls: Synthesis-Structure-Property Relationships - Room: Pacific Salon 3 Session D1 **Boron Nitride, Carbon Nitride-Based Multifunctional Materials and Group-III (Al, Ga, In) Nitride Materials** **Moderators:** M. Keunecke, Fraunhofer IST, A. Fernandez, nstituto de Ciencia de Materiales de Sevilla	**Tribology & Mechanical Behavior of Coatings & Thin Films Room: Pacific Salon 1 - Session E4/G4** **Coatings for Machining Advanced Materials and Advanced Manufacturing Methods** **Moderators:** W. Kalss, OC Oerlikon Balzers, H.G. Fuss, CemeCon
1:30 pm	**D1-1 Invited** A Novel Cubic Boron Nitride Coating Technology: Coating Design, Deposition, Analysis, and Performance in Turning Applications, W. JIANG, Duralor, LLC, **A.P. MALSHE**, University of Arkansas and NanoMech, LLC	**E4/G4-1** A Comparative Study on the Role of Solid Lubricant for Improving Tribological Properties in Turning Process, N.S. KUMAR REDDY, BITS-Pilani Hyderabad Campus, INDIA, **M. NOUARI**, Ecole Nationale Supérieure des Mines de Nancy, FRANCE
1:50 pm	Invited talk continued.	**E4/G4-2 Invited** Adaptive PVD Coating for Machining of Hard to Cut Materials, **G.S. FOX-RABINOVICH**, McMaster University, Canada, K. YAMAMOTO, Kobe Steel, Ltd., Japan, B. BEAKE, Micro Materials Ltd, United Kingdom, S. VELDHUIS, McMaster University, Canada
2:10 pm	**D1-3** Comparative Study of Chemical Bonding Observed for Ion-Implanted BN, B_4C and CN_x Films With B-C-N Films, **E. BENGU**, M.F. GENISEL, Bilkent University, Turkey	Invited talk continued.
2:30 pm	**D1-4 Invited** Challenges in the Industrial-Scale Deposition of Thick Amorphous and Fullerene-Like Carbon Nitride Coatings, **E. BROITMAN**, Carnegie Mellon University, L. HULTMAN, Linköping University	**E4/G4-4** Micro/Nanocrystalline Bilayered CVD Diamond Coated Tools for Hardmetal Machining, F.A. ALMEIDA, University of Aveiro, Portugal, N. DERKAOUI, F. BÉNÉDIC, UPR 1311 CNRS, Université Paris 13, France, **R.F. SILVA**, University of Aveiro, France, F.J. OLIVEIRA, University of Aveiro, Portugal
2:50 pm	Invited talk continued.	**E4/G4-5** Evaluating the Performance of Edge-Conditioned and Coated Milling Cutters using a Half-Length Approach, **M. SARWAR**, J. HAIDER, Northumbria University, United Kingdom
3:10 pm	**D1-6** Texture Development and Microstructure Characterization of Piezoelectric AlN Thin Films Fabricated by Pulsed Closed FieldUnbalanced Magnetron Sputtering, **M. HASHEMINIASARI**, J.J. MOORE, B. MISHRA, Colorado School of Mines	**E4/G4-7** Dry Stamping Feasibility Test for Various DLC-Cotaed Dies, **T. AIZAWA**, Shibaura Institute of Technology, Japan, S. KATAOKA, Shounan Institute of Technology, Japan, T. UEMATSU, Tokyo Metropolitan Industry Research Institute, Japan
3:30 pm	**D1-7** *In-situ* Stress Measurements During Growth of GaN(0001)/Al_2O_3(0001) by Reactive DC Magnetron Sputter Epitaxy, **M. JUNAID**, P. SANDSTRÖM, J. BIRCH, Linköping University, Sweden	**E4/G4-8** Antifriction Finishing Properties in Diamond Honing, **M. EL MANSORI**, Arts et Métiers ParisTech, France
3:50 pm		**E4/G4-9 Invited** γ-Al_2O_3 Coatings for Challenging Cutting Operations, K. BOBZIN, N. BAGCIVAN, **M. EWERING**, RWTH Aachen University, Germany
4:10 pm		Invited talk continued.
4:30 pm		**E4/G4-11** Factors Controlling the Behavior of Coatings Under Extreme Contact Loading in Dry Machining Processes, **F. KONE**, C. CZARNOTA, B. HADDAG, M. LAZARD, M. NOUARI, Ecole des Mines de Nancy, France
4:50 pm		**E4/G4-12** A New Hybrid Tribological Characterisation of Coating Delamination Process in Cutting Tools Wear, **S. BAHI**, GIP-INSIC, France, M. NOUARI, Ecole des Mines de Nancy, France, A. MOUFKI, LPMM, France, M. EL MANSORI, Arts et Métiers ParisTech, France, A. MOLINARI, LPMM, France
5:10 pm		
5:30 pm		
5:50 pm		

Wednesday Afternoon, April 28, 2010

	Tribology and Mechanical Behavior of Coatings and Thin Films **Room: Sunset - Session E5** **Nano- and Microtribology** **Moderators:** N. Randall, CSM Instruments, USA, J.H. Hahn, Korea Research Institute of Standards and Science	**New Horizons in Coatings and Thin Films** **Room: Royal Palm 4-6 - Session H2-1** **High Power Impulse Magnetron Sputtering** **Moderators:** R. Bandorf, Fraunhofer IST, J.-E. Klemberg-Sapieha, Ecole Polytechnique de Montreal
1:30 pm	**E5-1 Invited** Applications of Nano-Scale Coatings in Tribological Systems, **D.-E. KIM**, Yonsei University, Korea	**H2-1-1 Invited** Diagnostics of HPPMS Discharges; Sputtered Vapor Ionization, Transport and Transfer of Sputtered particles and Active Species, **J. BRETAGNE**, D. BENZEGGOUTA, C. BOISSE-LAPORTE, Université Paris Sud, France, L. DE POUCQUES, Université Henri Poincaré, France, M. GANCIU, National Insitute of Laser,
1:50 pm	Invited talk continued.	Invited talk continued.
2:10 pm	**E5-3** Evaluation of Thin PVD Coatings Using Rooms and High Temperature Nano-Testing, **N.M. RENEVIER**, University of Central Lancashire, United Kingdom, B. BEAKE, Micromaterials Ltd, United Kingdom	**H2-1-3** High Rate Copper Deposition by Gasless High Power Impulse Magnetron Sputtering, **J. ANDERSSON**, Uppsala University, Sweden, A. ANDERS, Lawrence Berkeley National Laboratory
2:30 pm	**E5-4** A Combination of Multiscale Hierarchical Patterns and DLC Coating for Enhancing Tribological Properties of Silicon Surfaces, D.-C. PHAM, K. NA, S. PIAO, S. YANG, J. KIM, **E.-S. YOON**, Korea Institute of Science and Technology, Korea	**H2-1-4** Spatial and Temporal Investigation of High Power Pulsed Magnetron Discharges by Optical 2D-Imaging, **B. LIEBIG**, University of Liverpool, United Kingdom, N.S. BRAITHWAITE, The Open University, United Kingdom, J.W. BRADLEY, University of Liverpool, United Kingdom, P. KELLY, Manchester Metropolitan University, United Kingdom
2:50 pm	**E5-5** Micro-Tribological Performance of Au-MoS_2 Nanocomposite and Au/MoS_2 Bilayer Coatings, **P. STOYANOV**, S. GUPTA, McGill University, Canada, J.R. LINCE, The Aerospace Corporation, R. CHROMIK, McGill University, Canada	**H2-1-5** Characterization and Simulation of HIPIMS Discharges in Gas Mixtures, **M.A. LANGE**, A.N. REED, Air Force Research Laboratory / Universal Technology Corporation, J. JONES, C. MURATORE, A.A. VOEVODIN, Air Force Research Laboratory
3:10 pm	**E5-6** Micro-Tribology Experiments on Low Friction Coatings, **M. GEE**, J.W. NUNN, National Physical Laboratory, United Kingdom	**H2-1-6** Density Measurement of Films Deposited by High Power Impulse Magnetron Sputtering, M. SAMUELSSON, D. LUNDIN, **D. MAGNFÄLT**, J. JENSEN, U. HELMERSSON, Linköping University, Sweden
3:30 pm	**E5-7** In Situ Accelerated Nano-Wear - a New Technique to Fill the Measurement Gap, **B. BEAKE**, Micro Materials Ltd, United Kingdom, T. LISKIEWICZ, Leeds University, United Kingdom	**H2-1-7** Time-Resolved Characteristics of Reactive HIPIMS Plasmas, M. HALA, **J.-E. KLEMBERG-SAPIEHA**, J. CAPEK, L. MARTINU, Ecole Polytechnique de Montreal, Canada
3:50 pm	**E5-8** Advancement in Nano Tribology with the Use of the Single Point Nanoscratching Technique, **E. POIRÉ**, EP Laboratories Inc	**H2-1-8** Influence of HIPIMS Plasma Ionization on the Microstructure and Texture of TiN Thin Films, **A.P. EHIASARIAN**, A. VETUSHKA, Sheffield Hallam University, United Kingdom, Y. ARANDA GONZALVO, Hiden Analytical Ltd., United Kingdom, G. SÁFRÁN, P.B. BARNA, Hungarian Academy of Sciences, Hungary
4:10 pm	**E5-9** Designing Robust Hydrophobic Surfaces, **M.M. GENTLEMAN**, Texas A&M University, J.A. RUUD, GE Global Research	**H2-1-9** HPPMS (Cr,Al,V)N and (Cr,Al,W)N Thin Films for Friction Reduction Through High Temperature Activation, K. BOBZIN, N. BAGCIVAN, **S. THEIß**, R.H. BRUGNARA, RWTH Aachen University, Germany
4:30 pm		**H2-1-10** Low Temperature Synthesis of α-Al_2O_3 Films by High-Power Pulsed Plasma Chemical Vapor Deposition, **K. JIANG**, K. SARAKINOS, RWTH Aachen University, Germany, S. KONSTANTINIDIS, Université de Mons, France, J.M. SCHNEIDER, RWTH Aachen University, Germany
4:50 pm		**H2-1-11** Tribological Properties of Cr_2AlC Coatings Manufactured via DCUMS and HPPMS, **A. FLORES RENTERIA**, C. LEYENS, BTU Cottbus, Germany, M. TO BABEN, RWTH Aachen, Germany, J.M. SCHNEIDER, RWTH Aachen University, Germany
5:10 pm		**H2-1-12** Exploring the Potential of High Power Pulsed Magnetron Sputtering for the Deposition of Diamond Like Carbon Films, **K. SARAKINOS**, A. BRAUN, C. ZILKENS, S. MRÁZ, J.M. SCHNEIDER, RWTH Aachen University, Germany, H. ZOUBOS, P.A. PATSALAS, University of Ioannina, Greece
5:30 pm		**H2-1-13** HPPMS – The Next Generation of Dedicated Coatings for High Precision Cutting Tools, **T. LEYENDECKER**, W. REICHERT, S. BOLZ, C. SCHIFFERS, CemeCon AG, Germany
5:50 pm		

NOTES

Thursday Morning, April 29, 2010

	Coatings for Use at High Temperature **Room: Sunrise - Session A3-1** **Thermal Barrier Coatings** **Moderators:** A. Bolcavage, Rolls-Royce Corporation, R.G. Wellman, Cranfield University, B.T. Hazel, General Electric	**Hard Coatings and Vapor Deposition Technology** **Room: Town & Country - Session B5-1** **Properties & Characterization of Hard Coatings and Surfaces** **Moderators:** M. Fenker, FEM Research Institute, Y.W. Chung, Northwestern University, G. Abadias, University of Poitiers
8:00 am	**A3-1-1 Invited** Models for Foreign Object Damage to Columnar Zirconia Thermal Barrier Coatings, M.W. CROWELL, University of California, Santa Barbara (now at Los Alamos National Lab), **R. MCMEEKING**, A.G. EVANS, University of California, Santa Barbara	**B5-1-1 Invited** Determination of Mechanical Properties of FIB-Based Cantilever Bending Technique, **R. PIPPAN**, K. MATOY, ST. MASSL, C. MOTZ, M. RESTER, Austrian Academy of Sciences, Austria
8:20 am	Invited talk continued.	Invited talk continued.
8:40 am	**A3-1-3** Lifetime of Thermal Barrier Coatings With MCrAlY-Bondcoats: Effects of Testing Procedure and Coatings Microstructure, **D. NAUMENKO**, P. SONG, L. SINGHEISER, W. QUADAKKERS, Forschungszentrum Jülich GmbH, Germany	**B5-1-3** Characterization of Nanoindented TiAlN/CrN Nano-Multilayer Films by Transmission Electron Microscopy, **P.-L. SUN**, Feng Chia University, Taiwan, C.-H. HSU, S.-H. LIU, Tatung University, Taiwan, C.-Y. SU, National Taipei University of Technology, Taiwan, C.-K. LIN, Feng Chia University, Taiwan
9:00 am	**A3-1-4** Role of Ceramic Deposition Temperature and Surface Finish on the Life of an EB-PVD TBC Deposited on Pt-Diffused Bondcoat, **L. CHIRIVI**, J.R. NICHOLLS, Cranfield University, United Kingdom	**B5-1-4** Influences of Annealing on the Microstructures and Mechanical Properties of Cr_2N/Cu Multilayered Thin Films, **C.-L. LI**, Tungnan University, Taiwan, L.-C. CHANG, Ming Chi University of Technology, Taiwan, J.-W. LEE, Tungnan University, Taiwan
9:20 am	**A3-1-5 Invited** Suspension Plasma Spray as a Route for Microstructural Design of New Thermal Barrier Coatings, **R.W. TRICE**, Purdue University	**B5-1-5** Microstructural and Mechanical Properties of TiN/VN Nano-Structured UMS Coatings, **Q. YANG**, M. BIELAWSKI, R.C. MCKELLAR, National Research Council Canada
9:40 am	Invited talk continued.	**B5-1-6** Co-development of Stress and Texture in TiN Films, Revealed by In-Situ Film Stress Measurments, **R. MACHUNZE**, G.C.A.M. JANSSEN, Delft University of Technology, The Netherlands
10:00 am	**A3-1-7** Proto-TGO Formation in TBC Systems Fabricated by Spark Plasma Sintering, **M. BOIDOT**, S. SELEZNEFF, D. MONCEAU, D. OQUAB, C. ESTOURNÈS, CIRIMAT, France	**B5-1-7** Effect of Grain Size on the Residual Stress State and Thermal Expansion in Magnetron Sputtered Thin Films, **R. DANIEL**, D. HOLEC, J. KECKES, C. MITTERER, Montanuniversität Leoben, Austria
10:20 am	**A3-1-8** Effect of Superalloy Substrate and Bond Coating on TBC Lifetime, **B.A. PINT**, J.A. HAYNES, Oak Ridge National Laboratory, Y. ZHANG, Tennessee Technological University	**B5-1-8** Influence of Multilayer Designs on their Residual Stresses and Mechanical Properties, W. TILLMANN, **E. VOGLI**, H.-A. CROSTACK, G. FISCHER, U. SELVADURAI-LASSL, J. HERPER, TU Dortmund, Germany
10:40 am	**A3-1-9 Invited** On The Design of Industrial Sensor Thermal Barrier Coating Systems, **J.P. FEIST**, Southside Thermal Sciences, A.L. HEYES, Imperial College London, United Kingdom, R. VA B EN, Forschungszentrum Jülich GmbH, Germany, J.R. NICHOLLS, Cranfield University, United Kingdom	**B5-1-9** Thermal Decomposition of Epitaxial Al-Cr-N Hard Coatings: Crystallography and Mechanical State of Individual Phases, **M. BARTOSIK**, R. DANIEL, C. MITTERER, J. KECKES, Montanuniversität Leoben, Austria
11:00 am	Invited talk continued.	**B5-1-10 Invited** Plasma Sprayed Ceramic-Carbon Nanotube Coatings with Tailored Mechanical Properties, **S. SEAL**, University of Central Florida, A. AGARWAL, Florida International University
11:20 am	**A3-1-11** Effect of Laser Remelting on the Tribological Performance of Thermal Barrier Coatings, **M.D. LOPEZ GONZALEZ**, F. SEVILLANO, A. RICO, C.J. MÚNEZ, J. RODRIGUEZ, P. POZA, M.V. UTRILLA, Universidad Rey Juan Carlos, Spain	Invited talk continued.
11:40 am	**A3-1-12** Microstructure Design and Mechanical Properties of Thermal Barrier Coatings with Layered Top and Bond Coats, Y.-G. JUNG, **S.-W. MYOUNG**, J.-H. KIM, W.-R. LEE, Changwon National University, Republic of Korea, U.G. PAIK, Hanyang University, Republic of Korea, K.-S. LEE, Kookmin Universiy, Republic of Korea	**B5-1-12** Elemental Characterization of Metallurgical Coatings and Films using Glow Discharge OES and Laser Ablation ICP-MS, **F. LI**, S. ANDERSON, Air Liquide Balazs NanoAnalysis
12:00 pm		

Thursday Morning, April 29, 2010

	Fundamentals and Technology of Multifunctional Thin Films: Towards Optoelectronic Device Applications **Room: Royal Palm 1-3 - Session C2-1** **Thin Films for Active Devices and Microstystems** **Moderators:** T. Miyata, Kanazawa Institute of Technology, N. Drolet, Konarka	**Carbon and Nitride Materials: Synthesis-Structure-Property Relationships** **Room: Pacific Salon 3 - Session D2-1** **Diamond and Diamond-Like Carbon Materials** **Moderators:** O. Shenderova, International Technology Center, R. Hauert, Empa
8:00 am	**C2-1-1 Invited** Organic Semiconductor Lasers, Optical Amplifiers and Detectors, Y. YANG, D. AMARASINGHE, G. TSIMINIS, J.W. LEVELL, M.E. GIARDINI, A. RUSECKAS, G.A. TURNBULL, **I.D.W. SAMUEL**, University of St. Andrews, United Kingdom	**D2-1-1 Invited** Synthesis, Properties, and Applications of Ultrananocrystalline Diamond (UNCD®) Thin Films, **J.A. CARLISLE**, Advanced Diamond Technologies, Inc.
8:20 am	Invited talk continued.	Invited talk continued.
8:40 am	**C2-1-3** Concepts for the Material Development for Solution Processable Phosphorescent Polymers and their Application in PLEDs, **S.J. JANIETZ**, H.K. KRUEGER, M.T. THESEN, A.W. WEDEL, FhG-IAP, Germany	**D2-1-3** HF-CVD of Diamond Coatings Onto Fluidized Bed Machined (FBM) CrN Interlayers, R. POLINI, **M. BARLETTA**, Università di Roma Tor Vergata, Italy, G. CRISTOFANILLI, Università di Roma Tor Vergata, Itlay
9:00 am	**C2-1-4** Synthesis and Characterization of 1-Phenyl-3-(4-phenyl-[1,2,3]triazol-1-yl)-4-Styryl-Azetidin-2-One Films for Light Emitting Applications, **A. MAHAJAN**, V. KUMAR, R.K. BEDI, Guru Nanak Dev University, India	**D2-1-4** Pretreatment of Cemented Carbides with Different Seeding Powders for Diamond Hot Filament CVD (HFCVD), **C. BAREISS**, W. REICHERT, O. LEMMER, CemeCon AG, Germany
9:20 am	**C2-1-5 Invited** Light Emission from Organic Field-Effect Transistors, E. FELDMEIER, M. SCHIDLEJA, C. SIOL, C. MELZER, **H. VON SEGGERN**, Technical University of Darmstadt, Germany	**D2-1-5** Growth of Diamond Thin Films on Al/AlN-Coated Copper Plates, L.S. XU, **Q. YANG**, University of Saskatchewan, Canada, X.H. CHEN, Hunan University, China
9:40 am	Invited talk continued.	**D2-1-6 Invited** Applications of Nanodiamond and Onion-Like Carbon Particles in Composites, **G. MCGUIRE**, International Technology Center, O. SHENDEROVA, Intl Technology Cntr & Adámas Nanotech, Inc, S. HENS, Intl Tech Cntr, V. KUZNETSOV, Boreskov Inst of Catalysis, Russia, M.G. IVANOV, Ural State Tech Univ, Russia
10:00 am	**C2-1-7** Polythiophene Thin Films Electrochemically Deposited on Sol-Gel Based TiO_2 for Photovoltaic Applications, R. VALASKI, Inmetro, N. YAMAMOTO, R. MELLO, M. OLIVEIRA, L. ROMAN, UFPR, Brazil, C. LEGNANI, W. QUIRINO, Inmetro, Brazil, **M. CREMONA**, PUC-Rio, Brazil	Invited talk continued.
10:20 am	**C2-1-8** Effect of Cationic Surfactant on the Sensing Behavior of Nanocrystallite CuO Films Deposited by Spray Pyrolysis, **R.K. BEDI**, Guru Nanak Dev University, India, I. SINGH, Khalsa College, Amritsar, India	**D2-1-8** Bi-Layer Diffusion Barrier Used to Optimized Diamond Deposit onto Cermets: A Proposal, **A. POULON-QUINTIN**, C. FAURE, J.-P. MANAUD, CNRS, Université Bordeaux, ICMCB, Pessac, France
10:40 am	**C2-1-9** Microstructural and Optical Properties of Ga-Doped ZnO Semiconductor Thin Films Prepared by the Sol-Gel Process, **C.-Y. TSAY**, C.-W. WU, Feng Chia University, Taiwan, C.-M. LEI, Chinese Culture University, Taiwan, F.-S. CHEN, Tatung University, Taiwan, C.-K. LIN, Feng Chia University, Taian	**D2-1-9** Design of Interlayer Materials for Adhering Diamond Coating on Steel Substrates, Y. LI, **Y. TANG**, University of Saskatchewan, Canada
11:00 am	**C2-1-10** Characteristics of Highly Transparent Conductive Ga-Doped ZnO on Polymer Substrates Prepared by Ion-Plating Deposition with DC Arc Discharge, **T. YAMAMOTO**, A. MIYAKE, T. YAMADA, H. MAKINO, N. YAMAMOTO, Kochi University of Technology, Japan	
11:20 am	**C2-1-11** Optical and Electrical Properties of Transparent Conductive Ga-Doped ZnO Thin Films, **H. MAKINO**, T. YAMADA, N. YAMAMOTO, T. YAMAMOTO, Kochi University of Technology, Japan	
11:40 am	**C2-1-12** Effect of Organic-Buffer-Layer on Electrical Properties and Environmental Reliability of GZO Films Prepared by RF Plasma Assisted DC Magnetron Sputtering on Plastic Substrates, **T. HINOKI**, C. KYUHARA, H. AGURA, K. YAZAWA, Oike & Co., Ltd., Japan, K. KINOSHITA, K. OHMI, S. KISHIDA, Tottori University, Japan	
12:00 pm		

Thursday Morning, April 29, 2010

	Applications, Manufacturing, and Equipment **Room: Pacific Salon 1 - Session G7** **Advances in Industrial PVD & CVD Deposition Equipment** **Moderators:** R. Cremer, KCS Europe GmbH, K. Yamamoto, Kobe Steel Ltd.	**New Horizons in Coatings and Thin Films** **Room: Royal Palm 4-6 - Session H2-2** **High Power Impulse Magnetron Sputtering** **Moderators:** R. Bandorf, Fraunhofer IST, J.-E. Klemberg-Sapieha, Ecole Polytechnique de Montreal
8:00 am	**G7-1 Invited** Functional Nano Color Coatings: Basics, Preparation and Applications, **R.W. DOMNICK**, M. BELZNER, Ara-Coatings GmbH & Co. KG, Germany	**H2-2-1 Invited** Reactive HiPIMS Processes for Optical Coatings, **M. VERGÖHL**, S. BRUNS, O. WERNER, R. BANDORF, V. SITTINGER, G. BRÄUER, Fraunhofer Institute for Surface Engineering and Thin Films, Germany
8:20 am	Invited talk continued.	Invited talk continued.
8:40 am	**G7-3** The New Platit Pi111 PVD Coating Unit, **B. TORP**, Platit Inc., USA, T. CSELLE, O. CODDET, A. LÜMKEMANN, M. MORSTEIN, Platit AG, Switzerland, P. HOLUBAR, M. JILEK JR, Pivot, Czech Republic	**H2-2-3** Measuring the Negative Oxygen Ion Density in a Reactive Pulsed DC Magnetron, J.W. BRADLEY, **R. DODD**, S. YOU, University of Liverpool, United Kingdom
9:00 am	**G7-4** Characterization of Inductively Coupled Plasmas in a Commercial Etcher, **B. O'SHAUGHNESSY**, S.H. LEE, University of Texas at Dallas, K.J. PARK, DMS, Korea, C.W. CHUNG, Hanyang University, Korea, M.J. KIM, G.S. LEE, University of Texas at Dallas	**H2-2-4** Process Control and Hysteresis in HiPIMS Reactive Deposition of Oxide Coatings, **G.T. WEST**, P. KELLY, Manchester Metropolitan University, United Kingdom
9:20 am	**G7-5** Tungsten Carbide Coatings on New Coating Machine RS50, **A. MUELLER**, M. ESSELBACH, H. RUDIGIER, OC Oerlikon Balzers AG, Liechtenstein	**H2-2-5** Control of Reactive High Power Impulse Magnetron Sputtering Processes, M. AUDRONIS, Gencoa Ltd., V. BELLIDO-GONZALEZ, B. DANIEL, **S. WILLIAMS**, Gencoa Ltd
9:40 am	**G7-6** Deposition of Low-Stress Thick Coating by Modified Cathodic Arc Source, **K. YAMAMOTO**, S. TANIHUJI, Y. KUROKAWA, H. FUJII, S. KUJIME, Kobe Steel, Ltd., Japan	**H2-2-6** Modulated Pulse Power Sputter Deposition of Thick Tantalum Coatings, **W.D. SPROUL**, J. LIN, J.J. MOORE, Colorado School of Mines, S. LEE, US Army ARDEC-Benet Labs, J. WANG, HeFei University of Technology, B. MISHRA, Colorado School of Mines
10:00 am	**G7-7** Mechanical Properties and Structure Determination of High Al Containing Al$_{1-x}$Ti$_x$N Coatings by High Ionization Plasma for Advanced Coatings, **J. ALAMI**, G. ERKENS, J. MUELLER, P. ZARUBA, Sulzer Metaplas GmbH, Germany	**H2-2-7** A Comparative Study of Conventional Magnetron Sputtering, Plasma Enhanced Magnetron Sputtering (PEMS) and HIPIMS, **R. WEI**, Southwest Research Institute, S. LEE, US Army ARDEC-Benet Labs, W.D. SPROUL, Colorado School of Mines
10:20 am		**H2-2-8** Effect of Substrate Bias Voltage on the Structure and Properties of ZrN Coating Deposited by HIPIMS Technology, **Y.P. PURANDARE**, A.P. EHIASARIAN, P.EH. HOVSEPIAN, Sheffield Hallam University, United Kingdom
10:40 am		**H2-2-9** Effect of Substrate Bias Voltage on the CrN Film Depositions Using Modulated Pulse Power Magnetron Sputtering, J. LIN, **J.J. MOORE**, W.D. SPROUL, B. MISHRA, Colorado School of Mines
11:00 am		**H2-2-10** Advances in HIPIMS$^+$ Deposited Hard Coatings for Tooling Applications, **F. PAPA**, R. TIETEMA, T. KRUG, Hauzer Techno Coating BV, Netherlands
11:20 am		**H2-2-11** High Rate Deposition of Thick Cr$_2$N and CrN Coatings Using Modulated Pulse Power (MPP) Magnetron Sputtering, **J. LIN**, J.J. MOORE, W.D. SPROUL, B. MISHRA, Colorado School of Mines, S. LEE, US Army ARDEC-Benet Labs, J. WANG, HeFei University of Technology
11:40 am		**H2-2-12** Reactive High Power Impulse Magnetron Sputtering of Titanium Carbide Thin Films, **M. SAMUELSSON**, Linköping University, Sweden, H. HÖGBERG, H. LJUNGKRANTZ, Impact Coatings AB, Sweden, U. HELMERSSON, Linköping University, Sweden
12:00 pm		

NOTES

Thursday Afternoon, April 29, 2010

	Coatings for Use at High Temperature **Room: Sunrise - Session A3-2** **Thermal Barrier Coatings** **Moderators:** A. Bolcavage, Rolls-Royce Corporation, R.G. Wellman, Cranfield University, B.T. Hazel, General Electric	**Hard Coatings and Vapor Deposition Technology** **Room: Town & Country - Session B5-2** **Properties & Characterization of Hard Coatings and Surfaces** **Moderators:** M. Fenker, FEM Research Institute, Y.W. Chung, Northwestern University, G. Abadias, University of Poitiers
1:30 pm	**A3-2-1 Invited** Novel Thermal Barrier Coatings that are Resistant to Molten-Deposits Attack, **P. PADTURE**, The Ohio State University	**B5-2-1 Invited** Transition Metal Nitride-Based Complex Coatings: Kinetic and Thermodynamic Effects Resulting to Ternary Films or Nanocomposites, **P.A. PATSALAS**, University of Ioannina, Greece, G. ABADIAS, University of Poitiers, France, G. MATENOGLOU, L.E. KOUTSOKERAS, University of Ioannina, Greece
1:50 pm	Invited talk continued.	Invited talk continued.
2:10 pm	**A3-2-3** Lifetime Approximation Based on Quantitative Microstructural Analysis for Air Plasma Sprayed Thermal Barrier Coatings, **C BARGRASER**, P. MOHAN, K. LEE, Y. SOHN, University of Central Florida	**B5-2-3** Thermal Stability of Arc-Evaporated $Nb_{1-x}Al_xN$ Hard Coatings, **R. FRANZ**, Montanuniversität Leoben, Austria, M. LECHTHALER, OC Oerlikon Balzers AG, Germany, C. POLZER, Plansee Composite Materials GmbH, Germany, C. MITTERER, Montanuniversität Leoben, Austria
2:30 pm	**A3-2-4** Delamination-Indicating Thermal Barrier Coatings Incorporating Luminescent Sublayers Produced by Continuous Versus Interrupted Deposition, **J.I. ELDRIDGE**, NASA Glenn Research Center, D.E. WOLFE, Pennsylvania State University	**B5-2-5** Influence of Zr on Structure, Mechanical and Thermal Properties of Ti-Al-N Thin Films, **P.H. MAYRHOFER**, L. CHEN, D. HOLEC, Montanuniversität Leoben, Austria, Y. DU, Central South University
2:50 pm	**A3-2-5** Insight into the Phase Evolution of Thermal Barrier Coatings Upon Aging, **J.A. KROGSTAD**, R.M. LECKIE, S. KRAEMER, University of California, Santa Barbara, Y. GAO, D.M. LIPKIN, GE Global Research Center, C. LEVI, Univrsity of California, Santa Barbara	**B5-2-6** Incorporation Effects of Si in TiC_x Thin Films, **O. TENGSTRAND**, Linköping University, Sweden, N. NEDFORS, Uppsala University, Sweden, A FLINK, Impact Coatings AB, Sweden, A. ANDERSSON, ABB AB, Corporate Research, Sweden, H. HÖGBERG, H. LJUNGKRANTZ, Impact Coatings AB, Sweden, U. JANSSON, Uppsala University, Sweden, P. EKLUND, L. HULTMAN, Linköping University, Sweden
3:10 pm	**A3-2-6 Invited** A UK Study of Failure Mechanisms in EBPVD Thermal Barrier Coatings, **A. ATKINSON**, D. BALINT, Imperial College, United Kingdom, J.R. NICHOLLS, Cranfield University, United Kingdom	**B5-2-7** Texture Effect on the Hardness Enhancement of Nanocomposite Ti-Si-N Thin Films Using Reactive Magnetron Co-sputtering, C.-K. CHUNG, **S.-C. CHANG**, J.J. JHU, T.-S. CHEN, B.-H. WU, National Cheng Kung University, Taiwan
3:30 pm	Invited talk continued.	**B5-2-8** Raman Spectroscopy Investigations of CVD Hard Coatings in the Ti-B-C-N System, **I. DREILING**, University of Tuebingen, Germany, D. STIENS, Walter AG, Germany, T. CHASSÉ, University of Tuebingen, Germany
3:50 pm	**A3-2-8** The Evolution of Y_2SiO_5 EBCs Under Combined CMAS and Water-Vapor Exposure, **K. GRANT**, S. KRAEMER, G. SEWARD, C. LEVI, University of California, Santa Barbara	**B5-2-9** High Oxidation Resistance and Phase Stability of Cr-Si-O-N Coatings, **L. CASTALDI**, Empa, Switzerland, D. KURAPOV, A. REITER, OC Oerlikon Balzers AG, Liechtenstein, V. SHKLOVER, ETH, Switzerland, P.S. SCHWALLER, J. PATSCHEIDER, Empa, Switzerland
4:10 pm	**A3-2-9** Durability Assessment of Electrophoretically Deposited Environmental Barrier Overlay for Air Plasma Sprayed Thermal Barrier Coating, **P. MOHAN**, T. PATTERSON, Y. SOHN, University of Central Florida	**B5-2-10** A Spectroscopic Scanning of Magnetron Sputtered FeSiN Thin Films: Variations of the Nanostructure Induced by the Deposition Parameters, **A. MÈGE-REVIL**, J.F. PIERSON, J.PH. BAUER, Ecole des Mines de Nancy, France
4:30 pm	**A3-2-10** An Integrated Approach Towards Reliable Operation of TBCs Through Design and NDT, **A.M.G. LUZ**, University of Lisbon, Portugal, D. BALINT, K. NIKBIN, Imperial College, United Kingdom	**B5-2-11** Characteristics of Pulsed DC Reactive Magnetron Sputtered Nanocomposite Cr-Zr-N and Cr-Zr-Si-N Thin Films, **S.-T. CHANG**, J.-W. LEE, C.-H. CHIEN, J.-J. CHEN, S.-S. SHIANG-SHIUNG, Tungnan University, Taiwan, L.-C. CHANG, Ming Chi University of Technology, Taiwan, C.-J. WANG, National Taiwan University of Science and Technology, Taiwan
4:50 pm	**A3-2-11** Simultaneous Synthesis of Thermal Barrier Coating Top Coat and Bond Coat by Spark Plasma Sintering, **J. SONG**, Wuhan University of Technology, China, K. MA, J.M. SCHOENUNG, University of California - Davis	**B5-2-12** Structure and Property of Nanocrystalline ZrN_xO_y Thin Film: Effect of Oxygen Content and Film Thickness, **K.-C. LAN**, J.-H. HUANG, G.-P. YU, National Tsing Hua University, Taiwan
5:10 pm		

Thursday Afternoon, April 29, 2010

	Fundamentals and Technology of Multifunctional Thin Films: Towards Optoelectronic Device Applications **Room: Royal Palm 1-3 - Session C2-2** **Thin Films for Active Devices and Microstystems** **Moderators:** T. Miyata, Kanazawa Institute of Technology, N. Drolet, Konarka	**Carbon and Nitride Materials: Synthesis-Structure-Property Relationships** **Room: Pacific Salon 3 - Session D2-2** **Diamond and Diamond-Like Carbon Materials** **Moderators:** O. Shenderova, International Technology Center, R. Hauert, Empa
1:30 pm	**C2-2-1** Investigation on Post-Deposition Annealing of Amorphous Indium-Zinc-Oxide Thin-Film-Transistors, **W.-F. CHUNG**, National Chiao-Tung University, Taiwan, T.-C. CHANG, National Sun Yat-Sen University, Taiwan, H.-W. LI, National Chiao-Tung University, Taiwan, Y.-C. CHEN, National Sun Yat-Sen University, Taiwan, T.-Y. TSENG, Y.-H. TAI, National Chiao Tung University, Taiwan	**D2-2-1** Comparison of DLC Deposited by Different Techniques, **I. GOROKHOVSKY**, K. COULTER, M.A. MILLER, R. WEI, C.A. ELLIS, Southwest Research Institute
1:50 pm	**C2-2-3** Leakage Current and Dielectric Constant Dependencies on Single and Double Layer of Oxides in MOS Structure, I. BANERJEE, P. LAHA, A. BIHARI PANDA, Birla Institute of Technology, India, B. SAHA, CHAKRABORTY, Saha Institute of Nuclear Physics, India, P.K. BARHAI, **MAHAPATRA**, Birla Institute of Technology, India	**D2-2-2** Surface and Structural Properties of DLC Coatings and their Influence on Protein Adsorption, **W. WALDHAUSER**, M. KAHN, B. POINTNER, Joanneum Research Forschungsgesellschaft GmbH, Austria, R. KARGL, Karl-Franzens University Graz, Austria, M. REISCHL, S. KÖSTLER, V. RIBITSCH, E. BRANDSTÄTTER, Joanneum Research Forschungsgesellschaft GmbH, Austria
2:10 pm	**C2-2-4** Dielectric Properties of Sc$_x$Al$_{1-x}$N Thin Films Deposited by Dual Reactive DC Magnetron Sputtering, **A. ZUKAUSKAITE**, G. WINGQVIST, F. TASNÁDI, J. BIRCH, L. HULTMAN, Linköping University, Sweden	**D2-2-3 Invited** Industrial Filtered Laser-Arc Film Deposition, New Quality of ta-C Films, J. ACOSTA, ITESM-CEM, Mexico, H.-J. SCHEIBE, Fraunhofer Institute for Materialsand Beam Technology IWS, Germany, MEYER, M. LEONHARDT, **A. LESON**, V. WEIHNACHT, Fraunhofer Institute for Material and Beam Technology, IWS, Germany
2:30 pm	**C2-2-5** Resistance Switching Mechanisms of Partial Doped SiO$_2$ With Fe Irons in a MIM Structure, **L.-W. FENG**, C.-Y. CHANG, National Chiao Tung University, Taiwan, T.-C. CHANG, National Sun Yat-Sen University, Taiwan	Invited talk continued.
2:50 pm	**C2-2-6** Broad Visible Photoluminescence from Two-Layer Si/C Film Deposited on Si (100) Substrate Under Rapid Thermal Annealing, C.-K. CHUNG, **C.-W. LAI**, National Cheng Kung University, Taiwan	**D2-2-5** Tetrahedral Amorphous Carbon (t-aC) Deposited by Filtered Cathodic Vacuum Arc (FCVA) Bombarded by Argon Ions, **C. MARQUES**, H. OLIVEIRA, F. MOTTA, Universidade Estadual de Campinas, Brazil
3:10 pm	**C2-2-7** Low-Temperature Fabrication of Superconducting FeSe Thin Films by Pulsed Laser Deposition, **T.K. CHEN**, J.-Y. LUO, C.-T. KE, Academia Sinica, Taiwan, H.-H. CHANG, National Tsing Hua University, Taiwan, T.-W. HUANG, K.-W. YEH, P.-C. HSU, C.-C. CHANG, M.-J. WANG, M.-K. WU, Academia Sinica, Taiwan	**D2-2-6** Multi-Pass Scratch Test of DLC Coatings Deposited by CFUBMS on Anodized-CP-Ti at the Different Temperatures and Potentials, **C. ALBAYRAK**, O. BARAN, Erzincan University, Turkey, A. ALSARAN, I. EFEOGLU, A. CELIK, Atatürk University, Turkey
3:30 pm		**D2-2-7** In Situ Real-Time Ellipsometry Study of Diamond-Like Carbon Films on Metal Substrates, D. ESCAICH, M. AZZI, O. ZABEIDA, J.-E. KLEMBERG-SAPIEHA, **L. MARTINU**, Ecole Polytechnique de Montreal, Canada
3:50 pm		**D2-2-8** Anisotropic Texturing of Diamond-Like Carbon Films by Colloidal Lithography with Sub-Micron Spheres, **C. CORBELLA**, S. PORTAL, M. RUBIO-ROY, M.A. VALLVÉ, J. IGNÉS-MULLOL, E. BERTRAN, J.-L. ANDÚJAR, University of Barcelona, Spain
4:10 pm		**D2-2-9** High Temperature Tribological Behaviour of Carbon Based (B$_4$C and WC-DLC) Coatings Against Aluminum, **A. ABOUGHARAM**, University of Windsor, Canada, M.L. LUKITSCH, GM Research & Development Center, A.T. ALPAS, University of Windsor, Canada
4:30 pm		**D2-2-10** Synthesis of Ultra-Smooth and Ultra-Low Friction DLC Based Nanocomposite Films on Rough Substrates, **K.P. SHAHA**, T. PEI, C. CHEN, J.T.M. DE HOSSON, University of Groningen, The Netherlands
4:50 pm		
5:10 pm		

Thursday Afternoon, April 29, 2010

	Tribology & Mechanical Behavior of Coatings & Thin Films - Room: Pacific Salon 1 - Session E1-1 - Friction & Wear of Coatings: Lubrication, Surface Effects & Modeling **Moderators:** E. Broitman, Carnegie Mellon University, J.C. Sanchez-Lopez, Instituto de Ciencia de Materiales de Sevilla (CSIC-US), O.L. Eryilmaz, Argonne National Laboratory	**New Horizons in Coatings and Thin Films** **Room: Royal Palm 4-6 - Session H4/C4** **Thin Films for Photovoltaics: Synthesis and Characterization** **Moderators:** S.V. Khare, University of Toledo, Z. Hong, University of Califronia
1:30 pm	**E1-1-1** Identification of Hard Turning Signature of Coated Tools on Cut Surface, **A. ZAWADA-TOMKIEWICZ**, Koszalin University of Technology, Poland, M. EL MANSORI, Arts et Métiers ParisTech, France	**H4/C4-1** The Characteristics of Zinc Oxide, Cadium Oxide and SnO$_2$ Prepared by RF Magnetron Sputtering, **Y. ZHOU**, F. WU, C. ZHENG, University of Science & Technology Liaoning, China
1:50 pm	**E1-1-2** On the Early Stages of Friction of Tetrahedral Amorphous Carbon Thin Films Deposited by Femtosecond Laser Ablation, P. PAOLINO, Ecole Centrale de Lyon, France, A. SIKORA, Université Jean Monnet, France, C. GUERRET-PIÉCOURT, **J. FONTAINE**, Ecole Centrale de Lyon, France, F. GARRÉLIE, C. DONNET, A.-S. LOIR, Université Jean Monnet, France, M. BELIN, Ecole Centrale de Lyon, France	**H4/C4-2** Three-Terminal Microcrystalline Silicon Solar Cell, **C.-H. TAI**, C.-H. LIN, National Dong Hwa University, Taiwan
2:10 pm	**E1-1-3 Invited** Recent Developments on DLC Films and Tribomechanical Characterizations, **V.J. TRAVA-AIROLDI**, P.A. RADI, F.R. MARCIANO, L.V. SANTOS, D.A. LIMA-OLIVEIRA, E.J. CORAT, Instituto Nacional de Pesquisas Espaciais, Brazil	**H4/C4-4 Invited** To Be Announced
2:30 pm	Invited talk continued.	Invited talk continued.
2:50 pm	**E1-1-5** Fretting Contact Study of Ti-6Al-4V/Carbon Couples in a Dry Shaft/Bearing Contact with Trust: Influence of a Plasma Nitridation of the Titanium Alloy, **M. SYLVESTRE**, H. ZAIDI, J.-P. RIVIÈRE, D. EYIDI, Université de Poitiers, France, F. DOYEN, Carbone Lorraine Composant, France	**H4/C4-6** Intergranular Microstructure and Residual Stress Investigation by EBSD on Laser-Crystallized Polycrystalline Si Thin Films on Glass Substrates for Photovoltaic Applications, **X MAEDER**, C. NIEDERBERGER, Empa, Sweden, S. CHRISTIANSEN, Max-Planck-Institute of Microstructure Physics, Germany, A. BOCHMANN, G. ANDRÄ, A. GAWLIK, F. FALK, Institute for Photonic Technology, Germany, J. MICHLER, Empa, Switzerland
3:10 pm	**E1-1-6** Tribological Evaluation of the Friction and Material Pick-Up Tendencies of VN and V$_2$N Coatings in Dry Sliding Contact Against Austenitic Stainless Steel, **M.X. FALLQVIST**, U.J.G. BEXELL, E. OLSSON, Dalarna University, Sweden	**H4/C4-7** Addition of Na into CuInS$_2$ Thin Film via Co-Evaporation, **W.-Z. TSAI**, C.-H. TSAI, C.-H. CHANG, J.-M. TING, National Cheng Kung University, Taiwan
3:30 pm	**E1-1-7 Invited** Nanoscale Deformation Mechanism in the Sliding Contact of TMD-C Nanocomposite Coatings, **T. POLCAR**, Czech Technical University in Prague and University of Coimbra, Portugal, A. CAVALEIRO, University of Coimbra, Portugal	**H4/C4-8** Fabrication of Densely Distributed Silver Indium Selenide Nanorods by Ag$^+$ Ion Irradiation, **D. PATHAK**, R. KUMAR, Guru Nanak Dev University, India, D. KAUR, IIT Roorkee, India, R. KUMAR, Inter University Accelerator Centre, India
3:50 pm	Invited talk continued.	**H4/C4-10** Impregnation of Nano-Particles in Glancing-Angle Deposited Titania Films for Efficiency Enhancement in Dye-Sensatized Solar Cells, **C.-L. CHEN**, C.H. HUANG, M.-S. WONG, National Dong Hwa University, Taiwan
4:10 pm	**E1-1-9** Growth, Structure and Tribological Properties of Atomic Layer Deposited Lubricious Oxide Nanolaminates, **B.A. MENSAH**, H. MOHSENI, T.W. SCHARF, University of North Texas	**H4/C4-11** Nano-Structured TiO$_2$ Films by Plasma Electrolytic Oxidation of Ti Combined with Chemical and Thermal Post-Treatments for Dye-sensitized Solar Cell Applications, **P.-J. CHU**, University of Sheffield, United Kingdom, S.-Y. WU, K.-C. CHEN, J.-L. HE, Feng Chia University, Taiwan, A. ALEKSEY, A. MATTHEWS, University of Sheffield, United Kingdom
4:30 pm	**E1-1-10** Sophisticated New Analyzing and Simulation Tools for Scratch, Impact, and Wear Tests, **M.C. FUCHS**, N. BIERWISCH, Saxonian Institute of Surface Mechanics, Germany	**H4/C4-12** Depth Profile Analysis of Thin Layers on Conductive or Nonconductive Substrates by Rf GD-OES (Semiconductor, Photovoltaic and PVD/CVD Applications), **P. HUNAULT**, HORIBA Jobin Yvon Inc., USA, C. TAUZIÈDE, P. CHAPON, A. TEMPEZ, HORIBA Jobin Yvon, France, M. GANCIU, NILPRP, Romania, P. GUILLOT, University JF Champollion, France, P. BELENGUER, Laplace CNRS, France
4:50 pm	**E1-1-11** Multi-Scale Contact Modelling of Textured Surfaces Under Dry Sliding Conditions, O. RASHWAN, **M. STOILOV**, University of Windsor, Canada	
5:10 pm	**E1-1-12** Tribological Properties of Water Confined by Self-Assembled Monolayers, **M. CHANDROSS**, Sandia National Laboratories, C.D. LORENZ, King's College London, United Kingdom, J.M.D. LANE, G.S. GREST, Sandia National Laboratories	

NOTES

Thursday Afternoon Poster Sessions

Coatings for Use at High Temperature
Room: Golden Pacific Ballroom - Session AP

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

AP-1

Thermal Cycling Behavior and Interfacial Stability in Thick Thermal Barrier Coatings, Y.-G. JUNG, Changwon National University, Korea, **P.-H. LEE**, S.-Y. LEE, Changwon National Unviersity, Korea, J.Y. KWON, S.-W. MYOUNG, Changwon National University, Korea, U.G. PAIK, Hanyang University, Korea

AP-2

Original Refractory Metallic Coatings on Fibers: Morphology and Behavior at High Temperature, A.-S. ANDRÉANI, **A. POULON-QUINTIN**, F. REBILLAT, Université de Bordeaux, France

AP-3

Pulsed Magnetron Sputtering of Hard Amorphous Si-B-C-N Coatings with High Thermal Stability and Oxidation Resistance, **P. STEIDL**, P. CALTA, J. VLCEK, P. ZEMAN, University of West Bohemia, Czech Republic

AP-4

Why Measurement at Higher Temperature is of Great Importance and How the Results Should be Used, **N. BIERWISCH**, L. GEIDEL, N. SCHWARZER, Saxonian Institute of Surface Mechanics, Germany

AP-5

Influence of APS Parameters on the Microstructural Properties of ZrO_2–10% Y_2O_3–18% TiO_2, **S.L. LISCANO**, L.G. GIL, UNEXPO, Venezuela, M.H. STAIA, Universidad Central de Venezuela, M. PRATO, UCV, Venezuela, A.S. SCAGNI, Plasmatec Ingenieros CA, Venezuela

AP-6

EBSD Study of Crystallographic Identification of Fe-Al-Si Intermetallic Phases in Al-Si Coating on Cr-Mo Steel, **W.-J. CHENG**, C.-J. WANG, National Taiwan University of Science and Technology, Taiwan

AP-7

CMAS Attack of Erbia Doped EB PVD TBCs, **R.G. WELLMAN**, Cranfield University, United Kingdom

AP-8

Oxidation Resistance and Mechanical Properties of Quasi-Amorphous Ta-Si-N Sputtered Films, C.-K. CHUNG, T.-S. CHEN, N.-W. CHANG, S.-C. CHANG, **M.-W. LIAO**, National Cheng Kung University, Taiwan

AP-9

A Study of High Temperature Oxidation Behaviors of Zr-Si-N Nanocomposite Thin Films at 900°C, **J.-W. LEE**, Y.-B. LIN, Tungnan University, Taiwan, L.-C. CHANG, Ming Chi University of Technology, Taiwan, F.-B. WU, National United University, Taiwan

AP-10

Degradation of CaO-Stabilized Zirconia Thermal Barrier Coating by Molten Salts, **M.D. LOPEZ GONZALEZ**, R. RODRIGUEZ, M.V. UTRILLA, C.J. MÚNEZ, P. POZA, Universidad Rey Juan Carlos, Spain

AP-11

Sol-Gel Thermal Barrier Coatings : Optimization of the Manufacturing Route and Durability Under Cyclic Oxidation, J. SNIEZEWSKI, Y. LEMAOULT, P. LOURS, Université de Toulouse, ICA Mines-Albi, France, V.M. BEKALE, D. MONCEAU, **D. OQUAB**, Université de Toulouse CIRIMAT-ENSIACET, France, J. FENECH, F ANSART, J.-P. BONINO, Université de Toulouse CIRIMAT-UPS, France

AP-12

Corrosion Resistance of Cr/CrN Multilayer Coatings Deposited by Unbalanced Magnetron, Y. CHIPATECUA, **J. OLAYA**, Universidad Nacional de Colombia

Hard Coatings and Vapor Deposition Technology
Room: Golden Pacific Ballroom - Session BP

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

BP-1

Effects of Substrate Radial Positioning for TiAlN Films Deposited by an Inverted Cylindrical Magnetron Sputtering System, **H. ABU-SAFE**, Lebanese American University, Lebanon, M. GORDON, University of Arkansas, K.N. ABUSHGAIR, Albalqa Applied University, Jordan

BP-2

Pressure Dependent Stability of Cubic and Wurtzite Phases Within the TiN-AlN and CrN-AlN Systems, **D. HOLEC**, F. ROVERE, P.H. MAYRHOFER, Montanuniversität Leoben, Austria, P.B. BARNA, Hungarian Academy of Sciences, Hungary

BP-3

Oxidation Resistance and Mechanical Properties of TiAlN/CrAlYN/TiAlN Three-Layer Film Deposited by Cathodic Arc Ion Plating Method, **M. TAKAHASHI**, N. FUKUMOTO, Keio University, Japan, H. HASEGAWA, Okayama University, Japan, T. WATANABE, Kanagawa Academy of Science and Technology, Japan, T. SUZUKI, Keio University, Japan

BP-4

Mechanical Properties of Ti-Al-Si-N Thin Film Coatings Prepared by Filter Vacuum Arc and Sputtering Techniques, **J.-K. KIM**, S. LEE, J.-Y. LEE, Korean Institute of Materials Science, Korea, I. SVADKOVSKI, Belarussian State University of Informatics and Radioelectronics, Russia, J.-D. KWON, D.-G. KIM, Korean Institute of Materials Science, Korea

BP-5

High Temperature Tribological Characterisation of AlTiISiN Coatings Produced by CAE-PVD Techniques, **F. FUENTES**, E. ALMANDOZ, R. MARTINEZ, R.J. RODRIGUEZ, Asociación de la Industria Navarra, Spain, J. CARO, M. VILASECA, CTM Centre Tecnologic, Spain

BP-6

Friction Properties and Microstructure of (Cr,Al)N-Based Coatings Deposited by Magnetron Sputtering Method, **H. HASEGAWA**, T. MIYAKE, A. KISHIMOTO, Okayama University, Japan

BP-7

Study on Characterization of Superlattice CrN/AlN Coating in Aluminum Alloy Die Casting Die Application, D.-Y. WANG, **H.-C. LIN**, W.-C. CHEN, MingDao University, Taiwan

BP-8

Mechanical Properties of Multilayered $Al_xCr_{1-x}N$/ZrN Coatings Synthesized by a Cathodic-Arc Deposition Process, Y.-Y. CHANG, **C.-Y. HSIAO**, Mingdao University, Taiwan

BP-9

Growth of AlN-Based Nanocomposites Grown by Pulsed Laser Deposition and Sputtering, H. ZOUBOS, RWTH Aachen University, Germany, **P.A. PATSALAS**, University of Ioannina, Greece

BP-10

Effect of Carbon on the Microstructure and Properties of Cr-C-N Coatings Deposited by Pulsed Closed Field Unbalanced Magnetron Sputtering, Z.L. WU, Dalian University of Technology, China, **J. LIN**, J.J. MOORE, Colorado School of Mines, M.K. LEI, Dalian University of Technology, China

BP-11

Shielded Cathodic Arc Deposition of Nanocomposite a-C:Cr Coatings, **L. YATE**, L. MARTÍNEZ-DE-OLCOZ, J. ESTEVE, A. LOUSA, Universitat de Barcelona, Spain

BP-12

Thermal Stability and Corrosion Performance of Cr-B-N Coatings Deposited Using Reactive Arc-Evaporation, **K. POLYCHRONOPOULOU**, A. HADJIAFXENTI, C.G. REBHOLZ, University of Cyprus, J. NEIDHARDT, Montanuniversität Leoben, Germany, K. KANAKIS, University of Sheffield, United Kingdom, M. O'SULLIVAN, PLANSEE Composite Materials GmbH, Germany, A. REITER, OC Oerlikon Balzers AG, Liechtenstein, A. MATTHEWS, The University of Sheffield, United Kingdom, C. MITTERER, Montanuniversität Leoben, Austria

BP-13

Corrosion Characteristics of CrN/NiP-Based Dual Layer Sputtering Coatings, Y.-Y. LI, **H.-H. HUANG**, F.-B. WU, National United University, Taiwan

BP-14

The Growth Mode, Microstructure, Texture and Residual Stress of Unbalanced Magnetron Sputtered Chromium Nitride Coatings, **Q. LUO**, Sheffield Hallam University, United Kingdom, T. HURKMANS, Hauzer Techno Coating Europe BV, The Netherlands, D.B. LEWIS, W.-D. MUNZ, Sheffield Hallam University, United Kingdom

BP-15

Thermal Stability of CrZrN/Si_3N_4 Multilayer Coatings Synthesized by Closed Field Unbalanced Magnetron Sputtering, Y.S. KIM, National Core Research Center for Hybrid Materials Solution, Korea, **S.-Y. LEE**, Korea Aerospace University, Korea, J.J. LEE, School of Materials Science and Engineering, Korea, W.Y. JEUNG, KIST, Korea

BP-16

Effect of (Ti,Zr) Interlayer on the Structure and Properties of (Ti,Zr)N Thin Films, Y.-W. LIN, Instrument Technology Research Center, Taiwan, J.-H. HUANG, **G.-P. YU**, National Tsing Hua University, Taiwan

BP-17

Resistance to Harsh Environnements of Ti-Zr-N Coatings for Future Nuclear Reactor Applications, **G. ABADIAS**, University of Poitiers, France, A.V. SEVRIUK, S.V. ZLOTSKI, V.V. UGLOV, Belarussian State University, Belarus, K.K. KADYRZHANOV, S.B. KISLITSIN, M.V. KOLODERDIN M.V, National Nuclear Center of Republic of Kazakhstan

BP-18

AC- Electrical Measurements - An Interesting Approach to Characterise the SiN Layer in Nanocomposite Zr N /SiN Thin Films, **C. SANDU**, S. HARADA, R. SANJINES, EPFL, Switzerland

BP-19

Evolution of the Crystallographic Preferred Orientation of NbN Films by Grazing Angle X-ray Diffraction, **G. RAMIREZ**, S.E. RODIL, J.G. GONZALEZ-REYES, S. MUHL, Universidad Nacional Autónoma de México, Mexico, E. CAMPS, L. ESCOBAR-ALARCON, Instituto Nacional de Investigaciones Nucleares, Mexico, J.L. BENITEZ, Universidad Nacional Autónoma de México, Mexico

BP-20

TiCN Thin Films Grown by the Simultaneous Laser Ablation of Two Targets, **E. CAMPS**, L. ESCOBAR-ALARCON, S. ROMERO, Instituto Nacional de Investigaciones Nucleares, Mexico, S. MUHL, I. CAMPS, Universidad Nacional Autónoma de México, Mexico, D.A. SOLIS-CASADOS, CIQS-UAEM, Mexico

BP-21

Structure and Mechanical Properties of Hafnium Carbide Coating on Cemented Carbide Cutting Tools, **W. LIU**, X. CHEN, S. WANG, Zhuzhou Cemented Carbide Cutting Tools Co., Ltd., China

BP-22

Performance Improvement of Metal-Core PCB Cutters Using Nanocomposite Coatings Deposited by Cathodic Arc Ion Plating Process, **S.-H. HUANG**, T.-E. HSIEH, National Chiao Tung University, Taiwan, J.-W. CHEN, Gigastorage Corporation, Taiwan

BP-23

Effect of CO_2 Reactive Gas on Abrasion Behavior of AISI 304 Stainless Steel Arc-Deposited Ti-C-O Composite Coatings, C.-H. HSU, C.-Y. LEE, S.-H. CHEN, Tatung University, Taiwan, **P.-L. SUN**, C.-K. LIN, Feng Chia University, Taiwan

BP-24

Control of Phase Formation During Synthesis of ZrO_2 Coatings by Magnetron Sputtering, **C. WALTER**, C. MITTERER, Montanuniversität Leoben, Austria

BP-25

Effect of Phase Transition and Microstructure of ZrO_2(N) Coating on the Corrosion Resistance AISI 304 Stainless Steel Substrate, **P.-H. HUANG**, J.-H. HUANG, G.-P. YU, National Tsing Hua University, Taiwan

BP-26

A Comparison of PVD Alumina Films Deposited Using AC and Pulsed DC Power Supplies, **K. GANGLUFF**, M. GORDON, A. BARITO, University of Arkansas

BP-27

Low-Temperature Deposition of Mixed-Phase Alpha Alumina by Physical Vapor Deposition without a Chrome Template Layer, **A. BARITO**, M. GORDON, University of Arkansas

BP-28

On the Phase Stability of Vapor Deposited γ-Al_2O_3 Films, **K. JIANG**, K. SARAKINOS, A. ATISER, A REINHOLDT, J. MAYER, J.M. SCHNEIDER, RWTH Aachen University, Germany

BP-29

Phase Analysis of Dual Magnetron Sputtered Thin Films in the Al-Cr-O System – a TEM Study, **W. ENGELHART**, V. SCHIER, Walter AG, Germany, O. EIBL, University Tübingen, Germany, W. DREHER, NMI Natural and Medical Sciences Institute, Germany

BP-30

Characteristics of Thickness Dependence of Vanadium Dioxide Thin Films Deposited by Pulsed-Laser Deposition Technique, **G.W. SEO**, ETRI/UST, Korea, B.-J. KI

M, ETRI, Korea, Y.W. LEE, ETRI/Pukyong National University, Korea, S. CHOI, H.-T. KIM, ETRI, Korea

BP-31

On the Formation of Off-Axis Texture in Nanostructured Thin Films, A. SHETTY, **A. KARIMI**, EPFL, Switzerland

BP-32

Oxidation Study of Ta-Ru Hard Coatings, **B.-N. TSAI**, Y.-I. CHEN, National Taiwan Ocean University, Taiwan

BP-33

Oxidation and Tribological Behaviors of Nanocomposite Ti-B-C-N-Si Films Deposited by Unbalanced Magnetron Sputtering, **I.-W. PARK**, J.J. MOORE, B. MISHRA, Colorado School of Mines, A.A. VOEVODIN, Air Force Research Laboratory, K.H. KIM, NCRC-HyMAS, Korea, E.A. LEVASHOV, Moscow State Institute for Steels and Alloys, Russia

BP-34

Mechanical and Tribological Properties of Nanocomposite MoN-Cu Coatings at Elevated Temperature, **H.N. LEE**, S.-Y. LEE, Korea Aerospace University, Korea, M.-H. RHEE, Korea Automotive Technology Institute, Korea

BP-35

Diffusion in Multilayer Coatings on Cemented Carbide by Chemical Vapor Deposition, **X. CHEN**, Zhuzhou Cemented Carbide Cutting Tools Co., Ltd., China, D. YI, Central South University, China, S. WANG, Zhuzhou Cemented Carbide Cutting Tools Co., Ltd., China

BP-36

Microstructure and Corrosion Behavior of Co-Sputtered Ni-Al-P Coatings, **K.-C. CHANG**, H.-H. HUANG, F.-B. WU, National United University, Taiwan

BP-37

Microstructure and Characterization of Magnetron Sputtered Stoichiometric Ni_3Al Coatings, C.-C. WU, **F.-B. WU**, National United University, Taiwan

BP-38

Effect of Annealing on Wettability, Microstructure and Electrical Property of RuN Thin Films, **C.-Y. WU**, W.-H. LEE, Y.-S. WANG, National Cheng Kung University, Taiwan, S.-C. CHANG, Y.-L. WANG, National Chia-Yi University, Taiwan

BP-40

Reliability Analysis of Coating-Substrate Systems Containing Inhomogeneities, **L.M. KEER**, K. ZHOU, Northwestern University

BP-41

Fabrication of Al Coated TiC Particles through Potential Hydrogen (pH), **W.-R. LEE**, Y.-G. JUNG, E.-H. KIM, Changwon National University, Korea

BP-42

Study by Optical Emission Spectroscopy of a Physical Vapour Deposition Process for AlCuFeB Deposition, T. DUGUET, **T. BELMONTE**, J.-M. DUBOIS, V. FOURNÉE, Ecole des Mines de Nancy, France

BP-43

Structural Characteristics of $BiFeO_3$/$LaNiO_3$ Artificial Superlattices Prepared by rf Magnetron Sputtering, **Y.-T. LIU**, C.-S. KU, H.-Y. LEE, National Synchrotron Radiation Research Center, Taiwan

BP-44

Reversible Resistive Switching Behaviors of Ga_2O_3 Memory Thin Films with Embedded Metal Layer, **D.-Y. LEE**, S.-Y. WANG, T.-Y. TSENG, National Chiao Tung University, Taiwan

BP-45

Ion Energy Distribution Studies of Ions and Radical in Ar/H_2 Radio Frequency Magnetron Discharge During a-Si:H Deposition Using Energy-Resolved Mass Spectrometry, **S.L. MENSAH**, M. GORDON, University of Arkansas, H. ABU-SAFE, Lebanese American University, H. NASEEM, University of Arkansas

BP-46

Stress Level / Deposition Parameters Correspondence in FeSiN Magnetron Sputtered Thin Films, **A. MÈGE-REVIL**, J.F. PIERSON, Ecole des Mines de Nancy, France

BP-47

Properties of Multi-Component CrBMoS Coatings by Pulsed Magnetron Sputtering from Powder Targets, **Y. ZHOU**, University of Science & Technology Liaoning, China, P. KELLY, Manchester Metropolitan University, United Kingdom, Z. ZHAO, University of Science & Technology Liaoning, China

BP-48

Characterization of Amorphous and Crystalline Zr-Cu-Ag-Al Metallic Thin Films with Different Thickness by Unbalanced Magnetron Sputtering, **P.-N. CHEN**, J.-H. HUANG, G.-P. YU, National Tsing Hua University, Taiwan

BP-49

Effect of Intercalated Metal Layer (M) on Photocatalytic Capabilities of TiO_2/M/ITO Film Catalysts, **K.R. WU**, National Kaohsiung Marine University, Taiwan, C.-W. YEH, Kao Yuan University, Taiwan, C.-H. HUNG, National Kaohsiung First University of Science and Technology, Taiwan

BP-50

Improved Damp Heat Stability of Ga-Doped ZnO Thin Film by Pre-Treatment of PET Substrate, D.-W. KIM, J.-H. KANG, Y.-S. LIM, **M.-H. LEE**, W.-S. SEO, Korea Institute of Ceramic Engineering and Technology, Korea, H.-H. PARK, Yonsei University, Korea, M.-G. PARK, K.-H. SEO, LG Display Co., Ltd., Korea

BP-51

Ferromagnetic Behavior of Fe-Cu co-doped ZnO Thin Films Grown by r.f. Sputtering, **Y.-S. CHANG**, National Formosa University, Taiwan, C.-W. CHEN, National Cheng Kung University, Taiwan, S. WU, Tung-Fung Institute of Technology, Taiwan, T.-H. FANG, National Formosa University, Taiwan

BP-52

Electric and Reliability Characteristics of Nitrogen-Incorporated Silicon Carbide Film Deposited by Chemical Vapor Deposition, **L.Y. CHENG**, T.-J. HIU, National Chi-Nan University, Taiwan

BP-53

Precipitate Formation and Effects on Electrical and Mechanical Properties of Fluorinated Silicon Oxide, **J. WU**, L.Y. CHENG, National Chi-Nan University, Taiwan

BP-54

Film Properties of Copper Barrier Films with Different Deposition Temperatures, **B.J. WEI**, L.Y. CHENG, J.H. WANG, National Chi-Nan University, Taiwan

BP-55

A Study of Silicon Compound Gas Barrier Thin Films Deposited on Polyimide Substrates by Pulsed DC Reactive Magnetron Sputtering, M.-H. TSAI, **H.-Y. WANG**, National Chin-Yi University of Technology, Taiwan, J.-W. LEE, Tungnan University, Taiwan, C.-Y. WANG, National Chin-Yi University of Technology, Taiwan, J.-C. HUANG, Tungnan University, Taiwan

BP-56

Triple Coatings: A Powerful Concept for Demanding Applications, **M. MORSTEIN**, O. CODDET, P. KARVANKOVA, A. LÜMKEMANN, Platit AG, Switzerland, B. TORP, Platit Inc., T. CSELLE, Platit AG, Switzerland

BP-57

Mechanical and Electrochemical Properties of Arc Ion Plated Titanium Dioxide on Polyetheretherketone, **H.-K. TSOU**, Feng Chia University & Taichung Veterans General Hospital, Taiwan, P.-Y. HSIEH, M.-H. CHI, Feng Chia University, Taiwan, C.-J. CHUNG, Central Taiwan University of Science and Technology, Taiwan, J.-L. HE, Feng Chia University, Taiwan

Fundamentals and Technology of Multifunctional Thin Films: Towards Optoelectronic Device Applications
Room: Golden Pacific Ballroom - Session CP

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

CP-1

Electro-Optical Property and Microstruture of Polymer Dispersed Liqid Crystal Doped with Various Reinforcing Materials, **S.-W. MYOUNG**, Y.-G. JUNG, E.-H. KIM, Changwon National University, Republic of Korea

CP-2

The Interface States Improvement of Pentacene Thin Film Transistors Through Self-Assemble Molecular Layers, Y WANG, Graduate Institute of Photonics, National Changhua University of Education, Taiwan R.O.C., **C.-Y. TSAY**, Feng Chia University, Taiwan

CP-3

Residual Stess Relaxation in ZnO Thin Films Deposited by Magnetron Sputtering on Si, F. CONCHON, **P.O. RENAULT**, P. GOUDEAU, E. LE BOURHIS, University of Poitiers-France, E. SONDERGARD, E. BARTHEL, S. GRACHEV, E. GOUARDES, V. RONDEAU, R. GY, Saint Gobain Research, France, R. LAZZARI, INSP-France, N. BRUN, LPS-France

CP-5

Hysteresis Effects on PVD Alumina Using an Inverted Cylindrical AC Magnetron Sputtering System, **J. MEHTA**, R. KILARU, M. GORDON, University of Arkansas

CP-6

Annealing Effects of ZnO Thin Film Growth on m-Plane Sapphire at Room Temperature by Atomic Layer Deposition, C.-S. KU, National Synchrotron Radiation Research Center, Taiwan, Y.-C. CHEN, J.-M. HUANG, **C.-M. LIN**, National Hsinchu University of Education, Taiwan, H.-Y. LEE, National Synchrotron Radiation Research Center, Taiwan

CP-7

The Effect of Varying Inert Gas Species on the Depositon of Thin Conducting Silver Films via Magnetron Sputtering, **G.T. WEST**, P. KELLY, Manchester Metropolitan University, United Kingdom

CP-8

Studies of the Structural Evolution and Film Properties of Pulsed Magnetron Sputtered Titania Coatings, **P. KELLY**, J. KULCZYK-MALECKA, N. FARAHANI, G.T. WEST, Manchester Metropolitan University, United Kingdom, C. HILL, J. STRATTON, Millennium Inorganic Chemicals Ltd., United Kingdom, G. CLARKE, Pilkington Technology Management Limited, United Kingdom, I. IORDANOVA, University of Sofia, Bulgaria, V. VISHNYAKOV, Manchester Metropolitan University, United Kingdom

CP-9

Depositing Low Temperature Passivation Layers for Flexible Display Application, P.-T. LIU, **Y.-T. CHOU**, A.-D. HUANG, B.-M. CHEN, S.-Y. TSAI, National Chiao Tung University, Taiwan

CP-10

Optical Properties of Multilayered Metal/Amorphous Carbon Coatings, Y.-Y. CHANG, R.H. YANG, K.-C. TSENG, **C.-Y. TSAI**, Mingdao University, Taiwan

CP-11

Effects of Additive Gases and Plasma Post-Treatment on Electrical Properties and Optical Transmittance of ZnO Channel Layers in Transparent Thin Film Transistors, **J.H. BANG**, W. KIM, H.S. UHM, J.-S. PARK, Hanyang University, Korea

CP-12

Effects of Post Plasma Treatment on Material Properties and Device Characteristics in Indium Zinc Oxide Thin Film Transistors, **W. KIM**, J.H. BANG, H.S. UHM, J.-S. PARK, Hanyang University, Korea

CP-13

Fabrication of Bottom-Gate Transparent Oxide TFTs Using a Novel Two-Mask Process, **H.S. UHM**, J.H. BANG, W. KIM, Hanyang University, Korea, S.Y. LEE, KIST, Korea, J.-S. PARK, Hanyang University, Korea

CP-14

Preparation of Nano-Structured Alumina Thin Films by Microwave-Assisted Hydrothermal Process, **J.W.-C. YU**, M.-S. LIN, YI-CHENG JAW, F.C.-N. HONG, National Cheng Kung University, Taiwan

CP-15

Electrochromic Properties Ni(V)Ox Films Deposited via Reactive Magnetron Sputtering 8V-92Ni Alloy Target, J.-M. YE, Y.-P. LIN, Y.-T. YANG, J.-T. CHANG, **J.-L. HE**, Feng Chia University, Taiwan

CP-16

Resistive Switching in Transparent ITO/Cu_2O/TiO_2/ITO Stacked Structure, L.-C. CHANG, Y.-C. PENG, J.-H. LU, Ming Chi University of Technology, Taiwan, **Y.-C. KUO**, National Taiwan Ocean University, Taiwan

CP-17

Cathodoluminescent and Photoluminescent Properties of Manganese-doped Rhombohedral Zinc Germanate Prepared by Radio Frequency Magnetron Sputtering, K.H. YOON, **J.H. KIM**, Chungbuk National University, Korea

CP-18

Effect of Buffer Layer on Preparation of Transparent Conducting Impurity-Doped ZnO Thin Films by dc Magnetron Sputtering, **J.-I. NOMOTO**, J.-I. ODA, T. MIYATA, T. MINAMI, Kanazawa Institute of Technology, Japan

CP-19

Color Control of the Various Activator-Co-Doped La_2O_3:Bi Phosphor Thin Films Prepared by Magnetron Sputtering, **T. MIYATA**, K. SAHARA, T. MINAMI, Kanazawa Institute of Technology, Japan

CP-20

Determination of Dopant Concentration in Spiro2-CBP:$Ir(ppy)_3$ Co-Deposited Thin Films Used as Active Layer in Phosphorescent OLED, Y. ANGULO, PUC-Rio, Brazil, E. GRAVINA, R. MACHADO, C. LEGNANI, W. QUIRINO, C.A. ACHETE, Inmetro, Brazil, **M. CREMONA**, PUC-Rio, Brazil

CP-21

MgF_2/SiO_xN_y Couple for Double Layer Antireflection (DLAR) Coating Applications, **K.C. MOHITE**, A.D. ADSOOL, University of Pune, India

CP-22

Effect of Concentration on Optical Properties of Cobalt Oxide Selective Coatings Prepared by Electrodeposition Method on Stainless and Copper Substrate, **P.N. SHELKE**, Baburaoji Gholap College, India, R.R. HAWALDAR, S.D. GUNJAL, R. UDDAWANT, K.C. MOHITE, M.G. TAKWALE, University of Pune, India

Carbon and Nitride Materials: Synthesis-Structure-Property Relationships
Room: Golden Pacific Ballroom - Session DP

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

DP-1

Optical and Electrical Response of Self-Assembled Single-Walled Carbon Nanotube Networks, **I.-J. TENG**, L.-C. WANG, H.-L. HSU, T. WANG, K.-L. CHEN, National Chiao Tung University, Taiwan, S.-R. JIAN, I-Shou University, Taiwan, C.-T. KUO, Min Dao University, Taiwan

DP-2

Coating of Carbon Nanotubes with Amorphous Carbon Nitride Thin Films and Characterization of Long-Term Emission Stability, **Y.-R. NOH**, J.-P. KIM, J.-S. PARK, Hanyang University, Korea

DP-3

The Gas Sensing Study of Nanocomposite Material Based on Functionalized Carbon Nanotubes, **L.C. WANG**, National Chiao Tung University, Taiwan, K.-T. TANG, National Tsing Hua University, Taiwan, C.-T. KUO, MingDao University, Taiwan, S.-R. YANG, Chung-Shan Institute of Science & Technolog, Taiwan

DP-5

HF-CVD of Nano (NDC) and Micro (MDC) Diamond Coatings onto CrN/Cr Bi-Layers: Morphology, Adhesion and Wear Resistance, R. POLINI, **M. BARLETTA**, Università di Roma Tor Vergata, Italy, G. CRISTOFANILLI, Università di Roma Tor Vergata, Itlay

DP-6

Effect of Nickel Incorporation on Structural, Nanomechanical and Biocompatible Properties of Diamond Like Carbon Thin Films Prepared by Low Energy Biased Target Ion Beam Deposition, P. VIJAIBHARATHY, Bharathiar University, India, D. NATARAJ, Bharathair University, India, **Y.-Y. CHANG**, Mingdao University, Taiwan, D. MANGALARAJ, Bharathiar University, India, S.-M. YANG, National University of Kaohsiung, Taiwan, Y. QIAOQIN, University of Saskatchewan, Canada, L. YANG, T.J. WEBSTER, Brown University

DP-7

Silicon Modified DLC Coatings Deposited by PACVD and PVD Sputter Techniques, **M. KEUNECKE**, I. BIALUCH, K. BEWILOGUA, Fraunhofer IST, Braunschweig, Germany, D. HOFMANN, S. KUNKEL, AMG Coating Technology GmbH, Hanau, Germany

DP-8

Wear Resistance and Interfacial Studies of Cu-Doped Diamond-Like Carbon on Aluminum Alloy, J.-Y. JAO, **Y.-C. LIU**, S.-Y. SHIU, F.-S. SHIEU, L.-S. CHANG, National Chung Hsing University, Taiwan, H.-C. SHIH, National Tsing Hua University, Taiwan

DP-9

Structural, Nanomechanical and Biocompatible Properties of Titanium Incorporated Diamond Like Carbon Thin Films, P. VIJAIBHARATHY, Bharathiar University, India, D. NATARAJ, Bharathair University, India, **Q. YANG**, University of Saskatchewan, Canada, D. MANGALARAJ, Bharathiar University, India, J.S. ALBERO, University of Alicante, Spain, T.J. WEBSTER, Brown University, Y.-Y. CHANG, Mingdao University, Taiwan

DP-10

Reaction Mechanism and Characteristics of High-Temperature Oxidation of sp^3 Rich Diamond-Like Carbon Films Synthesized by the Cathodic Arc Evaporation Process, D.-Y. WANG, **J.-L. LU**, W.-C. CHEN, M.-H. SHIH, MingDao University, Taiwan

DP-11

UV/O_3 Treatment of a-C:O and a-C:N Thin Films, W. KULISCH, University of Kassel, Germany, F. DANNEIL, H. VASILCHINA, S. ULRICH, **M. STUEBER**, Forschungszentrum Karlsruhe, Germany, G. CECCONE, D. GILLILAND, European Commission JRC, Italy, C. POPOV, University of Kassel, Germany

DP-12

Electrical Properties of Liquid-Phase Deposited Carbon Nitride Films, **H. KIYOTA**, M. HIGASHI, T. KUROSU, Tokai University, Japan

DP-13

Corrosion Performance of Diamond-Like Carbon (DLC)-Coated 316L SS in Simulated Body Fluid Environment, **E. GIL DE FUENTES**, Universidad Nacional Experimental Politecnica (UNEXPO), Venezuela, M.H. STAIA, R. FRAGIEL, E.S. PUCHI, Universidad Central de Venezuela (UCV), Venezuela, D.E. CHICOT, Université des Sciences et Technologies de Lille, France

DP-14

Pulse Plasma Nitriding and a-CN_x:H Coating Deposition on Hot Work Steel Samples, **M. ZLATANOVIC**, School of Electrical Engineering, Serbia, N. POPOVIC, Nuclear Science Institut Vinca, Serbia

DP-15

Surface Optical Raman Modes in Nano-Crystalline $In_xGa_{1-x}N$ Thin Films Prepared by Mixed Source Modified Activated Reactive Evaporation, **S. MEHER**, K.P. BIJU, M.K. JAIN, IIT Madras, Semiconductor Laboratory, India

DP-16

Growth of Vertically Aligned GaN Nanowires, **W.-C. HOU**, F.C.-N. HONG, National Cheng Kung University, Taiwan

DP-17

Improving Surface Smoothness of Gallium Nitride Nanowires by Introducing Hydrogen Plasma, **T.-H. WU**, F.C.-N. HONG, National Cheng Kung University, Taiwan

DP-18

Resistive Switching Effect in Zirconium Oxynitride Thin Film Deposited by Unbalanced Magnetron Sputtering, **C.H. LEE**, J.-H. HUANG, J.-P. YU, National Tsing Hua University, Taiwan

DP-19

Effect of Al-Doped on Structural and Optical Properties of ZnO Thin Films Grown by Atomic Layer Deposition, **C.-C. HSIEH**, S.-R. JIAN, I-Shou University, Taiwan, C.-S. KU, H.-Y. LEE, National Synchrotron Radiation Research Center, Taiwan, J.-M. HUANG, C.-M. LIN, National Hsinchu University of Education, Taiwan

DP-20

Effect of Carbon on the Tribological Performance of Nano-Structured AlTiCN Films, **H.-Y. KAO**, Y.-Y. CHANG, Mingdao University, Taiwan

DP-21

The Effect of Sulfur on the Structure of Nanomaterials Synthesized in Organic Liquids, **A. ARAI**, Toyo University, Japan, H. GAMO, Toppan Printing Co. Ltd., Japan, S. SHIBASAKI, Toyo University, Japan, A. ANDO, National Institute for Materials Science, Japan, M. NISHITANI-GAMO, Toyo University, Japan

DP-22

The Investigation of Scratch Behaviour of Composed Structured TiBN Hard Films Deposited on Cold Work Tool Steel at the Different Nitrogen Rates, H. CICEK, Atatürk University, Turkey, **O. BARAN**, Erzincan University, Turkey, Y. TOTIK, E. ASLAN, I. EFEOGLU, Atatürk University, Turkey

Tribology and Mechanical Behavior of Coatings and Thin Films
Room: Golden Pacific Ballroom - Session EP

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

EP-1

Characterizing (Ti,Al)N Film Coating Produced by Inverted Cylindrical Magnetron (ICM) Sputtering For Metal Machining Applications, **K.N. ABUSHGAIR**, Albalqa Applied University, Jordan, H. ABU-SAFE, Lebanese American University, Lebanon, M. GORDON, University of Arkansas

EP-2

Coating Performances When Dry Machining Refractory Titanium Alloys, **M. NOUARI**, M. CALAMAZ, F. GIROT, Ecole des Mines de Nancy, France

EP-3

Study of Self-Lubricated Coatings Deposited onto Radial and Angular Bearings, **N.M. RENEVIER**, University of Central Lancashire, United Kingdom, D.G. TEER, Teer Coatings Limited, United Kingdom

EP-4

Mechanical Properties of Two WC Base Thermal Spray Coatings, Determined by Means of Conventional and Instrumented Indentation Tests, **J.G. LA BARBERA-SOSA**, University of Venezuela

EP-5

Mechanical Properties Evaluation of HFCVD Diamond-Coated WC-Co Substrates With Hard Chromized Interlayers, **C.-C. CHOU**, National Taiwan Ocean University, Taiwan, LEE, Ming Chi University of Technology, Taiwan, H.-H. LIN, Y.-I. CHEN, Y.-C. CHU, National Taiwan Ocean University, Taiwan

EP-6

Correlation Between Pvd Coating Strength Properties and Impact Resistance at Ambient and Elevated Temperatures, **K.D. BOUZAKIS**, CERTH, Greece and IPT, Germany, G. SKORDARIS, Aristoteles University of Thessaloniki, Greece / Fraunhofer PCCM, Germany, Greece, E. BOUZAKIS, Fraunhofer PCCM, Germany, Greece, S. GERARDIS, M. PAPPA, Aristoteles University of Thessaloniki, Greece / Fraunhofer PCCM, Germany, Greece

EP-7

Mechanical Properties of Polyimide with Nanostructure Induced by Ion Beam Irradiation, **S.F. AHMED**, G.-H. RHO, M.-W. MOON, J.-H. HAN, K-.R. LEE, Korea Institute of Science and Technology, Korea

EP-8

Coefficient of Friction and Wear of Sputtered a-C Thin Coatings Containing Mo, **P. NOVAK**, J. MUSIL, R. CERSTVY, University of West Bohemia, Czech Republic

EP-9

Challenges and Applications of Elevated Temperature Nanoindentation to 75° C, **B. BEAKE**, P. ADEN, Micro Materials Ltd, United Kingdom, N. SCHWARZER, Saxonian Institute of Surface Mechanics, Germany, G.S. FOX-RABINOVICH, McMaster University, United Kingdom, W. HELLE, LOT Oriel GmbH, Germany

EP-12

Tribological Behavior of Thick-Layered TiCN Coatings, **H.-M. LIN**, J-.G. DUH, National Tsing Hua University, Taiwan

EP-13

Fretting Wear of HVOF WC-Co -Cr Alloy Deposited on SAE 1045 Steel, **E. CARRASQUERO**, Central University of Venezuela

EP-14

Fretting Wear of Duplex ZrN/electroless Ni-P Coating on 7075-T6 Aluminum Alloy, T. MORENO, UNEFA, Venezeula, **M.H. STAIA**, Universidad Central de Venezuela

EP-15

Sliding Wear Perfomance of ZrN PVD Coating on 7075-T6 Aluminum Alloy, **Y. SANTANA**, Universidad Central de Venezuela

EP-16

Cracking Behaviour vs. Wear Behaviour of CrSiN Nanocomposite Coatings, **T. SCHMITT**, J. FONTAINE, Ecole Centrale de Lyon, France, P. STEYER, G.P. POT, INSA de Lyon, France, F. SANCHETTE, CEA, France, C. ESNOUF, INSA de Lyon, France

EP-17

Impact Facture Resistance of CrAlSiN Hard Coatings, Y.-Y. CHANG, **C.M. CHENG**, Mingdao University, Taiwan

EP-18

Evaluation of Hardness and Mechanical Property of Cr$_2$N/Cu Multilayered Thin Films by Molecular Dynamics Simulations, **.-C. HUANG**, Tungnan University, Taiwan

EP-19

Direct Measurement of the Glass Transition Temperature of a Thin Polymer Film, **S. PAVAN**, J.-L. LOUBET, Ecole Centrale de Lyon, France, M. BEN SAAD, J. MALLÉGOL, ArcelorMittal Research Liège, Belgium

EP-20

Tribological and Corrosion Behavior of TiAlN/Pt and TiALN/TiAL Multilayers, **M. FLORES**, E. RODRIGUEZ, J. GARCIA, Universidad de Guadalajara, Mexico

EP-21

The Performance TiAlN + AlCrN Coated Grade in Milling of ADI, **W. MATTES**, SENAI-SC, Brazil, A.C. BOTTENE, USP, Brazil, R. DA SILVA, UNERJ, Brazil

EP-22

Tribological Studies of Mechano-Chemically Applied Topcoats on Nanolayered TiAlN-CrN PVD Coatings Deposited by Steered Arc, **A. MATTHEWS**, A. LEYLAND, University of Sheffield, United Kingdom, C.I. LENNARTZ, University of Sheffield, United Kingdom & Aachen University, Germany, G. CASSAR, J.W. EICHLER, University of Sheffield, United Kingdom, A. TOROSYAN, L.A. DONOHUE, Richter Precision Inc.

EP-23

Towards Redefining the Geometry of the Rockwell Stylus to Improve the Scratch Test, **N.M. JENNETT**, National Physical Laboratory, United Kingdom, G. FAVARO, CSM Instruments, Switzerland, N. RANDALL, CSM Instruments

EP-24

Temperature Dependent Comparison of Silver Molybdate and Silver Tungstate as Solid Lubricants to Understand Double Metal Oxides, **D. STONE**, D.P. SINGH, J. LIU, Southern Illinois University Carbondale, C. MURATORE, A.A. VOEVODIN, Air Force Research Laboratory, Q. GE, S.M. AOUADI, Southern Illinois University Carbondale

EP-25

Influence of Different Plasma Nitriding Treatments on the Wear and Crack Behaviour of Forging Tools Evaluated by Rockwell Indentation and Scratch Tests, **H. PASCHKE**, M. WEBER, P. KAESTNER, G. BRÄUER, Fraunhofer IST, Germany

EP-26

Nanocrystalline Diamond Films Coatings for Tungsten Carbide Tools, V.P. ADIGA, University of Pennsylvania, C.D. TORRES, P.J. HEANEY, A.V. SUMANT, University of Wisconsin-Madison, K. SRIDHARAN, Argonne National Laboratory, F.E. PFEFFERKORN, University of Wisconsin-Madison, **R.W. CARPICK**, University of Pennsylvania

EP-28

Impact of Uniaxial Strain on GIFBE in Partially Depleted SOI n-MOSFETs, **C.-H. DAI**, T.-C. CHANG, National Sun Yat-sen University, Taiwan

EP-29

Numerical Approach for the Description of Different Fracture Modes for Zr/ZrO$_2$ system - Deterministic and Probabilistic Aspects, **L. LI**, D. BRANCHERIE, J. FAVERGEON, J.M. ROELANDT, University of Technology of Compiegne, Roberval Laboratory, France

EP-30

The Effect of Surface Wettabiity on Friction and Wear of Nanopatterned DLC Film, Y.J. JANG, **H. KOUSAKA**, N. UMEHARA, Nagoya University, Japan

EP-31

Liquid Cyrstals onto Boron Nitride/Diamond-Like Carbon Multilayered Films for Ultralow Friction Applications, **V.B. AMARAL**, Commonwealth Scientific and industrial Research Organisation, Australia, T. AMANN, S. MEIER, M. KONIG, A. KAILER, Fraunhofer IWM, Germany

Characterization: Linking Synthesis Properties and Microstructure
Room: Golden Pacific Ballroom - Session FP

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

FP-1

Growth and Optical Properties of Uniform Tungsten Oxide Nanowires Bundles via a Two-Step Heating Process by Thermal Evaporation, Y.T. HSIEH, National Tsing Hua University, Taiwan, M.W. HUANG, National Chung Hsing University, Taiwan, C.C. CHANG, **C.H. CHIEN**, H.C. SHIH, National Tsing Hua University, Taiwan

FP-2

Charatcerization of CuCr Films Annealed Under Controlled Atmosphere, **H.-Y. CHEN**, H.-C. WANG, National Kaohsiung University of Applied Sciences, Taiwan

FP-3

Modulated IR Radiometry of Magnetron Sputtered Optically Active Coatings with Au Nanoparticles Dispersed in an Amorphous TiO$_2$ Dielectric Matrix, **F. VAZ**, F. MACEDO, R.T. FARIA JR., M. TORRELL, Minho University, Portugal, A. CAVALEIRO, University of Coimbra, Portugal, K.H. JUNGE, J. GIBKES, J. PELZL, B.K. BEIN, Ruhr-University, Germany

FP-4

The Effect of Thermal Annealing on the Structural Properties of ZnO Thin Films, **E. BROITMAN**, H-J. HSIEH, Carnegie Mellon University, B.H. HOWARD, National Energy Technology Laboratory, U.S. Department of Energy, J.B. MILLER, Carnegie Mellon University

FP-5

Residual Stress Gradients in Shot Peened TiN and TiCN Coatings Characterized by High Temperature X-ray Diffraction, **M. BARTOSIK**, Montanuniversität Leoben, Austria, R. PITONAK, Boehlerit GmbH & Co.KG, Austria, J. KECKES, Montanuniversität Leoben, Austria

FP-6

The Preparation and Photo-Sensing of Thermal Evaporated ZnS Nanowires, **Y.-W. CHENG**, Chinese Culture University, Taiwan

FP-7

Characteristics of Linear Polarization Selector and Polarization-Discriminatory Inverter Fabricated by Oblique Angle Deposition, **Y.J. PARK**, J.J. KIM, S.J. PARK, C.K. HWANGBO, Inha University, Korea

FP-8

Effect of Substrate Bias and Nitrogen Flow Rate on the Microstructure and Properties of TaN$_x$ Thin Films, C.-K. CHUNG, N.-W. CHANG, T.-S. CHEN, **S.-C. CHANG**, B.-H. WU, National Cheng Kung University, Taiwan

FP-9

Application of Modulated IR Radiometry to IR Semitransparent Coatings, R.T. FARIA JR., **F. MACEDO**, A.C. FERNANDES, F. VAZ, Universidade do Minho, Portugal, J. GIBKES, Ruhr-University, Germany, P. KIJAMNAJSUK, Kasetsart University, Thailand, J. PELZL, B.K. BEIN, Ruhr-University, Germany

FP-10

Stress Development in Amorphous Si Thin Films: an *in situ* Study, **A. FILLON**, G. ABADIAS, A. MICHEL, C. JAOUEN, University of Poitiers, France

FP-11

In-Situ Impedance Spectroscopy Studies into the Effects of Electric Field Distribution During Plasma Electrolytic Oxidation of Al, **C.-J. LIANG**, A. ALEKSEY, University of Sheffield, United Kingdom, E. PARFENOV, Ufa State Aviation Technological University, Russia, A. MATTHEWS, University of Sheffield, United Kingdom

FP-12

Composition and Structural Analysis of Ti-C(O,N) Sputter Deposited Thin Films, **J.M. CHAPPÉ**, L. CUNHA, C. MOURA, Universidade do Minho, Portugal, J.F. PIERSON, Ecole des Mines de Nancy, France, N. MARTIN, Institut FEMTO-ST, France, F. VAZ, Universidade do Minho, Portugal

FP-13

Study of Crystallization and Microstructure Evolution of TiO$_2$ Thin Films and Powders by XRD Total Pattern Fitting, **R. KUZEL**, Z. MATEJ, L. NICHTOVA, Charles University in Prague, Czech Republic

FP-14

Photo-Degrading of Azo Dye Acid Yellow 17 by La-Modified TiO_2, **Q.H. WANG**, Y.H. HSIEH, National Chung-Hsing University, Taiwan, K.S. YAO, Mingdao University, Taiwan, T.C. CHENG, National Pingtung University of Science and Technology, Taiwan, C.Y. CHANG, Mingdao University, Taiwan

FP-15

Comparative Study of Three Methods to Measure Thickness of PVD Coatings, **M.A. QUIÑONES-SALINAS**, R.D. MERCADO-SOLIS, Universidad Autonoma de Nuevo Leon, Mexico, J. SMOLIK, A. MAZURKIEWICZ, Institute for Sustainable Technologies, Poland

FP-16

Electrical Characteristics of High-k Dielectric Film Prepared by Atomic Layer Deposition, L.Y. CHENG, **A.S. CHEN**, National Chi-Nan University, Taiwan

Applications, Manufacturing, and Equipment
Room: Golden Pacific Ballroom - Session GP

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

GP-1

The Effects of Low Friction Coating on the Tribological Behaviors of the Piston Ring, B.C. NA, **J.H. SEO**, Korea Automotive Technology Institute, Korea, D.S. LIM, Korea University, Korea

GP-2

Nano-Columnar Amorphous Carbon Coating Design For Molding Dies of Optical Elements, **T. AIZAWA**, Shibaura Institute of Technology, Japan, T. FUKUDA, Mitue Mold Co. Ltd., Japan, E. IWAMURA, Arakawa Chemical Co. Ltd., Japan

GP-3

Structural and Mechanical Properties of Multilayered AlTiN/ZrN Coatings, Y.-Y. CHANG, **C.-C. HUNG**, W.-Y. CHANG, Mingdao University, Taiwan

GP-4

Effect of Embedded Metal Layer on $SrZrO_3$ Resistive Switching Memory Films, **C.-C. LIN**, W.-T. HO, National Dong Hwa University, Taiwan, C.-Y. LIN, National Chiao Tung University, Taiwan

GP-5

Low Temperature Synthesis of Amorphous Carbon Films by Using Microwave Plasma Jet, **Y. TACHIMOTO**, Keio University, Japan, A. SHIRAKURA, Kanagawa Academy of Science and Technology, Japan, H. KODAMA, Aoyama Gakuin University, Japan, T. HORIUCHI, Kanagawa Industrial Technology Center, Japan, T. SUZUKI, Keio University, Japan

GP-6

A New Method for Inner Surface Modification by Plasma Ion Implantation Based on Internal ICP Discharge, Z.J. WANG, **X.B. TIAN**, 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-7

Synthesis of TiO_x Thin Films by Atmospheric Pressure Plasma Enhanced Chemical Vapor Deposition, **S.S. KIM**, S.D. KIM, J.W. SHIN, S.C. OH, Institute for Advaned Engineering, Korea

GP-8

Self-Organised Nanostructuring of Composite Coatings at High-Temperatures for Drag Reduction and Self-Cleaning, **P. SCHAAF**, S. GÜNSCHMANN, Ilmenau University of Technology, Germany, J. WILDEN, V.E. DRESCHER, TU Berlin, Germany, M. HOPFELD, Ilmenau University of Technology, Germany

GP-9

Comparison of Crystalline La_2CuO_4 Thin Film Synthesis with Different Processes, **N. TRANVOUEZ**, Ecloe des Mines, France, J.-F. JEAN-FRANÇOISPIERSON, F. CAPON, Institut Jean Lamour, France, J.PH. BAUER, Ecole des Mines de Nancy, France

GP-10

Effect of Copper Acetate on Structure and Mechanical Properties of Plasma Electrolytic Oxidation Coatings on Al, **A. ALEKSEY**, University of Sheffield, United Kingdom, A. LHERMEROULT, ENSIACET, France, A. PILKINGTON, RMIT, Australia, A. MATTHEWS, The University of Sheffield, United Kingdom

GP-11

Vacuum Gas Nitriding of Electroplated Chromiun on H13 Steel, **H. CIFUENTES**, J.J. OLAYA, Universidad Nacional de Colombia

GP-12

Microstructural and Tribological Properties of Plasma Thermochemically Treated Ti-6Al-4V, **V.H. BAGGIO-SCHEID**, Institute of Advanced Studies, Brazil, L.F. BONETTI, National Institute of Space Research, Brazil

GP-13

The Effects of Post Heat Treatments on Wear Resistance of Plasma Sprayed Mo-NiCr Coatings, **M. RODRIGUEZ**, Universidad Central de Venezuela, L.G. GIL, UNEXPO, Venezuela, D. DA SILVA, R. HOYER, Universidad Central de Venezuela, R. GUEVARA, S.L. LISCANO, UNEXPO, Venezuela, M.H. STAIA, Universidad Central de Venezuela

GP-14

Material Properties and Cutting Performance of Cr-Al-N and Cr-Al-Mo-N Coated End-Mill Deposited by Hybrid Coating for Green Machining, **H.-S. TAK**, S-.H. KWON, Pusan National University, Korea, T.-J. JE, Korean Institute of Machinery and Materials (KIMM), Korea, M.-C. KANG, K.-H. KIM, Pusan National University, Korea

GP-15

Effect of Plasma Nitriding Pre-Treatment on Steel Surface Deformation Under Nitride Based Multilayer Coating (BELCOAT SS forStamping Mold of Ultra High-Tensile Steel), **T. OKUDE**, D.T. YASUNAGA, K. YAMAMOTO, Kobe Steel Ltd., Japan, T. KASHI, K. IMAI, Kams Co. Ltd., Japan, TAKAZAWA, J. YSHIDA, Nippon Koshuha Steel Co. Ltd., Japan

GP-16

Characterisation of PAPVD Coatings on Duplex-Treated Hot-Work Tool Steel, M.A. QUIÑONES-SALINAS, **R.D. MERCADO-SOLIS**, Universidad Autonoma de Nuevo Leon, Mexico, J. SMOLIK, A. MAZURKIEWICZ, Institute for Sustainable Technologies, Poland

GP-17

Nitriding of the CoCr Alloy as a Method for Improving the Adhesion of Hard Biocoatings, J.A. ORTEGA-SAENZ, **M.A.L. HERNANDEZ-RODRIGUEZ**, Universidad Autonoma de Nuevo Leon, FIME, Mexico, R. MICHALCZEWSKI, Institute for Terotechnology, Poland, J. SMOLIK, Institute for Sustainable Technologies, Poland, M. SZCZEREK, Institute for Terotechnology, Poland

GP-18

Tribology of Duplex Process of Plasma Nitriding Plus Hard Nanostructured Coating of Wear Resistance Applications in Tool Steels, **M. ARIZMENDI**, G. VARGAS, Centro de Investigacion en Materiales Avanzados, S.C., México, A. CHAVEZ, CINVESTAV-SALTILLO, Mexico

New Horizons in Coatings and Thin Films
Room: Golden Pacific Ballroom - Session HP

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

HP-1

Cobalt Nanocrystals Embedded in Silicon Oxide Fabricated by Incorporating Oxygen Elements During Sputtering Process, **C.-W. HU**, National Chiao Tung University, Taiwan, T.-C. CHANG, National Sun Yat-Sen University, Taiwan, C.-H. TU, National Chiao Tung University, Taiwan, Y.-H. HUANG, National Tsing Hua University, Taiwan, C.-C. LIN, National Chiao Tung University, Taiwan, M.-C. CHEN, National Sun Yat-Sen University, Taiwan, F.-S. HUANG, National Tsing Hua University, Taiwan, S.M. SZE, T.-Y. TSENG, National Chiao Tung University, Taiwan

HP-2

High Power Impulse Magnetron Sputtering of Zirconium, **J. REZEK**, J. LAZAR, J. VLCEK, University of West Bohemia, Czech Republic

HP-3

Impact of Strain Engineering on InGaAs NMOSFET with a InGaAs Alloy Stressor, **H.P. SUN**, S.-T. CHANG, C.-C. LEE, National Chung Hsing University, Taiwan

HP-4

Ir Nanocrystals Lying on Asymmetric SiO_2/Si_3N_4 Tunnel Barrier With Large Memory Window for Nonvolatile Memory Application, **T. WANG**, C.J. CHEN, I.-J. TENG, C.M. LIU, NCTU, Taiwan, C.-T. KUO, Min Dao University (MDU), Taiwan

HP-5

Structure and Properties of Nanocrystalline TiN Thin Film Produced by High Power Impulse Magnetron Sputtering: Effect of Ionization Rate, **C.-Y. SU**, J.-H. HUANG, National Tsing Hua University, Taiwan, G.-P. YU, National Tsing Hua University, J.-Y. WU, Institude of Nuclear Energy Research, Taiwan

HP-6

Effects of Seed Layer Precursor Type on the Synthesis of ZnO Nanowires using Chemical Bath Deposition, **W.-Y. WU**, National University of Tainan, Taiwan, T.-L. CHEN, J.-M. TING, National Cheng Kung University, Taiwan

HP-7

X-Ray Images Obtained from Cold Cathodes Using Carbon Nanotubes Coated with Gallium-Doped Zinc Oxide Thin Films, **J.-P. KIM**, Y.-R. NOH, Hanyang University, Korea, K.-C. JO, S.Y. LEE, KIST, Korea, H.-Y. CHOI, J.-U. KIM, KERI, Korea, J.-S. PARK, Hanyang University, Korea

HP-8

Fabrication and Photo-Sensing Properties of Sb-Doped SnO_2 Nanowire Sensors, **P.-S. LEE**, National Tsing Hua University, Taiwan

HP-9

Indium Layer Through Different Process in High-Quality $CuInSe_2$ Film for Solar Cell, **T.-W. CHANG**, W.-H. LEE, G.-S. LYU, National Cheng Kung University, Taiwan

HP-10

Reactive High Power Impulse Magnetron Sputtering of Titanium Oxide Thin Films, **M. AUDRONIS**, Gencoa Ltd., V. BELLIDO-GONZALEZ, Gencoa Ltd, P. KORGUL, A. MATTHEWS, The University of Sheffield, United Kingdom

HP-11

Forming $CuInSe_2$ Using Two-Step Electrodeposition of $CuSe_x$ and $InSe_x$ Layers, **S.-Y. HU**, Y.-X. SU, W.-H. LEE, National Cheng Kung University, Taiwan, S-.C. CHENG, Y.-L. WANG, National Chia-Yi University, Taiwan

HP-13

Gas Sensing Properties of SnO_2 Nanostructured Films by Electrophoretic Deposition, **S.-C. WANG**, M.-R. CHEN, Southern Taiwan University, Taiwan, R.-K. CHIANG, Far East University, Taiwan, ROC, C.-Y. TSAY, C.-K. LIN, Feng Chia University, Taiwan

HP-14

Modified Properites of NiCr for Use in Strain Gauges by HiPIMS Deposition, **R. BANDORF**, H. GERDES, U. HECKMANN, G. BRÄUER, Fraunhofer IST, Germany

HP-15

Parameters Influencing the Deposition Rate During High-Power Impulse Magnetron Sputtering, **S. KONSTANTINIDIS**, Université de Mons, Belgium, M. PALMUCCI, A. BALHAMRI, J.-P. DAUCHOT, M. HECQ, R. SNYDERS, University of Mons, Belgium

HP-16

The Influence of Differernt Eletrolyte and Co-Solvent on the Titanium Dioxide Nanotube Array Prepared by Anodic Pulse Oxidation, **S. CHEN**, National Chiao Tung University

HP-17

Fabrication of AlN Nanowires for Optical-Sensing Properties, **T.Y. LU**, National Tsing Hua University, Taiwan

HP-18

High Density of SiC Nanoparticle Formation from Three-Layer Si/C/Si on Si (100) Using Rapid Thermal Annealing, C.-K. CHUNG, T.Y. CHEN, **C.-W. LAI**, C.C. PENG, B.-H. WU, National Cheng Kung University, Taiwan

HP-19

Roughness-Enhanced Thermal-Responsive Surfaces by Surface Initiated Polymerization of Polymer on Ordered ZnO Pore-Array Films, **C.-J. CHANG**, E.-H. KUO, Feng Chia University, Taiwan

HP-20

Thermal Conductivity and Morphology of Silver-Filled Multi-Walled Carbon Nanotubes and Polyimide Nanocomposite Films, **M.-H. TSAI**, D.-S. CHEN, National Chin-Yi University of Technology, Taiwan, C.-J. CHANG, Feng Chia University, China, J.-M. YEH, Center for Nanotechnology at CYCU and R&D Center for Membrane Technology, Taiwan, J.-W. LEE, Tungnan University, Taiwan

HP-21

Preparation of $Zn_yCd_{1-y}S$ Thin Film by Chemical Bath Deposition and Application for Dye-Sensitized Solar Cell, C.-C. CHANG, C.-C. CHAN, W.-J. HSU, **L. LIN**, Feng Chia University, Taiwan

HP-22

Corrosion Behaviour in Artificial Seawater of Thermal Sprayed WC-Co Based Coatings on Mild Steel, S. BRIOUA, K. BELMOKRE, LCTS, Université de Skikda, Algérie, France, V. DEBOUT, Bodycote, CRDA, France, P. JACQUOT, Bodycote, France, E. CONFORTO, **J. CREUS**, Université de la Rochelle, France

HP-23

A Study of the Influence of Pulse Length and Duty Factor on Hafnium Films Deposited with High Power Impulse Magnetron Sputtering, **A.N. REED**, M.A. LANGE, Air Force Research Laboratory / Universal Technology Corporation, J. JONES, Air Force Research Laboratory, J.J. HU, UDRI / Air Force Research Laboratory, A.A. VOEVODIN, Air Force Research Laboratory

HP-24

Self-Organized Nanodots of SiO_x Deposited by Atmospheric Pressure Plasma Enhanced Chemical Vapour Deposition, **G. ARNOULT**, T. BELMONTE, G. HENRION, Ecole des Mines de Nancy, France

HP-25

Effect of Interlayers on Field Emission Characteristics of Ink-Jet Printed CNT Emitter, **D. SONG**, Korea University, Korea, K.-I. LEE, S.-H. KIM, J.-H. HAN, KETI, Korea, H.-G. YOON, Korea University, Korea, C.S. LEE, Korea Electronics Technology Institute, Korea

HP-26

Comparison of Ni-TiO_2 Nanocomposite Coating Fabricated by Conventional Electrolating (CEP) and Sediment Co-Deposition (SCD) on Low Carbon Steel, **A. SADEGHI**, R.A. KHOSROSHANI, Sahand University of Technology, Iran, Z. SADEGHIAN, Research Institute of Gas and Petroleum, Iran, N. PARVINI, Sahand University of Technology, Iran

H6-2

Improved Adhesion of Polymethylsilsesquioxane Hard Coatings on Polymer Substrates, **Y.-C. KAO**, F.C.-N. HONG, National Cheng Kung University, Taiwan

Session TS1-TS4
Room: Golden Pacific Ballroom - Session TSP

TS 1-4 Poster Session
5:00- 7:00 pm

TSP-1

Electrochemical Characteristics of HA Coated/Nanostructured Ti-30Nb-xZr and Ti-30Ta-xZr Alloys, **H.C. CHOE**, Y.M. KO, W.A. BRANTLEY, Chosun University, Korea

TSP-2

Improvement of Apatite-Forming Ability and Bonding Strength between TiO_2 Film and Ti Substrate by Micro-Arc Oxidation, **D.H. LEE**, M.H. HONG, Yonsei University College of Dentistry, Korea, B.Y. KIM, Incheon National University, Korea, K.Y. KIM, MST Technology, Ltd. Co., Korea, K.M. KIM, Y.-K. LEE, Yonsei University College of Dentistry, Korea

TSP-4

Anti-Bacterial TaN-Ag Coatings on Titanium Dental Implants, Y.-Y. CHANG, M.-C. LAI, **C-.R. LIN**, Mingdao University, Taiwan, H.-L. HUANG, China Medical University, Taiwan

TSP-5

Two-Functional DC Sputtered Cu-Containing TiO_2 Thin Films, **M. MEISSNER**, V. ONDOK, J. MUSIL, R. CERSTVY, University of West Bohemia, Czech republic, K. FAJFRLIK, Charles University in Prague, Czech republic

TSP-6

Electrochemical Performance of Magnetron Sputter Deposited $LiFePO_4$-Ag Composite Thin Film Cathodes, K.-F. CHIU, **C.-L. CHEN**, Feng Chia University, Taiwan

TSP-7

PTFE Coated Nafion Proton Conducting Membranes for Direct-Methanol Fuel Cells, K.-F. CHIU, Feng Chia University, Taiwan, **Y.-R. CHEN**, National Taiwan University, Taiwan

TSP-8

Bioactivity and Biocompatibility of Carbon Based Nanocomposites/Nanolaminates Formed on Template Surfaces, **C. TSOTSOS**, P. EPAMINONDA, S. GRAVANI, K. POLYCHRONOPOULOU, C. DOUMANIDIS, C.G. REBHOLZ, University of Cyprus

TSP-9

The Thermal Stability Studies for $LiMn_xFe_{1-x}PO_4$ Cathode Material, **Z.-C. LIN**, Chinese Culture University, Taiwan

TSP-10

Surface Phenomena of Nanostructured/Femtosecond Laser Textured Ti-35Nb-xZr Alloys for Bioimplants, **Y.H. JEONG**, H.C. CHOE, W.A. BRANTLEY, Chosun University, Korea

TSP-12

Influence of Humidity on the Tribological Performance of Unmodified Soybean and Sunflower Oils, M.T. SINIAWSKI, N. SANIEI, Loyola Marymount University, **P. STOYANOV**, McGill University, Canada

TSP-13

YSZ-Ag Composites With Adaptive Thermal Conductivity, **J. GENGLER**, S. ROY, Spectral Energies, LLC, J. GORD, C. MURATORE, J. JONES, A.A. VOEVODIN, Air Force Research Laboratory

TSP-14

Thermodynamic Approach for DC Reactive Sputtering Process, **S. FADDEEVA**, J. OSEGUERA, ITESM, Mexico

TSP-15

Molecular Dynamics Simulations of the Sputtering Process of Boron Nitride, **A.-P. PRSKALO**, S. SCHMAUDER, University of Stuttgart, Germany, S. ULRICH, C. ZIEBERT, J. YE, Karlsruhe Institute of Technology, Germany

NOTES

Friday Morning, April 30, 2010

	Hard Coatings and Vapor Deposition Technology **Room: Town & Country - Session B3** **CVD Coatings and Technologies** **Moderators:** F. Maury, CNRS-CIRIMAT, H. Holzschuh, SuCoTec Ag, Germany	**Carbon & Nitride Materials: Synthesis-Structure-Property Relationships - Room: Pacific Salon 3 - Session D3** **Carbon and Nitrogen-Containing Nanostructured Composite and Nanolaminated Films** **Moderators:** J.-M. Ting, National Cheng Kung University
8:00 am	**B3-1 Invited** MOCVD Processed Metallic Alloy Coatings: Requirements, Achievements and Challenges, **D. VAHLAS**, CIRIMAT, France	**D3-1 Invited** Optical and Electronic Properties of Carbon- and Nitrogen-Based Nanostructured Inorganic Thin Films, **A. SCHULER**, Ecole Polytechnique Federal de Lausanne (EPFL), Switzerland
8:20 am	Invited talk continued.	Invited talk continued.
8:40 am	**B3-3** Upscaling of an a-C:H:Si Triplex Treatment Process in an Industrial DC PACVD System, **C. FORSICH**, University of Applied Sciences, Austria, D. HEIM, University of Appliced Science, Austria, T. MUELLER, Rubig, Austria	**D3-3 Invited** Development of TiVCr-Based High Entropy Alloy Coatings, **F.-S. SHIEU**, R.-S. YU, D.-C. TSAI, National Chung Hsing University, Taiwan
9:00 am	**B3-4** Epitaxial and Polycrystalline Growth of AlN by High Temperature CVD : Experimental Results and Simulation, **R. BOICHOT**, A. CLAUDEL, N. BACCAR, E. BLANQUET, M. PONS, Grenoble Institute of Technology, France	Invited talk continued.
9:20 am	**B3-5** High Temperature Chemical Vapour Deposition of AlN/W Coatings on Bulk SiC, **F.-Z. ROKI**, C. BERNARD, M. PONS, E. BLANQUET, M. MORAIS, Grenoble Institute of Technology, France, A. CLAUDEL, G. HUOT, ACERDE, France, S. POISSONNET, CEA Saclay, France	**D3-5** Non-Uniform Elastic Deformation of MAX Phases, **C. HUMPHREY**, H.J. STONE, W.J. CLEGG, University of Cambridge, United Kingdom, M.G. TUCKER, Rutherford Appleton Laboratory, United Kingdom
9:40 am	**B3-6 Invited** Scale-up Industry Application, and Up-Scale for Three-Dimensions: Process Design Study for Pulsed-Pressure MOCVD, **S. KRUMDIECK**, V. SIRIWONGRUNSON, C.W. LIM, M. JERMY, CAVE, D. PONS, M. ALKAISI, University of Canterbury, New Zealand	**D3-6** Properties of Thin MAX Phase Films Produced by Ion-Beam-Assisted Deposition, **R. VALIZADEH**, V. VISHNYAKOV, J. COLLIGON, Manchester Metropolitan University, United kingdom
10:00 am	Invited talk continued.	**D3-7** Tilting of Self-Organized Layered Arrays of Encapsulated Metal Nanoparticles in C:Ni Nanocomposite Films by Means of Hyerpthermal Ion Deposition, **G. ABRASONIS**, Forsch Dresden-Rossendorf, & Univ of Sydney, T.W.H. OATES, G.J. KOVACS, J. GRENZER, FDR, P. PERSSON, Linkoping Univ K.H. HEINIG, A. MARTINAVICIUS, N. JEUTTER, C. BAETHZ, Forsch Dresden-Rossendorf, , M. TUCKER, M.M.M. BILEK, Univ of Sydney, W. MOLLER,
10:20 am	**B3-8** Aluminium-Rich TiAlCN Coatings by LPCVD, **I. ENDLER**, M. HÖHN, M. HERRMANN, Fraunhofer IKTS Dresden, Germany, H. HOLZSCHUH, Walter AG, Germany, R. PITONAK, Boehlerit GmbH & Co.KG, Austria, S. RUPPI, Seco Tools AB, Sweden, H. VAN DEN BERG, H. WESTPHAL, Kennametal Technologies GmbH, Germany, L. WILDE, Fraunhofer CNT Dresden, Germany	**D3-8** Nano Composite TiNiC-Coatings for Low Friction and Low Contact Resistance, **B. ANDRÉ**, E. LEWIN, U. JANSSON, U. WIKLUND, Uppsala University, Sweden
10:40 am	**B3-9** In-Situ Oxidation of CVD TiC, **S. CANOVIC**, Chalmers University of Technology, Sweden, B. LJUNGBERG, Sandvik Tooling, Sweden, M. HALVARSSON, Chalmers University of Technology, Sweden	**D3-9** Nanometer-Thick Protective Films for Miniature Applications Deposited Using Reactive Magnetron Sputtering, **C. TSOTSOS**, K. POLYCHRONOPOULOU, University of Cyprus, N.G. DEMAS, R. MESCHEWSKI, University of Illinois, C.G. REBHOLZ, University of Cyprus, A.A. POLYCARPOU, University of Illinois
11:00 am	**B3-10** TiO_xN_y Coatings Grown by Atmospheric Pressure MOCVD, **F. MAURY**, CNRS-CIRIMAT, France, F.D. DUMINICA, CIRIMAT, France	**D3-10** Magnetron Sputtered Ti_3SiC_2 as Ohmic Contact to SiC, **K. BUCHHOLT**, Linköping University, Sweden, R. GHANDI, KTH - Royal Institute of Tech, Sweden, P. EKLUND, Linköping Univ, Sweden, M. DOMEIJ, C.M. ZETTERLING, KTH - Royal Institute of Tech, Sweden, L. HULTMAN, A. LLOYD SPETZ, Linköping Univ Sweden
11:20 am	**B3-11** Thermal Stability of Doped CVD κ-Al_2O_3 Coatings, D. HOCHAUER, Materials Center Leoben, **C. MITTERER**, Montanuniversität Leoben, Austria, M. PENOY, C. MICHOTTE, CERATIZIT Luxembourg S.a.r.l., Luxembourg, H.-P. MARTINZ, Plansee Se, Austria, M. KATHREIN, CERATIZIT Austria GmbH, Austria	
11:40 am	**B3-12** Deposition of Chromium-Containing Al_2O_3-CVD-Coatings, **M. HÖHN**, I. ENDLER, Fraunhofer IKTS Dresden, Germany, H. VAN DEN BERG, H. WESTPHAL, Kennametal Technologies GmbH, Germany	
12:00 pm	**B3-13** Synthesis and Properties of $(Al,Cr)_2O_3$, **K. TOMITA**, M. IGARASHI, E. NAKAMURA, A. OSADA, Mitsubishi Materials Corporation, Japan	

Friday Morning, April 30, 2010

	Tribology & Mechanical Behavior of Coatings &Thin Films **Room: Pacific Salon 1 - Session E1-2 - Friction & Wear of Coatings: Lubrication, Surface Effects & Modeling** **Moderators:** E. Broitman, Carnegie Mellon University, J.C. Sanchez-Lopez, Instituto de Ciencia de Materiales de Sevilla (CSIC-US), O.L. Eryilmaz, Argonne National Laboratory	**Applications, Manufacturing, and Equipment** **Room: Royal Palm 4-6 - Session G3** **Atmospheric and Hybrid Plasma Technologies** **Moderators:** V.H. Baggio-Scheid, Institute of Advanced Studies, D. Pappas, U.S. Army Research Laboratory
8:00 am	**E1-2-1** Microstructure and Properties Evolution of AlSi Coated Surfaces, **O. RASHWAN**, M. STOILOV, University of Windsor, Canada	**G3-1 Invited** Scaling Down Atmospheric Pressure PECVD Processes, **T. BELMONTE**, G. ARNOULT, G. HENRION, Ecole des Mines de Nancy, France
8:20 am	**E1-2-2** Tribological Properties of CrN/AlN Thin Films Deposited on H13 Steel by Reactive Unbalanced Magnetron Sputtering, A. ROJO, ITESM-TOL, Mexico, **J. SOLIS-ROMERO**, DGEST-ITTLA/ITESM-CEM, Mexico, J. OSEGUERA-PENA, O. SALIS-MARTINEZ, ITESM-CEM, Mexico	Invited talk continued.
8:40 am	**E1-2-3** Influence of the Nitriding and TiAlN/TiN Coating Thickness on the Sliding Wear Behavior of Duplex Treated AISI H13 Steel, **R. TORRES**, P. SOARES, Pontifícia Universidade Católica do Paraná, Brazil, C. SCHMITZ, C. SIQUEIRA, Universidade Federal do Paraná, Brazil	**G3-3** Fundamentals of Voltastatic Method for Kinetic Studies of High-Voltage Plasma-Assisted Anodising in Alkaline Solutions, **L.O. SNIZHKO**, Ukrainian State Univ for Chemical Eng, Ukraine, A. ALEKSEY, Univ of Sheffield, UK, N.L. GUREVINA, Ukrainian State Univ for Chemical Eng, Ukraine, E. PARFENOV, Ufa State Aviation Technological Univ, Russia, A. MATTHEWS, Univ of Sheffield, UK
9:00 am	**E1-2-4 Invited** Polymer Monolayers as Lubricious Coatings, **N.D. SPENCER**, ETH Zurich, Switzerland	**G3-4** High Density Large Area Hydrogen Plasma by Hollow Cathode Plasma Array, J. CHO, J. YANG, PSK Inc., Korea, H. PARK, D. PARK, **S. PARK**, Inha University, Korea
9:20 am	Invited talk continued.	**G3-5 Invited** Thin Film Deposition and Surface Modification with Atmospheric Pressure Dielectric Barrier Discharges, **F. FANELLI**, F. FRACASSI, R. D'AGOSTINO, University of Bari, Italy
9:40 am	**E1-2-6** On the Relationships Between the Fretting and Ball Cratering Behaviors of Solid Lubricant Coatings, **V. FRIDRICI**, Ecole Centrale de Lyon - LTDS, France, D.B. LUO, Ecole Centrale de Lyon - LTDS & Southwest Jiaotong University, France, PH. KAPSA, Ecole Centrale de Lyon - LTDS, France	Invited talk continued.
10:00 am	**E1-2-7** Temperature Effects on the Wear Behavior of Molybdenum Disulfide Solid Lubricant Films, **R.S. COLBERT**, J.H. KEITH, W.G. SAWYER, University of Florida	**G3-7** Nanoparticles of Polypyrrole Obtained by Atmospheric Pressure Plasma, M. VASQUEZ-ORTEGA, CINVESTAV-IPN, Mexico, **J. MORALES-CORONA**, Universidad Autonoma Metropolitana, Mexico, M. ORTEGA, CINVESTAV-IPN, Mexico, G. CRUZ-CRUZ, G. OLAYO, ININ, Mexico, R. OLAYO, Universidad Autonoma Metropolitana, Mexico
10:20 am	**E1-2-8** Tribological Properties in Different Test Conditions of Thin Films TiTaBN Deposited by CFUBMS, **O. BARAN**, Erzincan University, Turkey, I. EFEOGLU, Atatürk University, Turkey, B. PRAKASH, Luleå University of Technology, Turkey	**G3-8** Atmospheric Pressure Non-Thermal Plasma for Surface Modification of UHMW-PE Fibers, **J. YIM**, Drexel University, D. PAPPAS, U.S. Army Research Laboratory, A. FRIDMAN, G. PALMESE, Drexel University
10:40 am	**E1-2-9** Comparison of Abrasive Wear Resistance of Low Carbon Steels Subjected to Carburizing, Nitriding, Nitrocarburizing, and Boriding Treatments, **V. SISTA**, Argonne National Laboratory, G. KARTAL, Istanbul Technical University, Turkey, A. ERDEMIR, O.L. ERYILMAZ, G. KRUMDICK, Argonne National Laboratory, S. TIMUR, Istanbul Technical University, Turkey	**G3-9 Invited** Atmospheric Pressure Plasma-Enhanced Chemical Vapor Deposition of Thin Films, **R.F. HICKS**, Surfx Technologies LLC
11:00 am	**E1-2-10** Influences of Cooling Rates on the Mechanical Property and Tribology of High Entropy Alloy Thin Film by Atomistic Simulations, **J.-C. HUANG**, Tungnan University, Taiwan	Invited talk continued.
11:20 am	**E1-2-12** The Effect of Rhenium on The Tribological Properties of Al-Ti-Re-N and Cr-Re-N Coatings, **Z. KAHRAMAN**, K. KAZMANLI, Istanbul Technical University, Turkey, A. ERDEMIR, Argonne National Laboratory, M. URGEN, Istanbul Technical University, Turkey	
11:40 am		
12:00 pm		

Friday Morning, April 30, 2010

New Horizons in Coatings and Thin Films
Room: Royal Palm 1-3 - Session H6
Coatings for Compliant Substrates
Moderators: B. Beake, Micro Materials Ltd,
R.M. Souza, University of São Paulo

8:00 am	**H6-1** Processes Controlling Delamination and Buckling in Thin Hard Film-Compliant Substrate Systems, **N. MOODY**, E.D. REEDY, JR., E. CORONA, D. ADAMS, Sandia National Laboratories, J. YEAGER, D. BAHR, Washington State University, D. HUBER, H. FRASER, Ohio State University	
8:20 am	**H6-4 Invited** Mechanical Integrity of Thin Inorganic Coatings on Polymer Substrates Under Quasi-Static, Thermal and Fatigue Loadings, **Y. LETERRIER**, A. MOTTET, N. BOUQUET, D. GILLIÉRON, P. DUMONT, A. PINYOL, L. LALANDE, J.H. WALLER, J.-A.E. MANSON, Ecole Polytechnique Fédérale de lausanne (EPFL), Switzerland	
8:40 am	Invited talk continued.	
9:00 am	**H6-6** Tribological Behaviors on Nano-Structured Surface of the Diamond-Like Carbon (DLC) Coated on Soft Polymer, **M.-W. MOON**, G.-H. NOH, S.F. AHMED, K-.R. LEE, KIST, Korea	
9:20 am		
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11:40 am		
12:00 pm		

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Hard Coatings and Vapor Deposition Technology
Room: Pacific Salon 3 - Session B1-1

Sputtering Coatings and Technologies
Moderator: P. Eklund, Linköping University, M.-S. Wong, National Dong Hwa University

10:00am **B1-1-1 Structure and Properties of AlCrSiON Oxynitrides Prepared Using Pulsed DC Magnetron Sputtering**, *H. Najafi*, ***A. Karimi*** *(ayat.karimi@epfl.ch)*, EPFL, Switzerland, *M. Morstein*, Platit AG, Switzerland

Addition of oxygen into nitride-based nanocomposite coatings represents many possibilities in microstructural design, but also challenges in processing and characterisation. In this paper, we present recent results on the formation, microstructure, and mechanical properties of Al-Cr-Si-O-N coatings deposited usingpulsed dc magnetron sputtering under Ar/(N_2+O_2) atmosphere. A wide range of oxynitrides varying from pure nitrides to pure oxides was prepared by changing the O_2/N_2 ratio of the reactive gas flow. The content of Si as well as the ratio of Al/Cr were varied within a significant range. The coatings were analysed by EPMA, SIMS, XRD, TEM, and nanoindentation to demonstrate, in particular, the role of O:N ratio and deposition temperature between 400°C-700°C on structural evolution.

Chemical analysis revealed that the incorporation of oxygen into the films increases much faster than the fraction of oxygen in the gas flow so that the pure oxides can be formed from the gas ratio of about $O_2/(O_2+N_2) = 20\%$. Addition of oxygen alters the crystallinity of nitride phases due to the incorporation of interstitial atoms and formation of metal vacancies, but nitride lattices seem to survive up to the oxygen incorporation of about 40%. Beyond this limit, the amorphisation of films continues up to the pure oxides which show the formation of crystalline a-Al_2O_3, stimulated by the presence of a-Cr_2O_3 and SiO_2 in the films. Transition from nitride to oxide has strong consequences on films hardness, which changes from 30-33 GPa for nitrides to 12-13 GPa for amorphous layers, and increases again to 20-25 GPa for pure oxides. The relationship between structure, mechanical properties, and thermal barrier capability of coatings will be discussed.

10:20am **B1-1-2 Plasma-Enhanced Cylindrical Magnetron Deposition of Tantalum Coatings on Interior Surfaces of Steel Cylinders**, ***S. Lee*** *(sabrina.l.lee@us.army.mil)*, US Army ARDEC-Benet Labs, *M. Cipollo, F. Yee*, US Army RDECOM, *R. Wei, E. Langa, K. Coulter*, Southwest Research Institute

Electrochemically deposited high contraction chromium (HC Cr) coatings have been used for decades to protect the interior surfaces of cylindrical structure for extended cycle life. However, chrome electroplating process generates hexavalent chrome, mandated for reduction or elimination. HC Cr also possesses as-deposited and operation-induced cracks to cause accelerated wear and erosion of the substrate. In this paper, we describe two approaches using plasma-enhanced cylindrical magnetron sputtering systems to deposit pollution-free tantalum on the interior surfaces of 120mm cylinders. In a stand-alone plasma-enhanced DC cylindrical magnetron sputtering system where the barrel acted as the anode, substrate biasing capability and a MPP (modulated pulse power) plasma generator power supply were incorporated. The addition of biasing and the MPP was to increase the degree of ionization and ion bombardment for improved coatings qualities. The system utilizes an in-situ plasma cleaning device for pre-deposition substrate and target cleaning to enhance adhesion. In the other plasma-enhanced DC cylindrical magnetron system which sits in a vacuum chamber, a HIPIMS (high power impulse magnetron sputter) power supply was added to generate high flux high ionization plasma. Tantalum coatings were deposited using biased DC and HIPIMS technology. The system utilizes a new double glow discharge (DGD) process for pre-deposition surface cleaning. Several cylinders of 120mm inside diameter were successfully coated directly with tantalum coatings of 100-200 µm thickness; and the coated steel cylinders are being analyzed. The Plasma-Enhanced Cylindrical Magnetron technologies using biased DC, MPP, and HIPIMS generated plasma, their effects on the hardness, phase, residual stress, topography and microstructure of the coatings will be discussed.

10:40am **B1-1-3 Industrial Scale Sputter Deposition of Photocatalytic and Solid Electrolyte Oxide Coatings**, ***L.P. Nielsen*** *(Lars.Pleth.Nielsen@teknologisk.dk), S. Sønderby, K.P. Almtoft, I.H. Andersen, B.H. Christensen, M.B. Sørensen,* Danish Technological Institute, Denmark, *A.J. Nielsen, J. Bøttiger*, University of Aarhus, Denmark **INVITED**

Industrial scale synthesis of advanced oxides with tailored properties is of utmost importance for bringing the more fundamental R&D research results onto a commercial production platform.

At the Tribology Centre at Danish Technological Institute we have performed large-scale reactive pulsed sputter deposition of TiO_2 and doped TiO_2 for photocatalytic applications. In addition cerium gadolinium oxides (CGO) and yttrium stabilized zirconium oxides (YSZ), and alternating layers hereof, have been synthesized for low temperature fuel cell applications. The various coatings were deposited on a commercial CC800/9 CemeCon Sinox unit.

For the TiO_2 system it will be shown that reproducible growth of dense, as well as highly porous TiO_2 coatings can be synthesized in the rutile and the anatase crystal phase (or mixtures hereof) as evident from SEM, RBS and XRD results. The photocatalytic activity has been quantified by photocatalytic oxidation of acetone into CO_2 and correlated to the obtained micro-/nanostructure, film thickness and choice of substrate material. The effect on the micro/-nanostructure by doping with, e.g., Cu and the impact on antimicrobial properties will be addressed.

For application of YSZ electrolytes and CGO diffusion layers it is of outmost importance to be able to control the film morphology and to avoid pinholes leading to gas penetration of the electrolyte, which is detrimental to the overall performance of the fuel cells. In order to increase the propability of depositing thin YSZ films it has been necessary to grow multi-layer YSZ/CGO coatings. The structure of single-layer YSZ and CGO films will be discussed and compared with the YSZ/CGO multilayer systems for various process parameters. The oxygen ion conductivity of the coatings and the strontium diffusion barrier ability of CGO films will be compared for different experimental process parameters.

11:20am **B1-1-5 Modelling and Experimental Characterization of Serial Co-Sputtering**, ***T. Kubart*** *(Tomas.Kubart@angstrom.uu.se), T. Nyberg,* Uppsala University, Sweden, *A. Pflug,* Fraunhofer IST, Germany, *M. Austgen, D. Koehl, M. Wuttig,* RWTH Aachen, Germany, *S. Berg*, Uppsala university, Sweden

Serial co-sputtering is an efficient and flexible method for the deposition of multi-component thin films. In contrast to conventional co-sputter processes, material mixing occurs at a rotatable primary target. While sputtering the primary target of material A its rear face is simultaneously coated with material B from an auxiliary target. This results in a mixture of both elements A and B being sputtered from the rotatable target. The main advantage of this process is the flexibility in controlling the ratio [B]/[A] by the power ratio of the discharges. At the same time the drawbacks of traditional co-sputtering processes are avoided and the constraints in flexibility surpassed. There are further advantages beyond traditional co-sputtering such as the sputtering yield amplification effect, which results from implanting adequate dopants into the primary target and enables a significantly increased overall sputter erosion rate.

In this study, a detailed analysis of the serial co-sputtering setup has been performed. In order to evaluate the process, it is essential to understand the dynamic processes on the rotatable target and e.g. the influence of its rotational speed. Dynamical simulations of deposition, implantation and sputter erosion on this target has been carried out by the TRIDYN code using binary collision approximation. The effect of the power ratio between the primary and auxiliary cathode and the influence of target material properties and the rotational speed has been analyzed. Transport of sputtered material and deposition at the substrate was simulated by a Direct Simulation Monte Carlo (DSMC)) model. By computational and experimental means we have evaluated optimum conditions for a sputtering yield amplification in a non-reactive process. The homogeneity of sputtered films and the functionality of the yield amplification mechanism crucially depend on the implantation and sputtering dynamics of materials A and B at the primary erosion site. This dynamical behaviour is mapped into a compositional lateral in-homogeneity in the deposited films. From our investigation of this in-homogeneity the influence of different process parameters like e.g. rotational speed or discharge voltage on the dynamics of material mixing is concluded.

11:40am **B1-1-6 Significant Reduction of Arc Caused Sputtering Losses**, *P. Lach (piotr.lach@pl.huettinger.com), P. Ozimek,* ***M. Zelechowski,*** HUETTINGER Electronic Sp Z.o.o., Poland*, G. Hintz*, Hüttinger Elektronik GmbH, Germany

Abstract

Sophisticated arc management with extremely short detection time and fast recovery are of great importance in modern DC power supplies for plasma applications.

However, opportunity of improvements in hardware already almost ends. By u sing the best available elements it is possible to extinguish an arc within less then 2ms. Further improvements are still possible by software related changes.

This paper presents a method of significant (tenfold) reduction of sputtering losses caused by arc extinguishing breaks . Moreover, reduction of the detection time to a range of tens of nanoseconds is obtained by using new-developed software algorithms and advanced microprocessor techniques. Decreasing detection and reaction time minimize arc energy which results in elimination of cathode damage and prevents droplets formation on a substrate. Introduced software algorithm also focuses on new control solutions to optimize arc quenching power circuitry.

Power supplies equipped with the mentioned features are able to handle arcs with energy lower then 0.4mJ/kW, which is additional significant reduction in comparison with currently best on the market generators. Also the number of arcs per second that power supply is able to manage is substantially increased. This is crucial for some processes in which arcing rate may reach up to 10,000 arc/s and dynamically - even up to 100,000 arc/s.

All presented improvements allow using standard DC power supplies in applications reserved so far for expensive pulsed generators. Increase of deposition rate and process time savings are an additional gain.

Practical results of above mentioned improvements obtained on industrial TCO processes will be presented.

Hard Coatings and Vapor Deposition Technology Room: Town & Country - Session B4

Laser and Ion Beam Surface and Coating Engineering

Moderator: K. Sarakinos, RWTH Aachen University, W. Waldhauser, Joanneum Research Forschungsgesellschaft GmbH

10:00am **B4-1 An Oveerview of Laser Ablation: Thin Films and Nano-Particles**, ***J. Mazumder*** *(mazumder@umich.edu)*, University of Michigan **INVITED**

A laser Ablation technique was used to synthesize nanocrystalline powders and films of intermetallic compounds. Nanocrystalline versions of intermetallic materials offer the prospect of mitigating the brittleness of these materials while retaining their strength and oxidation resistance. To this end, nanocrystalline powders of near-stoichiometric $NbAl_3$and multilayer microlaminates of alternating $NbAl_3$and Al thin film layers have been fabricated using a laser ablation deposition technique. During processing, a laser absorption spectroscopy probe of Nb atoms within the ablation plume provides data regarding plume temperature and density. High purity powders with mean grain sizes of <10 nm were produced. Standard deviation of the particle size distributions were typically 2–6 nm. HRTEM was used to confirm the DO_{22}crystal structure of $NbAl_3$. Multilayer thin films of 15 and 20 layers and individual layer thickness of 80 nm were synthesized on copper and silicon substrates under various processing conditions. Diffusion of elements between layers, observed by STEM-EDS, was minimal. SEM suggests the possibility to tailor microstructure by varying process conditions. Typical grain sizes for crystalline microstructures was 30 nm.

10:40am **B4-3 Deposition of Nanolaminate Films by Pulsed Laser Deposition from Pre-Synthesized MAX-Phase Targets**, ***P. Schaaf*** *(peter.schaaf@tu-ilmenau.de), C. Lange,* Ilmenau University of Technology, Germany*, M. Wilke,* MFPA Weimar, Germany*, M. Hopfeld*, Ilmenau University of Technology, Germany

Pulsed laser deposition (PLD) with a Nd:YAG laser was used to grow thin films from a pre-synthesized MAX-phase formulated ablation targets onto oxidized Si(1 0 0), MgO(1 0 0) and stainless steel substrates with and without an 200V Ar or nitrogen ion beam directed at the substrate surface during deposition. The depositions were carried out in a substrate temperature range from room temperature to 650°C.

The properties of the films have been investigated by glow discharge optical emission spectroscopy (GDOES) for film thickness and stoichiometric composition and X-ray diffraction for the crystallinity of the films. X-ray diffraction measurements for all samples show no signs of the MAX phase Ti3SiC2, but only reflections of crystalline TiC. GDOES measurements however showed that silicon is distributed highly inhomogenously through the films. Even in the samples grown without ion beam there is a diffusion like silicon profile in the samples with an increased silicon concentration at the substrate surface. The application of the ion beam enhances this effect. Diffusion length and concentration gradient of these profiles depend on the deposition temperature and the substrate material. Obviously, the silicon shows a much higher mobility during film growth than the two other elements titanium and carbon, which can be explained by a preferred formation of titanium carbide TiC.

These results for deposition from prefabricated MAX-phase targets will be compared with depositions from elemental targets.

The work is supported by the German Research Foundation under grant DFG Scha 632/10.

11:00am **B4-4 Laser Assisted Deposition of Industrial CAE-PVD TiN Thin Films**, ***J. Esparza*** *(jegorraiz@ain.es),* Asociación de la Industria Navarra, Spain, *X. de la Fuente*, ICMA-CSIC, Spain

This work reports on recent advances in Cathodic Arc Evaporation-PVD process assisted by a medium IR fiber laser (1055-1090nm). The main objective of this study is to improve the mechanical properties of titanium nitride (TiN) coatings by the “in-situ” application of laser in the deposition area during the coating growth process. The modification of the characteristic parameters of the laser source (Frequency, power and beam velocity) allows to obtain different effects, both on the final film properties and also on the substrate if the laser treatment is done before the deposition process. All the coatings have been produced in a commercial METAPLAS PVD chamber equipped with 6 arc sources.

The composition and morphology of these new laser assisted coatings have been studied by FE-SEM and GD-OES, thus changes in the chemical composition profile of the TiN coatings have been observed. The characterization of the films produced includes measurement of the mechanical properties such as film adhesion (scratch test), microhardness and tribology (wear coefficient).

11:20am **B4-5 Surface Nanostructures Induced by Low Energy Ion Sputtering**, ***S. Facsko*** *(s.facsko@fzd.de), A. Keller, M. Ranjan, W. Möller*, Forschungszentrum Dresden Rossendorf e.V., Germany **INVITED**

Under special conditions low energy ion sputtering of solid surfaces leads to the formation of regular nanopatterns. These surfaces represent an interesting example of spontaneous pattern formation in non-equilibrium systems exhibiting different features like wavelength coarsening or a transition to spatiotemporal chaos. Different pattern types are observed for different experimental conditions, i.e. wavelike ripple patterns and hexagonally ordered dot arrays under oblique and normal ion incidence, respectively [1]. These patterns have gained increasing interest in recent years as templates for thin film growth.

According to the model of Bradley and Harper (BH) [2], the regular patterns result from the competition between curvature dependent roughening and smoothing of the surface. Since the local erosion rate is higher in the valleys than on crests, the eroded surface is unstable. In the presence of smoothing mechanisms, however, a wave vector selection occurs and a periodic pattern with one spatial frequency is observed. The pattern formation can be described by continuum equations based on the BH model. Several extensions have been proposed in the last years, with the stochastic Kuramoto-Sivashinsky (KS) equation being the most prominent one [3]. However, although most experimental investigations on ion-induced pattern formation were performed under oblique ion incidence, only few theoretical studies focused on the corresponding anisotropic KS (aKS) equation.

We will also present studies of thin film growth on these patterns. Depending on the interface energy of the metal film with the substrate the films grow in a conformal way reproducing the surface topography or as nanoparticles on the substrate surface. Furthermore, depending on deposition angle, substrate temperature, beam flux, and deposition time, the nanoparticles align parallel to the ripples, eventually coalescing and forming nanowires. Metal thin films grown in this way exhibit distinct optical properties due to their localized surface plasmon resonance. Because of the alignment these nanoparticles exhibit a strongly anisotropic plasmonic resonance [4]. In addition, the magnetic properties of ferromagnetic thin films grown on rippled surfaces are drastically change by the presence of the interface and surface periodic roughness [5].

[1] W. L. Chan and E. Chason, J. Appl. Phys. **101**, 121301 (2007)

[2] R. Bradley and J. Harper, J. Vac. Sci. Technol. A **6**, 2390 (1988)

[3] R. Cuerno and A.-L. Barabási, Phys. Rev. Lett. **74** 4746 (1995)

[4] T.W.H. Oates, A. Keller, S. Facsko, et al., Plasmonics 2, 47 (2007).

[5] M. O. Liedke, B. Liedke, A. Keller, et al., Phys. Rev. B 75, 220407 (2007).

12:00pm **B4-7 Pulsed Laser Deposition of Low Work Function Coatings for Field Emission cathodes***, **S. Fairchild** (Steven.Fairchild@WPAFB.AF.MIL),* Air Force Research Laboratory*, T. Murray,* University of Dayton*, B. Towne,* Air Force Research Laboratory*, M. Cahay,* University of Cincinnati*, T. Back*, University of Dayton

Field emission DC cold cathodes continue as 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. The Air Force Research Laboratory (AFRL) began research on such DC cathodes for use in a THz traveling wave tube (TWT). The TWT requires an electron beam of 100 micron diameter or less which necessitates the need for small diameter cathodes. Various single fiber cathodes have been tested for their field emission properties including those made from graphite and single walled carbon nanotubes (SWNTs). Additionally, low work function coatings have been applied to these fibers to optimize their performance. Pulsed laser deposition (PLD) is initially used to coat planar graphite substrates so that the coating work function can be measured with an in-situ Kelvin Probe. Subsequently the coatings are applied by PLD to single fiber cathodes and their field emission properties are characterized. The fibers are heated during deposition to promote adhesion of the coatings. HfC, ZrC, TiC, and WC have been investigated. Preliminary results with HfC coated graphite fibers show a 3x improvement in emission current.

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

Tribology of Nanostructured and Amorphous Films
Moderator: J. Fontaine, Ecole Centrale de Lyon, R.D. Evans, Timken Company

10:00am **E3-1-1 Tribological and Mechanical Properties of Nanostructured Hydrogenated Amorphous Carbon and Titanium Diboride Films***, B. Zhao, **Y.W. Chung** (ywchung@northwestern.edu)*, Northwestern University

Hydrogenated amorphous carbon films are of great interest due to their favorable ultra-low friction and low wear rate properties in dry environments. Our work demonstrated that sulfur doping of hydrogenated carbon films enabled them to achieve ultra-low friction performance in both dry and humid environments. However, these films have a hardness of 7 - 10 GPa and an elastic modulus around 80 GPa, which are too low for some high stress applications. Formation of nanostructured coatings is known to improve hardness. With the aim to produce hard, low-friction coatings, we synthesized nanolayered and nanocomposite films of sulfur-doped and undoped hydrogenated carbon and titanium diboride as a hard second phase using dual-target magnetron sputtering. Titanium diboride deposited by this method had a hardness >30 GPa. This paper will discuss the film structure and how such structure correlates with its tribological and mechanical properties.

10:20am **E3-1-3 Tribology of Nanocrystalline Diamond Coatings***, **N.D. Theodore**,* US Naval Research Laboratory*, M. Wiora,* Ulm University*, K.J. Wahl (kathryn.wahl@nrl.navy.mil)*, US Naval Resarch Laboratory

Reciprocating sliding tests of sapphire balls against the nanocrystalline diamond have been performed to examine the effects of moisture in the surrounding ambient environment. Microstructure of the diamond coatings was confirmed by X-ray diffraction (XRD) to be nanocrystalline with crystallite sizes ranging from to 20 to 70 nm, with a preferred texture in the (220) orientation. These diamond coatings had similar visible wavelength Raman absorption bands that were deconvolved into 5 peaks: a single sharp peak at 1332 cm^{-1} typical of crystalline diamond; broad peaks at 1340 cm^{-1} and 1580 cm^{-1} characteristic of the *D* and *G* peaks in sp^2 hybridized carbon; and, additional peaks at 1135 cm^{-1} and 1470 cm^{-1} that are commonly attributed to transpolyacetylene bonding. All nanodiamond coatings initially possessed high friction (0.5 - 0.8) before running-in to a steady-state value of ~0.05; each coating had a characteristic run-in profile to low friction (<0.1) occurring between 300 to 1000 cycles. Coatings with larger crystallites and higher surface roughness were more sensitive to changes in humidity, with faster run-in occurring as humidity increased between 3 and 45%. For these larger-crystallite coatings, wear of the sapphire counterface increased by an order of magnitude between 5 and 45% RH. However, coatings having smaller grain sizes and lower roughness exhibited similar run-in and counterface wear regardless of humidity. Coating tribological performance as a function of humidity will be related to the microstructural and compositional differences among the nanocrystalline diamond coatings.

10:40am **E3-1-4 Influence of Ultraviolet Ray Irradiation on CN$_x$ Coating's Tribological Characteristics***, **T. Tokoroyama** (tokoroyama@mech.nagoya-u.ac.jp), N. Umehara,* Nagoya University, Japan*, Y. Fuwa*, Toyota Motors Co., Ltd., Japan

Carbon Nitride (CNx) coating is one of the promising materials as well tribological property, especially low friction coefficient. The superlow friction phenomena of CNx coating slid against Si_3N_4 ball in N_2 gas was suggested to be taken place when the topmost surface of CNx changed to graphitic structure. It was reported that nitrogen atoms included CNx coating desorbed during the friction. From the view point of nitrogen desorption from CNx coating, it was assumed that ultraviolet ray could break C-N single bond when the ray power exceeded C-N single bonding energy. In this study, we hypothesized that ultraviolet ray irradiation could make the CNx coating topmost surface graphitic without friction in N_2 gas. We carried out preparing the CNx coating irradiated ultraviolet ray as 254, 312, and 365 nm wave length, because the C-N single bond is 305 kJ/mol and the other ultraviolet rays are 469, 382, and 327 kJ/mol, then these specimens were tested in N_2 gas to compare frictional property of with and without irradiation. CNx coating was synthesized with Ion beam assisted deposition method as 100 nm thickness on Si(100) substrate. Ar ion beam irradiated to carbon target, sputtered carbon was deposited on the substrate and nitrogen ion beam was irradiated to the specimen, simultaneously. Friction test was done with ball-on-disk type frictional tester which was set in vacuum chamber and the test conditions were that normal load was 0.1 N, sliding speed was approx. 0.04 m/s, and counter material was Si3N4 ball with 8 mm diameter. Before the friction test, the vacuum chamber was evacuated to approx. 0.1 Pa, then nitrogen gas was filled into the chamber approx. atmospheric pressure. All specimens did not show superlow friction coefficient at the initial of friction test, however, the coatings which were irradiated showed superlow friction phenomena gradually. We defined that the running-in period was friction coefficient became lower than 0.05, all irradiated specimens showed shorter running-in period than as-deposit CNx. The average of initial several cycle friction of as-deposit CNx showed 0.04, on the other hand, in the case of 312 nm ultraviolet ray irradiated CNx showed 0.01 or lower average friction coefficient. These results indicated that ultraviolet ray could break the C-N single bond, these broke bonds were restructured to C=C double bond, and nitrogen atoms desorbed from the coating as the cause of restructuring to N2 molecule.

11:00am **E3-1-5 Tribology of Nanocrystalline Diamond and Amorphous Carbon Films: Achieving Ultralow Friction and Wear***, **R.W. Carpick** (carpick@seas.upenn.edu)*, University of Pennsylvania **INVITED**

Ultrastrong carbon-based films that are characterized by high amounts of sp^3-bonded carbon and very little hydrogen can possess extremely low friction and wear. Examples include nanocrystalline and ultrananocrystalline diamond (NCD and UNCD, respectively), and tetrahedral amorphous carbon (ta-C). It is well-known that smooth surfaces are required to achieve this, but in addition, the vapor environment is also crucial. It has been long known that some partial pressure of water or hydrogen is needed, or else high friction and wear will result. In this talk, I will describe our experimental work which has demonstrated new insights into these phenomena. We have observed friction coefficients as low as 0.005 in atmospheres as dry as 0.7%RH. We show that the mechanism of low friction and wear in these materials has nothing to do with the formation of crystalline graphitic layers, as had been postulated previously. Rather, we present spatially-resolved surface chemical and bonding analysis obtained by synchrotron-based photoemission electron microscopy (PEEM) that proves that passivation by dissociative adsorption of water is the primary mechanism responsible for maintaining low friction and wear of self-mated contacts of UNCD and ta-C in humid environments. We propose that the dynamic competition between the rate of dissociative passivation and the rate of trans-interfacial bonding of dangling bonds produced during sliding is the key to understanding the threshold between low and high friction states. We find that the transition from low to high friction is both reversible and extremely sharp. A possible explanation for these newly observed phenomena based on the energetics and kinetics of dissociation will be discussed.

Characterization: Linking Synthesis Properties and Microstructure
Room: Royal Palm 1-3 - Session F2

In Situ Characterization
Moderator: F. Giuliani, Imperial College London, C.. Scheu, Ludwig-Maximilians-University of Munich

10:00am **F2-1 Plasticity and Debonding of Thin Metallic Films Studied by in Situ Tensile Testing**, ***G. Dehm*** *(gerhard.dehm@mu-leoben.at), M.J. Cordill,* Montanuniversität Leoben, Austria*, C. Kirchlechner,* Austrian Academy of Sciences, Austria*, J. Keckes,* Montanuniversität Leoben, Austria*, M. Smolka,* Kompetenzzentrum Automobil- und Industrie-Elektronik GmbH, Austria*, F. Fischer*, Montanuniversität Leoben, Austria **INVITED**

In microelectronic devices or flexible electronic components the metallic interconnects are prone to failure due to limited plasticity or debonding at the interface between the metal and the adjacent materials. In order to study the mechanical behaviour of the metallic films and the film/substrate interface quantitative approaches are required. Two examples will be provided in this talk:

(i) Lithography techniques can be used to fabricate free-standing tensile samples into the metallic film material. As a consequence of the small dimensions of several micrometers down to a few hundred nanometers electron microscopy is employed to perform controlled tensile tests. The in situ straining experiments provide quantitative load and displacement data as well as insights in the deformation mechanisms. Complementary synchrotron experiments are performed to unravel the deformation induced dislocation structures.

(ii) The “adhesion energy” of thin metallic films on compliant substrates can be probed by in situ tensile testing. Cracking of the metallic film occurs under tensile load, while the lateral contraction can impose compressive film stresses which lead to buckling and debonding. Quantification of the buckle dimensions and the debonded area is used to deduce the “adhesion energy” of the interface by a thermodynamically based energy consideration. The concept and its limits will be discussed in the talk.

10:40am **F2-3 Stress and Microstructure Evolution During Polycrystalline Metallic Film Growth : Influence of the Nucleation Conditions**, ***A. Fillon*** *(amelie.fillon@etu.univ-poitiers.fr), G. Abadias, A. Michel, C. Jaouen*, University of Poitiers, France

The origin of stress in polycrystalline thin films has gained recently a renewed interest with the potentiality offered by real-time techniques to measure stress evolution during growth. Such in situ measurements not only yield the magnitude of the growth stress, but also provide insights into the growth mechanism itself. Stress models have been proposed in the literature to explain mainly the complex behaviour of high-mobility materials grown by evaporation or sputtering.

The present work is focused on the stress development during growth of low mobility metallic thin film. For this purpose, Mo and Mo$_{1-x}$Si$_x$ alloy thin films, with x ranging from 0 to 0.4 and film thickness up to 200 nm, were grown by magnetron sputtering at 300K onto either amorphous Si (*a*-Si) or crystalline *bcc* Mo buffer. The stress evolution during growth was monitored *in-situ* with a multiple-beam optical stress sensor. Very distinct stress evolutions were observed as a function of the Si content and type of buffer layer. For films grown on *a*-Si, the different stages of stress evolution were correlated to change in surface stress, growth of an interfacial amorphous layer, followed by an amorphous-to-crystal phase transition occurring at a concentration-dependent critical thickness. While a significant tensile stress contribution was observed for crystalline alloys grown on a-Si, a steady-state compressive stress evolution was noticed for the equivalent films grown on bcc-Mo. The results are interpreted and discussed based on microstructural features revealed by ex-situ XRD, cross-sectional HRTEM and AFM surface topography. Finally, these results show the importance of the initial crystalline nucleation conditions on the different stress generation and relaxation mechanisms.

11:00am **F2-4 *In Situ* Tribology of Hard, Protective Coatings**, ***H.W. Strauss*** *(holger.strauss@mail.mcgill.ca),* McGill University, CANADA*, S. Hassani, J.-E. Klemberg-Sapieha, L. Martinu,* Ecole Polytechnique de Montreal, Canada*, R. Chromik*, McGill University, Canada

The tribological performance of hard, protective coatings is largely governed by their mechanical properties; great hardness and a moderate elastic modulus are most desirable and generally lead to reduced wear. In many tribological studies on protective hard coatings, the formation and retention of transfer film material within the contact interface is given only little or no attention. This may be the case because of technical limitations with respect to transfer film detection or because the influence of a transfer film on the tribological behaviour of protective hard coatings is underestimated.

Within this research, the influence of transfer film formation and –retention on friction and wear is studied in tribological experiments on a variety of nano-composite hard coatings consisting of carbides, nitrides, or carbonitrides of titanium and silicon. An *in situ* Raman tribometer is employed to study tribomechanical and –chemical processes determining friction and wear in interfacial sliding. Featuring a 1/4” diam. sapphire hemisphere as counterface, the tribometer allows the recording of transfer film formation and fluctuation by means of video microscopy. It is additionally possible to study chemical changes occurring within the sliding interface by means of Raman spectroscopy.

Initial tests were conducted on nano-composite carbide coatings with varying TiC/SiC ratios between 100:0 and 50:50, deposited onto Si wafers by means of Plasma-Enhanced Chemical Vapor Deposition (PE-CVD). The experiments were performed as stripe tests, implementing 600 cycles at a track length of 6 mm, half-way overlapped by an additional 1,800 cycles at a track length of 3 mm. The average Hertzian contact stress was 460 MPa; relative humidity was kept between 40 and 50 %. The coefficient of friction was recorded at high spatial resolution as well as processed as averages over cycle. To determine the variation of transfer film thickness with proceeding cycle number, video frame shots were analyzed by means of a Newton’s rings method [Wahl, Chromik, 2008]. *Ex situ* white-light interferometry was applied additionally to measure coating and counterface wear, as well as final transfer film thickness and morphology.

In situ tribometry generally revealed rapid build-up of transfer film material during run-in followed by variability in the transfer film thickness. In this initial test series, *in situ* Raman tribometry proved to be an effective tool for the study of dynamic changes within third bodies produced when sliding on hard coatings. Future tests will explore the correlations between transfer film changes and friction of further coating chemistries.

11:20am **F2-5 Growth Process of Zirconium Diboride Thin Films Prepared by Ultrahigh-Vacuum CVD**, ***Y. Yamada-Takamura*** *(yukikoyt@jaist.ac.jp), S. Bera*, JAIST, Japan

Metal diborides have attracting properties such as high hardness, high melting point, high electrical and thermal conductivities. Most of the diborides have a very simple crystal structure, which consists of alternating hexagonal metal layers and honeycomb boron layers. Refractory and conductive diborides in the form of thin films allow them to be integrated with other materials. It has been demonstrated that zirconium diboride (ZrB$_2$), which has a very good lattice matching to a wide-gap semiconductor hexagonal gallium nitride (GaN), serves as a conductive and reflective buffer layer for the GaN growth on an economical substrate Si(111), when the film with good crystallinity was realized through an epitaxial growth[1].

In order to grow high purity, high crystallinity film through epitaxy, the understanding of growth process and the control of surface and interface are critical. UltraHigh Vacuum Chemical Vapor Deposition (UHV-CVD) using zirconium borohydride (Zr(BH$_4$)$_4$) as a source has advantages in the purity of source material compared to solid source processes, and also in *in situ* surface characterization capability[1,2]. A unique UHV-CVD apparatus with Reflection High Energy Electron Diffraction (RHEED) system was constructed, and the epitaxial growth of ZrB$_2$ on Si(111) and sapphire(0001) were carried out successfully[3,4].

RHEED pattern evolution during the growth on both substrates was studied. On Si(111), two-dimensional nucleation of ZrB$_2$ with streaky ZrB$_2$(0001)-(2x2) pattern, and then ZrB$_2$(0001)-(1x1) pattern with increased thickness was observed, which is consistent with earlier report using low energy electron diffraction[2]. On sapphire substrate, transmission diffraction pattern was observed upon the nucleation of ZrB$_2$ indicating three-dimensional nucleation, and then under optimized conditions, ZrB$_2$(0001)-($\sqrt{3}$x$\sqrt{3}$) was observed with increased thickness. The difference in surface reconstruction during the growth seems to originate from substrate atoms segregating to the surface, and clear surfactant effect of these atoms was observed as an order of magnitude difference in growth rate for films grown on different substrates, but otherwise under same conditions.

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[2] C. W. Hu, A. V. G. Chizmeshya, J. Tolle, J. Kouvetakis, and I. S. T. Tsong, J. Cryst. Growth 267, 554 (2004).

[3] S. Bera and Y. Yamada-Takamura, Kyoto-Advanced Nanotechnology Network JAIST Report H19-028 (2008).

[4] S. Bera, Y. Sumiyoshi, and Y. Yamada-Takamura, J. Appl. Phys. 106, 063531 (2009).

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

Innovations in Surface Coatings and Treatments
Moderator: M. Rodmar, Sandvik Tooling, A. Leyland, University of Sheffield

10:00am **G1-1-1 Commercialization of Filtered Cathodic Arc Technology - Progress and Prospects**, ***R.P. Welty*** *(rwelty@magplas.com)*, Magplas Technik LLC **INVITED**

Coating deposition using cathodic arc technology has become widely commercialized during the last 3 decades, e.g. for hard coatings on tools and mechanical components and for durable decorative coatings. In such applications the advantages of an ionized and energetic coating stream for promoting adhesion and controlling coating structure have been found to outweigh the disadvantages of the splattered droplets (“macroparticles”) generated by the arc and incorporated into the coating. Although “filtering” of the coating stream, using magnetic and electric fields to divert the plasma while mechanically blocking the macroparticles, has been known since the late 1970s, the inefficiency and complexity of available equipment has hindered commercialization of this technology. Improvements in filtered source design in recent years by several groups, notably in increasing the ion current output, have made it practical to use filtered arc coatings in a number of products now being manufactured on an industrial scale. This presentation will review some current applications of filtered arc deposition, and examine factors influencing industrial adoption, including source and equipment design and cost, materials capabilities, and the emergence of competing methods providing ionized coating atoms.

10:40am **G1-1-3 Plasmaphysical Characterization and Technological Application of a Hollow Cathode Plasma Source with an Axial Magnetic Field**, ***F. Fietzke*** *(fred.fietzke@fep.fraunhofer.de), B. Zimmermann*, Fraunhofer Institute for Electron Beam and Plasma Technology FEP, Germany

Hollow cathode arc discharges with hot emitters have been studied for some decades in basic research and different fields of practical application. Especially in physical vapor deposition (PVD) they are often used for metal evaporation and the generation of plasma. Shortcomings preventing a broader application were found in the high throughput of working gas necessary for a stable operation and in the very inhomogeneous, locally concentrated ionization efficiency.

A promising way to overcome these limitations was found by arranging the hollow cathode in a strong axial magnetic field, allowing for a drastic reduction of working gas flow without loss of discharge stability. Moreover, with the reduction of gas flow not only a strong increase of the discharge impedance was observed, but also a multiplication of ion current density together with a highly expanded volume of plasma plume.

By means of spatially resolved Langmuir probe measurements, combined with the usage of an energy-resolved mass-spectrometer, plasma density profiles and energy distribution functions of electrons and ions have been measured. Generally, with an increase of the magnetic field and with the reduction of the working gas flow those energy distribution functions shift from mean values of a few eV to 10 eV and more, while charge carrier densities increase from 10^{16} m^{-3} to more than 10^{19} m^{-3}. A systematic overview of the measurements will be presented and conclusions for the application of the plasma source in different fields of surface treatment technologies will be derived.

In the second part of the presentation two promising applications related to the coating of cutting tools in industrial batch devices will be discussed in detail: the sputter etching with argon ions and the reactive pulse magnetron sputter deposition of wear resistant nitride layers. Whereas the first mentioned process provides pre-heating and etching rates higher than all actually used in tool coating industry, the second one offers great advance for film growth kinetics leading to significant improvements in structure, surface morphology, elastic modulus and hardness of the deposited layers.

11:00am **G1-1-4 Internal Plasma Processing of Narrow Halls and Tubes with Microwave Propagation Along Plasma-Sheath Interfaces**, ***H. Kousaka*** *(kousaka@mech.nagoya-u.ac.jp), K. Mori, N. Umehara,* Nagoya University, Japan*, N. Tamura, T. Shindo*, Contamination Control Services Inc., Japan

Recently, internal plasma processing of halls and tubes such as DLC (Diamond-Like Carbon) coating of molds and mechanical parts is strongly desired. Uniform processing of such a 3-dimensional metal surface is typically obtained by RF and DC plasmas where negative voltage is applied to a metal substrate against a grounded chamber at low gas pressures. However, the plasma electron density, n_e of RF and DCplasmas is typically no more than 10^9–10^{10} cm^{-3}, by which high-speed processing can not be expected. Furthermore, such low-density plasma can not steadily exist inside small halls and tubes less than 1 cm in width under typical processing conditions, In order to solve the latter problem for iinternal plasma processing of narrower metal halls and tubes, the use of higher-density (n_e>10^{11} cm^{-3}) plasma is essential. Therefore, we proposed a new method which can steadily generate such high-density plasma along 3-dimensional metal surfaces by using microwave propagation along plasma-sheath interfaces bounded by metal surfaces.

In our previous works, it was demonstrated by using the new method that plasma column is steadily sustained inside a narrow metal tube whose inner diameter is in the range of millimeters and the length is more than 10 times of it. Furthermore, in this work, we developed a new plasma CVD apparatus by using the plasma column, and prepared DLC film on the inner surface of a stainless-steel tube (SUS304, JIS) 4.4 mm in inner diameter and 50 mm in length. Here, the flow rate ratio of source gases, methane and tetramethylsilane (TMS), were controlled to be 5:1, at a total gas pressure of 27 Pa, where a negative voltage of −180 V was applied to the pipe with 2.45-GHz microwaves injected at a forward power of 120 W.

In order to investigate the tribological properties of the DLC film deposited, rotational friction test of the film a was conducted against cast iron shaft (FC250, JIS) 4.2 mm in outer diameter and 10 mm in length; as a result, friction coefficient was 0.17 at the position about 40 mm from the bottom end of the pipe where microwaves were injected during deposition. However, the friction coefficient was 0.4 at the rest positions (10 and 25 mm from the bottom end), where the films were peeled off the substrate.

This work was partly supported by a Grant-in-Aid for Young Scientists (B), No. 19740343 (2007-2008), from the Japan Society for the Promotion for Science, and Tokai Region Nanotechnology Manufacturing Cluster, Knowledge Cluster Initiative (The Second Stage, 2008-).

11:20am **G1-1-5 Theoretical Investigation of Plasma Ion Implantation into Cylindrical Bore Based on Internal Inductively-Coupled Radio-Frequency Discharge***, X.B. Tian (xiubotian@163.com), Z.J. Wang, B.Y. Guan, 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 ion implantation has proven to be an effective tool to enhance surface properties. Many attempts have been made to implant internal wall of cylindrical bore using this technique. However the difficulties have been well demonstrated due to severe non-uniformity of incident dose stemming from external plasma source. A novel technique has been proposed in our lab based on internal inductively-coupled radio-frequency discharge. The RF coil acts as both plasma source and grounded electrode to eliminate the overlapping effect of plasma sheath in tubes. In order to comprehend the implantation dynamics, numerical simulation based on particle-in-cell/Monte Carlo method has been performed. The uniformity of injected ions, the influence of ion-neutral collisions on the impact energy, incident dose and impact angle have been investigated at different gas pressure. The shadow effect of RF coil appears in the implanted wall and minimum incident dose happens at the center of shadow regions. Incident ions fly towards the internal wall at about ±30°off normal with higher impact energies. As the gas pressure increases, the uniformity of incident dose is improved slightly however the impact energy decreases significantly. A higher gas pressure leads to wider distribution of impact energy and angle of incident ions. The numerical results have demonstrated that this novel technique is capable for implanting internal wall of cylindrical bore and a manipulation system has to be utilized to achieve uniform implantation.

11:40am **G1-1-6 EnFACE – a Maskless MicroScale Pattern Transfer Technique**, ***S. Roy*** *(s.roy@ncl.ac.uk)*, Newcastle University, United Kingdom

In a typical micro-fabrication process, micro scale pattern transfer is achieved by using photolithography. In this process, each substrate is covered by a light sensitive resist. The resist covered substrate is then exposed to light through a patterned mask – this either develops or destroys the resist in the areas exposed to light. Thereafter, materials can be plated on or etched off from the exposed areas. This platform technology, therefore, allows micro sized patterns of materials to be transferred on to a substrate.

We have developed a process to transfer micro scale patterns on a fully exposed substrate. The method uses electrochemical means and a specialised electrochemical reactor for pattern transfer. This process uses a metallic material with a resist pattern, which serves as an electrochemical tool. The substrate, which is fully exposed, is placed facing the tool, within close proximity. The tool and the substrate are electrically connected so that the tool is the cathode and the substrate is the anode. Electrolyte is pumped through the system to deliver fresh solution to the anode and cathode as well as remove reaction by products.

Our experiments, involving copper as the tool as well as substrate material, showed that micro scale patterns by electrochemical etching and plating could be transferred with good reproducibility. In our reactor, they were placed within a distance of 500 microns. We have successfully transferred micro patterns which are significantly smaller than the electrode gap, namely, 50, 100 and 200 microns. The steep walls and cubic shape demonstrate the feasibility of the process. The process has also been applied to metal deposition and lines to 100 microns width have been reproduced. Copper deposits up to 2.5 microns thick has been plated using the technique.

We have developed a model which describes the underlying physical phenomemenon of the micropattern transfer process. The model is a reaction distribution model (which, in electrochemical engineering is called a potential or current distribution) model. We used modelling software, ElSyCA-2D, to understand the critical processes enable micropattern transfer. The model is tested against the experimental data obtained in the experiments.

Since a single tool can be used to transfer a pattern numerous times, this opens the the possibility of greatly reducing the use of photolithography for pattern transfer on to metallic substrates. This means that chemical solvents used for photolithography can be minimised. In addition clean room use can also be greatly reduced. Finally, the technique requires very dilute solutions, which means that the process is non-hazardous.

12:00pm **G1-1-7 Alumina-Graphite Coating by a Novel Technique: Friction Oxidation Deposition (FOD) Applied on Ti6Al4V Alloy***, **J. Diabb**, M.A.L. Hernandez-Rodriguez (mhernandez@gama.fime.uanl.mx)*, Universidad Autonoma de Nuevo Leon, FIME, Mexico

Friction oxidation deposition (FOD) is a coating method where mechanical effect and thermochemical reactions are involved in order to get coating films. In this process a contact pair between a cotton mop and a Ti6Al4V substrate was performed under a speed of 22,000 rpm and a load of 0.35Nw until achieve one second; after that, an equivalent mixture of fine powders of Al_2O_3 and graphite were supplied by a dispenser device for about two seconds. As a result a coating was achieved by triboadhesion mechanisms. Finally to complete this process, three coated samples were exposed to an oxy-butane flame by 30, 60 and 90 seconds respectively. Each of the samples was characterized with metallographic techniques, scanning electronic microscope (SEM), energy dispersive spectroscopy (EDS), X-ray diffraction, micro scratch and nanoindentation test. The results exhibited the formation of a coating film with different kinds of oxides which presented a strong relation between film thickness, adherence and the exposition oxidation time. The hardness was improved with respect to substrate for all conditions.

Applications, Manufacturing, and Equipment
Room: Royal Palm 4-6 - Session G5/H5

Coatings for Renewable Energy Harvesting Systems
Moderator: L. Bardos, Uppsala University, S. Roy, Newcastle University

10:00am **G5/H5-1 Evaluation of the Anti-Fouling Properties of Atmospheric Plasma Deposited Siloxane Coatings***, **D.P. Dowling** (denis.dowling@ucd.ie), C.E. Nwankire*, University College Dublin, Ireland **INVITED**

Both organic and inorganic fouling is a significant problem for a range of surfaces used in industries as diverse as milk pasteurization and paper making. The objective of this study is to evaluate the anti-fouling properties of fluorinated and non-fluorinated siloxane coatings. These nm thick coatings were deposited onto silicon wafer and stainless steel substrates using the atmospheric plasma jet system called PlasmaStream^{TM}. The plasma polymerised coatings were obtained from a range of fluorinated and non-fluorinated siloxanes precursors, which were nebulized into the atmospheric plasma. The adhesion of both inorganic (calcium carbonate) and organic (Casein protein) foulants were assessed with changes in coating chemical functionality and surface roughness (Ra). The properties of the deposited coatings were examined using optical profilometry, SEM, ellipsometry, contact angle and XPS. These techniques were used to evaluate surface morphology, thickness, surface energy and chemical functionality respectively. The erosive wear resistance of the nm thick coatings was compared using an ultrasonic jet treatment in an aqueous slurry of silicon carbide particles for periods up to 30 minutes. Casein adhesion was evaluated under dynamic flow conditions from aqueous mixtures of the protein using the spectroscopic ellipsometry technique. The optical measurements enabled the rate of protein adhesion and its thickness to be measured. The thickness of the protein layer was verified using quartz crystal microbalance measurements. In the case of calcium carbonate the quantity of the inorganic fouling was assessed on steel substrates after immersion of the coated and uncoated metal in an aqueous slurry of the carbonate. For both the inorganic and protein foulants investigated in this study the level of foulant adhesion was found to be influenced by both the coating chemistry and roughness.

10:40am **G5/H5-3 Cold Atmospheric Plasma Treatment of Energy System Components***, **H. Barankova** (Hana.Barankova@angstrom.uu.se), L. Bardos*, Uppsala University, Sweden

Fused hollow cathode (FHC) atmospheric plasma source and Hybrid Hollow Electrode Activated Discharge (H-HEAD) source have been tested for surface treatments of epoxy glass laminates used for wind turbine blades and of steel surfaces used in ocean buoys driving the linear wave energy converters. Argon, neon, nitrogen and air mixtures have been used for the plasma treatments and the resulting surface energy has been examined by contact angle measurements. Plasma parameters and process conditions leading to highly hydrophobic surfaces in wind turbine blades preventing for example formation of ice have been tested. Conditions for hydrophilic surfaces have been examined on steel surfaces before subsequent painting or coating suitable for long protection lifetimes in harsh ocean environment. Results of tests under different plasma parameters are presented and discussed.

Hard Coatings and Vapor Deposition Technology
Room: Pacific Salon 3 - Session B1-2

Sputtering Coatings and Technologies

Moderator: P. Eklund, Linköping University, M.-S. Wong, National Dong Hwa University

1:30pm **B1-2-1 Measurement of Residual Stress and Elastic Constants of Transition Metal Nitride Thin Films**, ***J.-H. Huang*** *(jhhuang@mx.nthu.edu.tw)*, National Tsing Hua University, Taiwan **INVITED**

The measurement of residual stress in crystalline thin films by X-ray diffraction (XRD) method is somewhat problematic, especially for those films with texture and the thickness in the range of a few hundred nm or less. The difficulties are from small diffraction volume and few diffraction peaks. To solve the problem, we proposed a XRD cos^{2}asin^{2}y method using grazing incident X-ray to increase both diffraction volume and diffraction peaks. The method has been successfully applied on transition metal nitride thin films such as TiN, ZrN, CrN, and VN. For the coatings with interlayer, the cos^{2}a sin^{2}y method can respectively measure the stresses in coating and interlayer. The technique has also been applied on determining the stresses in multiphase thin films such as ZrN_xO_y containing ZrO_2 and ZrN. However, there is a major issue in using XRD techniques on residual stress measurement. Elastic constants are necessary for calculating stress after the strain is acquired from XRD measurements. Unfortunately, the elastic constants are normally not available for thin films and the data measured from the bulk counterparts are not fully reliable. In our study, we proposed a nondestructive method combining optical curvature and XRD sin^{2}y techniques to simultaneously measure the Young's modulus and Poisson's ratio for transition metal nitride thin films. The proposed method can measure the six strain components for a thin film sustaining a biaxial stress; combining with the stress obtained from optical curvature method the elastic constants can be calculated. In addition, the measured elastic constants were used in the cos^{2}a sin^{2}y method to determine the stress of the same specimen, and the result was compared with that determined by the optical curvature method. The results indicated that the stresses from both methods were consistent and therefore the elastic constants obtained from the proposed method were verified.

2:10pm **B1-2-3 Thermal Stability and Oxidation Resistance of Magnetron Sputtered Ti-Zr-N and Ti-Ta-N Thin Films**, ***G. Abadias*** *(gregory.abadias@univ-poitiers.fr),* University of Poitiers, France*, L.E. Koutsokeras,* University of Poitiers, France University of Ioannina, Greece*, P.A. Patsalas*, University of Ioannina, Greece

Ternary transition metal nitride (TMN) films are offering superior mechanical properties, oxidation resistance or tribological performance compared to their binary counterparts. Among them, Ti-Al-N and Cr-Al-N systems are intensively studied. Their deposition by PVD techniques results in the formation of (meta)-stable solid solutions or nanocomposites, depending on growth conditions, concentration of substituting elements, or subsequent thermal treatments.

In the present work, we investigate the growth, structure, thermal stability and oxidation resistance of Ti-Zr-N and Ti-Ta-N systems, which represent archetypes of iso-structural (*B1*-type) and non-isostructural TMN systems. These coatings, with thickness up to 300 nm, were grown by dc reactive magnetron co-sputtering in Ar/N_2 plasma discharges at 300°C on Si substrate. The growth parameters were optimized from the hysteresis curves of N_2 partial pressure vs. N_2 flow. X-ray Diffraction patterns reveal the stabilization of solid solutions with *B1*-type structure in the whole composition range for $Ti_{1-x}Zr_xN$ and up to y=0.75 for $Ti_{1-y}Ta_yN$. Due to the difference in the average deposited energy, the two systems exhibit distinct texture and surface morphology. Post-growth thermal annealing (up to 850°C under vacuum and 600°C under air) were performed to study their structure stability and stress relaxation. *In situ* temperature XRD experiments were also implemented on selected samples to investigate the onset of oxidation process.

2:30pm **B1-2-4 Modified TiAlN Coatings for Cutting Tools Prepared by Magnetron Sputtering**, ***M. Keunecke*** *(martin.keunecke@ist.fraunhofer.de), C. Stein, K. Bewilogua,* Fraunhofer IST, Germany*, W. Koelker,* Cemecon AG, Germany*, D. Kassel, H. van den Berg*, Kennametal Technologies GmbH, Germany

Coatings like TiN or TiAlN are well established as hard and wear resistant tool coatings. These coatings often will be prepared by PVD techniques like arc evaporation or d.c. magnetron sputtering. Typical micro hardness values of such hard coatings are in the range of 30 GPa. As a clear advancement compared to d.c. magnetron sputtering processes the pulsed magnetron sputter deposition technique could be shown. TiAlN hard coatings as well as modified TiAlN coatings with additional elements like Si, Cr, W and C were prepared using the pulsed magnetron sputter technique in a CC800/9 batch coater equipped with 4 targets. Coatings prepared with the pulsed sputter process showed both high hardness and high wear resistance. Beside hardness and wear other properties like adhesion or friction coefficient were determined. Cross sectional SEM images revealed the growth structure in dependence of the applied substrate bias and of the added elements. The chemical composition of the coatings was investigated by electron microprobe analysis and the phase and crystal size were determined by X-ray diffraction. Using the pulsed magnetron sputter process the coating properties, especially the hardness could be significantly improved. With HU_{plast} > 40 GPa the range of superhard materials could be reached The application potential of these coatings will be demonstrated by turning and milling tests results of coated cemented carbide cutting inserts.

2:50pm **B1-2-5 Structure, Wear, and High Temperature Oxidation of SiAlON and SiZrON Films Grown by RF Reactive Magnetron Co-Sputtering**, *M.S. Byrne, B.J. Nugent, G.P. Bernhardt,* ***R.J. Lad*** *(rjlad@maine.edu)*, University of Maine

In bulk form, both SiAlON and SiZrON ceramic materials exhibit useful properties such as high hardness and fracture toughness. However, thin films of these materials have received very little attention. In this study, both homogeneous and nanolaminate structured SiAlON and SiZrON thin films ranging in thickness from 100nm to 1µm were grown on sapphire substrates by RF reactive magnetron co-sputtering of Si+Al or Si+Zr targets in $Ar/O_2/N_2$ gas mixtures. The films were found to be extremely smooth (< 2nm average roughness measured by atomic force microscopy) and to exhibit amorphous glass-like structure at substrate growth temperatures up to 600^{o}C. Post-deposition annealing in vacuum up to 1200^{o}C induces nanocrystallite formation in SiZrON films whereas the SiAlON films remain amorphous as determined by X-ray diffraction. Negligible changes in film stoichiometry were evident after the vacuum annealing as measured by X-ray photoelectron spectroscopy. Post-deposition annealing in air up to 1200^{o}C leads to film oxidation and a loss of nitrogen in the surface region for both types of films. The kinetics of SiAlON and SiZrON film oxidation as a function of stoichiometry was measured for homogeneous films using argon ion depth profiling combined with X-ray photoelectron spectroscopy, and the results were found to be comparable to the oxidation kinetics of nano-laminate structured films in which layer interdiffusion becomes important. Pin-on-disk wear measurements at room temperature both immediately after film deposition and following the annealing treatments indicate that the amount of wear increases as the film nitrogen content increases, with SiAlON films being more wear resistant compared to SiZrON films.

3:10pm **B1-2-6 TiCN/TiNbCN Multilayer System with Enhanced Tribological Properties**, *J. Caicedo (jcaicedoangulo@gmail.com), C. Amaya, M. Gomez,* Universidad del Valle, Colombia*, L. Yate, A. Lousa, J. Esteve,* Universitat de Barcelona, Spain*,* ***P. Prieto***, Centro de Excelencia en Nuevos Materiales, Colombia

$[TiCN/TiNbCN]_n$ multilayer coatings were grown onto Si (100) and steel substrates by reactive r.f. magnetron sputtering technique using two targets (TiC and Nb) and alternating deposition conditions. The bilayer period (Λ) was varied from the micrometric to the nanometric range, maintaining the total thickness of the coatings in the range of a few microns by depositing a suitable number of bilayers (n). The structure of the coatings was characterized by x-ray diffraction (XRD) and scanning electron microscopy (SEM). The stress was calculated by measuring the curvature of the films onto Si (100) substrates with a profilometer. Hardness measurements were performed by using nanoindentation. The tribological properties were determinate via dynamic contact test using a Microtest MT 4001-98 tribometer and Scratch Test Microtest MTR2 system; from them, the friction coefficient and critical load for the different samples were measured. An enhancement of both hardness and elastic modulus was observed when the bilayer period (Λ) in the coatings was reduced. Sample with the smallest bilayer period (Λ = 15 nm, n = 200 bilayers) showed the lowest friction coefficient (~0.1) and the highest critical load (80 N), corresponding to 2.2 and 1.6 times better than those values for the coating with n = 1, respectively. The enhancement effects in the $[TiCN/TiNbCN]_n$ multilayer coatings can be attributed to the Hall Petch effect in multilayered coatings, in which the interfaces act as a barrier against the movement of the dislocations and the bilayers of materials having different mechanical properties generate an inhomogeneous system prohibiting the advancement of potential micro-cracks.

This work was supported by the Center of Excellence for Novel Materials (CENM) under Colciencias/CENM contract # RC-043-2005. Colciencias-Univalle and J. C. Caicedo thank Colciencias for the doctoral fellowship.

3:30pm **B1-2-8 Growth Behavior of Magnetron Sputtered Nanocomposite Films: Experimental Observation and Simulation**, ***T. Pei*** *(y.pei@rug.nl), K.P. Shaha, C. Chen,* University of Groningen, The Netherlands, *A. Turkin,* Kharkov Institute of Physics & Technology, Ukraine, *I. Vainshtein, J.T.M. De Hosson*, University of Groningen, The Netherlands

In film growth, the competition between interface roughening and smoothening essentially determines the nano-/microstructure and consequently the properties of a deposited film. This paper reports several new findings on the breakdown of dynamic roughening in thin film growth. With increasing energy flux of concurrent ion impingement during pulsed DC magnetron sputtering, a transition from dynamic roughening to dynamic smoothening is observed in the growth behavior of TiC/a-C nanocomposite films. The nanocomposite films show a negative growth exponent and ultra-smoothness (RMS roughness ~0.2 nm at film thickness of 1.5 µm). Based on high resolution cross-sectional transmission electron microscopy observations, we conclude that an amorphous front layer 2 nm thick covers the nanocomposite film during growth and suppresses the influence of nanocrystallites on the roughness evolution of the nanocomposite films, which is a solid experimental proof of the impact-induced downhill flow model [1] and subplantation model [2-4]. We were able to predict the evolution of surface roughness based on a linear equation of surface growth which contains two diffusivity parameters that control the atomic mobility along the growing outer surface. The model is in good agreement with atomic force microscopy measurements of roughness evolution [5, 6].

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3:50pm **B1-2-9 Amorphous Metal Carbides: Magnetron Sputtering of Glassy Zr-Si-C Films**, ***M. Hanson*** *(matilda.hanson@mkem.uu.se), S. Urbonaite, E. Lewin, U. Jansson*, Uppsala University, Sweden

Metallic glasses are a well-known group of materials with interesting physical and chemical properties. The glass forming ability (GFA) during solidification of alloys have been studied by Inoue and certain rules for high GFA have been formulated [1]. These rules can also be partly applied on thin film deposition of e.g. metal carbides. Sputtering of amorphous metal carbides films have previously been observed in some systems such as Cr-C, W-Ni-C and W-Fe-C (see e.g. ref. [2]). In the present study we have investigated magnetron sputtering of Zr-Si-C thin films. Krzanowski et al. [3] have found evidence for GFA in this ternary system but no systematic study has been performed before.

The coatings were deposited with non-reactive DC magnetron sputtering with elemental targets. The silicon content was varied between 0-30 at% and the zirconium content between 30-60 at%. Chemical composition and bonding was analyzed using XPS while the microstructure was studied using XRD, SEM and TEM. Mechanical and electrical properties were analyzed using nanoindentation, resistivity measurements and contact resistance measurements. We have found that Zr-Si-C thin films deposited at 250 °C are amorphous in a large composition range and that the GFA is highly depending on the Si content in the film. Initial results of mechanical and electrical properties show a resistivity of 300-400 µΩ cm, a hardness of 9-16 GPa and a Young's modulus of 200-300 GPa. The GFA as well as the influence of the structure on the chemical and physical properties of the coatings will be discussed.

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4:10pm **B1-2-10 Characterizing an Inverted Cylindrical Magnetron During Aluminum and Alumina Depositions: Ion Energy Distribution and Langmuir Probe Studies**, ***S.L. Mensah*** *(smensah@uark.edu), M. Gordon*, University of Arkansas

Ion energy distributions and plasma parameters for plasmas used to deposit low-temperature Al_2O_3 without a chrome template layer were investigated as a function of oxygen partial pressure in the vicinity of the substrate using a Langmuir probe and energy-resolved mass spectroscopy (EQP). The thin films were deposited using a mid-frequency AC reactive magnetron sputtering system operating at 40kHz. In this work, 4kW power, and total flow rates of 40 and 70sccm were used. The gate valve was set such that the pressure in the system reads 2 and 5mTorr for a pure argon discharge for each flow rate. Oxygen partial pressures ranging from 0-70% were investigated. Monitored species include Ar^+, O^+, O_2^+, and Al^+. The growth rate and the elemental composition of the deposited film was investigated

EQP results show that at constant chamber pressure changes in the ratio of the partial pressures of Ar/O_2 affects the high energy tail of ions in the discharge. At high oxygen partial pressures the high energy peak diminishes and all the sputtered alumina atoms are consumed. Deposition with low oxygen results in aluminum thin film growth while alumina was deposited with high concentrations of oxygen. Similarly, changes in pressure influence the characteristics of the Al_2O_3 films deposited. Preliminary studies show that the introduction of oxygen results in the formation of plasma layers which in turn affect the ion energies. Correlations between the ion energy distribution of the discharge particles, plasma layers and the elemental composition in the films deposited are analyzed.

Hard Coatings and Vapor Deposition Technology
Room: Town & Country - Session B6-1

Hard and Multifunctional Nano-Structured Coatings
Moderator: C.P. Mulligan, U.S. Army ARDEC, Benét Laboratories, R. Sanjines, EPFL, P. Zeman, University of West Bohemia

1:30pm **B6-1-1 Morphological and Structural Development of AlTiN Coatings Deposited by Cathodic Vacuum Arc**, ***J. Vetter*** *(joerg.vetter@sulzer.com), J. Mueller,* Sulzer Metaplas GmbH, Germany, *J. Andersson, J. Jolen, L. Karlsson,* Seco Tools AB, Germany, *J. Alami, G. Erkens*, Sulzer Metaplas GmbH, Germany

Coating structure and morphology often play a dominating rule in applications (i.e. cutting tools, components). The morphological and structural development of AlTiN coatings deposited by cathodic vacuum arc are high lightened. The observed morphologies include the fine columnar growth and the super fine growth. Deposition conditions (pressure, bias, voltage, temperature) are influencing both the coating morphology and the phase composition, e.g. the existence of a minor hcp phase for coatings with Al/Ti-content larger than 1. It will be shown that the Al content in the coating and the type of evaporators influence the coating growth. Experimental results will be shown for different Al/Ti compositions at different growth conditions. Experimental methods used were X-ray investigations and SEM. The possibility to generate super fine growth will be discussed.

1:50pm **B6-1-3 New Generation Nanscale Multilayer Coatings to Serve High Temperature, Corrosion and Tribological Applications Deposited by HIPIMS**, ***P.Eh. Hovsepian*** *(p.hovsepian@shu.ac.uk), A.P. Ehiasarian,* Sheffield Hallam University, United Kingdom, *R.I. Braun*, DLR-German Aerospace Centre, Germany **INVITED**

Oxidation resistant and wear resistant coatings for environmental protection of light weight materials such as gama-TiAl alloys for future applications in aero and automotive engines are in high demand. CrAlYN/CrN coatings utilising nanoscale multilayer structure with a typical bi-layer thickness of 4.2nm were successfully produced on large scale by utilising the High Power Impulse Magnetron Sputtering (HIPIMS) technology. HIPIMS was employed for surface pre-treatment as well as for coating deposition. The surface pre-treatment was carried out by bombardment with Cr^+ ions. For comparison CrAlYN/CrN was deposited by Unbalanced Magnetron Sputtering, (UBM) as well.

Scanning Transmission Electron Microscopy, (STEM) revealed that the coating/substrate interface was extremely clean and sharp. Large areas of coating grown epitaxially were observed. STEM-Energy Dispersive Spectroscopy (EDS) profile analysis further showed that during the HIPIMS ion bombardment Cr had been implanted into the substrate to a depth of 5 nm. HIPIMS deposited coatings showed extremely sharp interfaces between the individual layers in the nanolaminated material and almost no layer waviness. This improved structure resulted in further enhancement of the coatings barrier properties.

CrAlYN/CrN showed potential for reliable protection of gama-TiAl alloys against wear and aggressive environmental attack. For coated gama-TiAl alloys, thermo gravimetric quasi-isothermal oxidation tests in air at 750^0 C after 2000 hours exposure showed four times smaller weight gain compared to the uncoated material. HIPIMS coatings were superior to UBM deposited coatings. Tested even at higher, 850^0 C temperature the HIPIMS coatings showed by factor of 2 lower mass gain as compared to the UBM deposited coatings.

In sulphidation tests after 1000 hours exposure to aggressive H_2 /H_2S/H_2O atmosphere the CrAlYN/CrN protected gama-TiAl alloys showed reduced weigh gain by factor of four as compared to the uncoated substrate. High temperature pin-on-disc tests revealed that CrAlYN/CrN reduces its friction coefficient from 0.56 at room temperature to 0.4 at 650^0C, which demonstrates the excellent high temperature tribological behaviour of the coating. HIPIMS deposited coatings showed extremely low wear coefficient of K_C= 1.83 E-17 m^3 $N^{-1}m^{-1}$ at this temperature. Importantly HIPIMS deposited coatings retained the ultimate tensile strength of the gama-TiAl and reduced the fatigue strength only by 9%, compared to 20 % measured for the UBM deposited coatings, which opens perspectives for turbine blade application.

2:30pm **B6-1-5 Application Oriented Characterization of Nitride Coatings for Cutting Tools**, ***M. Lechthaler*** *(markus.lechthaler@oerlikon.com), D. De Gregorio, M. Raschke*, OC Oerlikon Balzers AG, Liechtenstein

The tribomechanical environment during cutting operations differs highly between machining techniques and cutting conditions. One important circumstance regards the temperature at the cutting edge, which varies between values close to room temperature for applications such as thread tapping and values higher than 1000°C for continuous cutting applications.

Generally, temperature dependent coating properties have to be considered in the characterization and later on in the selection of coatings for cutting tools. Mechanisms such as oxidation, phase transformation, recovery and chemical reactions in the contact area can occur. The measurement of the hardness at different temperatures is a characterization method which indicates presence of mentioned effects in form of changing the coating properties.

Hence, the hardness in relation to the temperature is discussed based on measurements which were conducted on TiAlN, AlCrN and alloyed AlCrN coatings deposited on polished cemented carbide (WC / 6% Co) substrates. The micro-hardness indents were performed under a non-oxidizing gas atmosphere at temperatures between 25°C and 1000°C. Furthermore, residual hardness after the annealing sequence was determined to distinguish between permanent and reversible transformations.

Finally, basic cutting tests serve to support the findings obtained in the hardness investigations and the results are discussed in combination with data from the literature.

2:50pm **B6-1-6 Theoretical Thermodynamics of Hard Coatings Materials - Beyond the Mean Field Approximation**, ***B. Alling*** *(bjoal@ifm.liu.se)*, Linköping University, Sweden

During the past few year, theoretical calculations from first-principles has provided important insights, increased understanding and fundamental physical explanations to structural, mechanical and thermodynamics properties of hard coatings materials. However, in order for theory to go beyond explanations, towards predictions, quantitative methods needs to be applied to account for temperature effects. In this work we present both difficulties and solutions to the application of state-of-the-art alloy theory to hard coatings materials. We show results for important systems such as TiAlN and discuss prospects and limitations of theoretical design of hard coatings materials in the future.

3:10pm **B6-1-7 Controllably Manipulating AlN Incorporation in $Hf_xAl_{1-x}N$(001) Single-Crystal Thin films During Magnetically–Unbalanced Reactive Magnetron Sputter Deposition by Low-Energy (10 to 80 eV) Ion-Bombardment**, ***B. Howe*** *(bhowe@uiuc.edu), E. Sammann, J.-G. Wen, M.R. Sardela, T. Spila, J.E. Greene,* University of Illinois at Urbana-Champaign, *A.A. Voevodin,* Air Force Research Laboratory, *L. Hultman,* Linköping University, Sweden, *I. Petrov*, University of Illinois at Urbana-Champaign

We show that the AlN incorporation in single crystal $Hf_{1-x}Al_xN$(001) films can be controllably manipulated between ~ 0 and 100% by varying the ion energy (E_i) incident at the growing film over a narrow range, 10 – 40 eV. The layers are grown on MgO(001) at 450°C using ultrahigh-vacuum reactive magnetically-unbalanced magnetron sputtering from a single Hf/Al 70/30 (at. %) alloy target in 5% N_2/Ar mixtures at a total pressure of 20 mTorr. The ion-to-metal flux ratio incident at the growing film is maintained constant at 8, while E_i is varied from 10 to 80eV. Film compositions vary from x = 0.3 with E_i = 10 eV to 0.27 with E_i = 20 eV, 0.17 with E_i = 30 eV, and $\leq$ 0.02 with $E_i \geq$ 40 eV. Thus, the AlN incorporation probability decreases by greater than two orders of magnitude! This extraordinary range in real-time manipulation of film chemistry during film deposition is due to the efficient resputtering of Al atoms (27 amu) by Ar ions (and fast Ar atoms, both 40 amu) scattered off heavy Hf atoms (178.5 amu) in the film. This effect can be used to grow planar heterostructures and superlattices with abrupt interfaces at high deposition rates from a single target by controllably switching E_i. The choice of E_i values determines the layer compositions and the switching speed controls the layer thickness. Here, we present the effects of film micro- and nanostructural properties on film hardness in $Hf_{0.70}Al_{0.30}N$/HfN superlattices with bilayer thicknesses ranging from 1 to 7 nm using high-resolution transmission electron microscopy (HR-TEM), HR-STEM, HR-XRD and nanoindentation.

3:30pm **B6-1-8 Design Concepts for Superhard Nitride Thin Films; Superlattices, Solid Solutions, and Nanocomposites**, ***L. Hultman*** *(larhu@ifm.liu.se)*, Linköping University, Sweden **INVITED**

Transition metal nitrides processed by PVD methods are strategic materials in advanced surface engineering applications. Recent findings of nanostructuring by design and self-organization in different compounds will be presented herein. Analysis of the materials (nanoindentation, XRD, TEM, 3D Atom Probe, et.c.) is coupled with ab initio calculations. The latter is used to assess the miscibility gap in the phase diagram of the MeAlN (Me = Ti, Sc, Zr, Hf) systems. This allows for the investigation of different explanations for phase stabilities or decomposition behavior such as lattice mismatch and electronic band structure effects. [1]

For TiN/NbN(001) superlattices, dislocation glide within the layers is the dominant deformation mechanism. That confirms the present models for superhardening that presumes plasticity and postulates dislocation hindering at interfaces between layers of different shear modulus. In consequence, these coatings also exhibit crystal rotation during deformation. [2]

Superhardening occurs in TiN/Si_3N_4 nanocomposites due to Si segregation forming a few-monolayer (ML)-thick SiN_x tissue phase, which can be amorphous or crystalline. In the latter case, we show the existence of a cubic-SiN_x layer that is epitaxially stabilized to TiN. A hardness maximum at 34 GPa is observed in TiN/SiN_x(001) superlattices at the epitaxial break-down limit for the epitaxial SiN_x layers of 2-5 ML, well above the percolation limit. [3]

Our concept of age hardening in supersaturated cubic-phase transition metal nitride alloy systems is presented for the pseudobinary MeAlN systems. Secondary phase transformation including spinodal decomposition of TiAlN into isostructural (cubic-phase) nm-size domains of TiN and AlN is thus demonstrated. [4] The as-formed domains hinder dislocation glide in films annealed to temperatures corresponding to cutting tool operations. The effects of pressure [5], temperature, composition, disorder, and stoichiometry (vacancies) will also be discussed.

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4:10pm **B6-1-10 Epitaxial Growth of ZrAlN Alloy and Superlattice Thin Films: Mechanical Properties and Structural Characterization**, ***N. Ghafoor*** *(naugh@ifm.liu.se), J. Birch, J. Jensen, L. Hultman, M. Odén*, Linköping University, Sweden

Ternary transition metal nitrides are commonly used as wear resistant coatings on cutting tools. In particular, the metastable TiAlN has proven to be both oxidation resistance and exhibit age-hardening due to spinodal decomposition. The purpose of this work is to study the related, but less explored ZrAlN system for which *ab initio* calculations [1,2] and experiments [3,4] show a relatively large miscibility gap. In order to elucidate the solid-solubility limit and any phase transformation occurring during growth, we propose to study single-crystal ZrAlN films. In this work, $Zr_{1-x}Al_xN$ and $Zr_{1-x}A_xN$/ZrN superlattice films with $0 \leq x \leq 1$ were deposited on MgO(001), MgO(111), Al_2O_3(0001), and WC-Co substrates at Ts = 700-800°C using high vacuum dual cathode unbalanced magnetron sputtering in a mixture of Ar and N_2. The substrates were kept at floating potential providing an ion assistance of ~18-25 eV. Ion beam analysis (ERDA and RBS) revealed that all films were stoichiometric with N/(Zr+Al)=1±0.02. High resolution X-ray diffractometry shows that high-quality B1-NaCl structure ZrN(001) films form on MgO(001) substrates.

Breakdown of the epitaxial crystal into nanosize crystallites takes place at x>0.2 accompanied by a shift in the 200 diffraction peak towards low 2θ values along with a progressive broadening. Alloying with Al yields films with increasing hardness from~22 Gpa (x=0) to 27 Gpa (x=0.7). $Zr_{1-x}Al_xN$/ZrN superlattices with varying composition modulation periodicities show higher hardness compared to monolithic alloy films. Preliminary tests show hardness as high as 38 Gpa for a 1.5 µm thick multilayer film with a compositional modulation period of 30 nm.

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4:30pm **B6-1-11 Effect of the Aluminium Contents and the Bias Voltage on the Microstructure Formation in the $Ti_{1-x}Al_xN$ Protective Coatings**, ***Ch. Wüstefeld*** *(wuestefeld@ww.tu-freiberg.de), D. Rafaja, V. Klemm,* TU Bergakademie Freiberg, Germany*, M. Kathrein,* CERATIZIT Austria GmbH, Austria*, C. Michotte,* CERATIZIT Luxembourt S.a.r.l., Austria*, C. Baehtz*, Forschungszentrum Rossendorf, Germany

Microstructure features like phase composition, crystallite size and lattice strain are usually related to the formation and mobility of microstructure defects and influence always the properties of protective hard coatings. Among the parameters of the deposition process, which are employed to adjust the microstructure of the Ti-Al-N coatings deposited by cathodic arc evaporation (CAE), the aluminium contents and the bias voltage play a crucial role. In this study, the influence of both parameters on selected microstructure parameters of the CAE $Ti_{1-x}Al_xN$ coatings deposited from the Ti-Al cathodes was investigated by using X-ray diffraction and transmission electron microscopy.

The microstructure of the coatings was described in terms of the chemical and phase composition, local distribution of the phases, crystallite size and lattice strain, which results from the interaction between neighbouring crystallites and from the presence of the dominant microstructure defects. The microstructure model based on the knowledge of the above microstructure parameters allowed the microstructure formation during the deposition process to be explained and correlated to the parameters of the deposition process. The correlation between the microstructure formation and the parameters of the deposition process contributed substantially to the understanding of the effect of the aluminium contents and the bias voltage on the microstructure formation in CAE $Ti_{1-x}Al_xN$ coatings.

This study was performed on coatings with the chemical compositions $Ti_{0.60}Al_{0.40}N$, $Ti_{0.50}Al_{0.50}N$ and $Ti_{0.40}Al_{0.60}N$, which were deposited at the bias voltages (U_B) ranging between -20 V to -120 V. Disregard the chemical composition, the coatings deposited at $U_B \leq -40$ V contained face centred cubic (Ti,Al)N as a single phase. With increasing U_B, Al segregated from the (Ti,Al)N and created AlN. The segregation of Al contributed to the reduction of the crystallite size and to the increase of the lattice strains in the coatings. Both these phenomena are related to the increase of the hardness. A departure from the monotonous reduction of the crystallite size and from the monotonous increase of the lattice strain was observed at the highest bias voltage (U_B = -120 V).

The non-monotonous effect of the bias voltage on the phase composition, on the crystallite size and on the kind and density of the microstructure defects will be discussed with respect to several competing processes, which are related to the energy of impinging particles, to the mobility of the deposited species, to the formation, arrangement and mobility of microstructure defects and to the mechanical interaction of neighbouring crystallites.

4:50pm **B6-1-12 Microstructure and Characterization of Ni-Alloy/CrN Nanolayered Coatings with Various Bilayer Periods**, ***H.-H. Huang****, F.-B. Wu (fbwu@nuu.edu.tw),* National United University, Taiwan*, J.-W. Lee,* Mingchi University of Technology, Taiwan

In this study, the Ni-alloy/CrN nanolayered coatings were fabricated on (100) silicon wafer and 420 stainless substrates by dual-gun sputtering technique. The influence of the interlayer alloy coatings on microstructure, morphology, and corrosion behavior of the nanolayered thin films were investigated. The bilayer thickness was controlled approximately 10-20 nm with a total coating thickness of 1µm . The microstructure evolution of the NiAl, NiP and Ni-alloy/CrN coatings under various process temperatures were evaluated. Through phase identification, precipitation or transformation was observed in the Ni alloy layers. The period stacking and theoretical values of bilayer period were analysis by low-angle XRD diffraction technique. The nanolayered coatings showed a higher corrosion resistance as compared to single layer coatings. The corrosion mechanisms of the coatings were compared through AC impedance and equivalent electrical circuit results in the frequency range of 0.1Hz -10kHz. Through Tafel curves analysis, the corrosion resistance improved effectively by nanolayered structure was evident. Through nanoindentation analysis, the hardness and Young's modulus were also improved by multilayer configuration. The correlation between microstructure evolution, corrosion and indentation behaviors was discussed.

5:10pm **B5-2-4 3D-Atom Probe Investigations of Ti-Al-N Thin Films**, ***R. Rachbauer*** *(richard.rachbauer@unileoben.ac.at), S. Massl, E. Stergar,* Montanuniversität Leoben, Austria*, P. Felfer,* University of Sydney, Australia*, P.H. Mayrhofer*, Montanuniversität Leoben, Austria

State of the art three-dimensional atom probe tomography (3D-APT) enables the simultaneous investigation of morphology and chemical composition with near atomic resolution. Since spinodal decomposition in $Ti_{1-x}Al_xN$ thin films results in the formation of a nanostructure and an increase in hardness at high temperatures, this process has attracted increasing interest and is in the focus of many research activities on the design and modification of chemical and phase-modulated nanostructured thin films.

We employ a local electrode 3D-atom probe in laser-mode to study the morphological and chemical development of $Ti_{1-x}Al_xN$ coatings. The results obtained clearly indicate compositional fluctuations of Ti and Al atoms of cubic $Ti_{0.46}Al_{0.54}N$ coatings, prepared by dc magnetron sputtering at 500 °C, already in the as-deposited state [1]. This is in good agreement to results reported for epitaxially grown $Ti_{0.50}Al_{0.50}N$ coatings [2]. Vacuum annealing to 900 °C induces an increase in the compositional amplitude of the fluctuations and the formation of a 3D-interconnected network of cubic Ti- and Al-rich domains. Detailed 3D-APT studies exhibit diffuse domain boundaries, which highlight the spinodal character of the decomposition process. During vacuum annealing to 1450 °C the aluminium enriched domains phase-transform in the stable modification, hexagonal (B4) AlN, whereas the titanium enriched domains maintain the cubic (B1) structure while transforming into TiN.

Based on our studies, we can conclude that starting from an almost randomly distributed input of 22.9 at.% Ti, 26.4 at.% Al and 50.5 at.% N in the as-deposited single-phase cubic $Ti_{0.46}Al_{0.54}N$, the complexity of the system increases upon annealing to temperatures above 900 °C. The decomposition process into TiN and AlN via spinodally formed Ti- and Al-rich domains also causes a rearrangement of the initially randomly incorporated 0.13 at.% oxygen impurities. After decomposition, the oxygen is preferentially incorporated in the AlN phases. Consequently, 3D-APT studies will have a strong impact on future developments of super-saturated, chemically and phase-modulated hard coatings and thin films, especially involving investigations on the effect of minority trace elements.

[1] R. Rachbauer, E. Stergar, S. Massl, M. Moser, P.H. Mayrhofer, Scripta Materialia 61 (2009) 725-728.

[2] F. Adibi, I. Petrov, L. Hultman, U. Wahlström, T. Shimizu, D. McIntyre, J.E. Greene, J.E. Sundgren, J. Appl. Phys. 69 (1991) 6437-6450.

Tribology and Mechanical Behavior of Coatings and Thin Films

Room: Pacific Salon 1 - Session E3-2

Tribology of Nanostructured and Amorphous Films

Moderator: J. Fontaine, Ecole Centrale de Lyon, R.D. Evans, Timken Company

1:30pm **E3-2-1 Friction, Wear and Solid Lubrication Mechanisms of $MoS_2/Sb_2O_3/Au$ Composite Coatings**, ***T.W. Scharf*** *(scharf@unt.edu),* The University of North Texas*, P.G. Kotula, S.V. Prasad,* Sandia National Laboratories

Amorphous $MoS_2/Sb_2O_3/Au$ composite sputtered coatings are well known for their solid lubricating behavior and environmental robustness. In the current study, we have investigated the fundamental mechanisms of friction and interfacial shear strength, and the role of contact stress and environment on their tribological behavior. Friction and wear measurements were made from 0.3 to 1.1 GPa contact pressures in dry (<1% RH) nitrogen or humid (50% RH) air, with precise control of dew point and oxygen content. The friction coefficient of $MoS_2/Sb_2O_3/Au$ in dry nitrogen was extremely low, ~0.007, whereas in humid air it increased to ~0.16, with minimal amount of wear in both environments with wear factors of 1.2-1.4 x 10^{-7} mm^3/Nm. The coatings also exhibited non-Amontonian friction behavior, with friction coefficient decreasing with an increase in Hertzian contact stress. 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. The interfacial shear strength, computed from friction coefficient - inverse Hertzian contact stress plots, was found to be 20 MPa in dry nitrogen and 38 MPa in humid air (both very low values for solid lubricant coatings). Cross-sectional transmission electron microscopy (XTEM) with Automated eXpert Spectral Image Analysis (AXSIA) software for X-ray spectral images and high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) were used to study the solid lubrication mechanisms of the wear tracks and corresponding transfer films. It was determined that that in dry nitrogen, frictional contact transformed the amorphous coating into crystalline 2H-MoS_2 basal (0002) planes oriented parallel to the sliding direction inside the wear track. This amorphous to crystalline transformation resulted in a continuous MoS_2 film across the entire wear track, while in the humid air, the wear track was also enriched with Au islands leading to the slightly higher friction coefficient and interfacial shear strength. In both environments, the transfer films also exhibit (0002)-orientated basal planes along their entire section resulting in predominantly self-mated 'basal-on-basal' interfacial sliding, and thus low wear. This presentation will also discuss the interrelationships between interfacial structure/tribochemsitry and the pressure-induced transfer film shear strength to explain the observed friction and wear behaviors in the two environments.

1:50pm **E3-2-2 Friction Behaviour of Fullerene-Like WS_2 Nanoparticles in Ni-Matrix Coating Compared to PVD WS_2 and MoS_2 Coatings**, ***F. Gustavsson***, *S. Jacobson (staffan.jacobson@angstrom.uu.se)*, Uppsala University, Sweden

MoS_2 and WS_2 are widely used as solid lubricants in coatings for tribological applications and have shown super-low friction in non-humid atmospheres and vacuum. They are known for their non-Amontonian behaviour, meaning a decreased coefficient of friction μ with increasing load. The big drawback is their sensitivity to humidity, leading to tribo-induced oxidation of WO_3 and MoO_3, respectively. These oxides are much harder to shear, thus resulting in higher μ. Inorganic Fullerene like nanoparticles (IFLs) of WS_2 and MoS_2 have been proposed to perform better, based on that their closed structure would make them more stable against oxidization.

This paper compares the friction behaviour of three MeS_2 based coatings in various atmospheres under different loads and sliding velocities against ball bearing steel balls.

A novel electrodeposited composite coating with IFL-WS_2 in a Ni-P-matrix is compared with a PVD coating with a columnar WS_2 structure and with a commercial MoS_2 PVD coating. The tests were performed in a pin-on-disc setup. Wear tracks and the transfer films were analysed with EDX, XPS and TEM.

In dry nitrogen atmosphere the IFL-WS_2 coating shows μ below 0.01, which is as good as the commercial PVD coating. The IFL-WS_2 coating shows very little wear under these conditions. In more humid atmospheres the IFL-coating performs better then the planar WS_2 coating but not as good as the commercial MoS_2 coating. Tests at elevated temperature, when no water is adsorbed to the surface, show some very promising results for the IFL-WS_2 coating. It has also been observed that the IFL-WS_2 coating performs better under higher normal load. Transfer films were observed for all contacts and their characteristics were investigated and are believed to have an important role for the friction behaviour.

The results clearly show that coatings containing IFL-nanoparticles can become an attractive alternative for specific tribological situations.

2:10pm **E3-2-3 High-Power Ion Beam Deposition of Nanocomposite and Nanolaminate Multilayer Coatings: Synthesis and Characterization***, ***T.J. Renk*** *(tjrenk@sandia.gov), T.E. Buchheit, P.G. Kotula, S.V. Prasad*, Sandia National Laboratories

We have formed self-assembled nanocomposite thin-films using ablation/redeposition by high-power ion beams. The films were formed using the the Repetitive High Energy Pulse Power (RHEPP-1) facility at Sandia National Laboratories with deposited energy densities up to 10 J/cm^2 energy per pulse. Individual deposited layers are ~ 10 nm thick, and hundreds of layers have been assembled to form films of up to several microns thickness. Films of alternating bi-metal composition (e.g. Mo-Ti or Mo-Ir), exhibit a well-delineated multi-layer structure of up to 20 GPa hardness. When a third element is added (in the form of MoS_2 instead of pure Mo), the growth of smooth individual layers was disrupted and the resultant structure comprised of 100 nm-sized single-crystal Mo spheres periodically spaced through the film thickness. Characterization of the films was performed on cross-sections of wear scars suitable for TEM analyses prepared using focused ion beam (FIB) microscopy. Friction and wear measurements were performed using a Si_3N_4 ball in dry nitrogen and air with 50% relative humidity (RH). The MoS_2 film with self-assembled spheres was found to exhibit both low friction and low wear, even in humid air with 50% RH. The spheres seem to provide a hard wear-resistant surface, while the MoS_2 contributes low friction. The formation of MoO_3 is inhibited in this structure. The latter is mechanically unstable, and contributes to the breakdown of MoS_2 in humid conditions. Sulphur appears to catalyze the sphere formation in an as-yet unknown way. Sphere growth occurs only under specific conditions, e.g. when the depositional substrate is heated to 350°C, MoS_2 and Ti layers are deposited separately, and a relatively high amount of Ti is deposited, more than the 20 at% mentioned by most researchers who have investigated Ti additions to MoS_2. Substitution of vanadium in place of the Ti leads to the same Mo sphere formation. This is significant, as Mo and Ti are immiscible, whereas Mo and V are fully miscible. We have also formed nanocomposites using WS_2 and Zr in place of MoS_2 and Ti (or V). The WS_2-Zr layer exhibits the same sphere microstructure, with single-crystal W spheres in place of the Ti spheres. This suggests that there are other examples of self-assembled nanocomposites possible. Analysis is continuing, and latest results will be presented.

*Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under Contract DE-AC04-94AL85000.

2:30pm **E3-2-4 Mapping Tribocorrosion Behaviour of ZrN_xO_y Nano-Structured Thin for Decorative Applications**, ***M.T. Mathew*** *(mathew_t_mathew@rush.edu)*, Rush University Medical Center, *E. Ariza, L.A. Rocha, P. Carvalho, F. Vaz*, Universidade do Minho, Portugal

Recently, there is a large growth in the nanotechnology research focused on the fabrication and evaluation of nano-structured devices and system, having several novel properties and applications including the decorative commodities. High surface area to volume ratio, tunable optical properties and enhanced mechanical properties are some of the key characteristics. However during the practical usage, such surfaces are also exposed to movements (For example: holding door handles) in diverse chemical environment (For example: human sweat). In such situations the wear and corrosion resistance of the surfaces are significant and influences the durability/performance of the component itself. Tribocorrosion is a new laboratory testing method, where prior evaluation of the surfaces can be made. This testing method represents a powerful and unique tool that can give precious information about the future in-service behavior of several tolls and machine parts and, most important, parts that are coated with a certain functional thin film system.

Among the different examples that one can imagine, decorative thin film systems are certainly among the most important examples, since this kind of materials are subjected to simultaneous wear and corrosion environments whenever they are put in service. In order to gain further knowledge, both in the test method itself,, as well as in the study of the future behavior of a particular decorative-like system, ZrN_xO_y thin films were tested for their tribocorrosion properties on a standard reciprocating sliding tribometer (TE 67/E) in an environment of artificial sweat solution. The study was conducted as a function of load (3-6-9N) and electrode potential (-0.5, 0, +0.5 V (E vs SCE)). The evolutions of the friction coefficient and current have been measured during the test. Electrochemical impedance test were used to comprehend the changes in the surface chemistry before and after the sliding test. For the in-depth understanding of the tribocorrosion process, wastage map, mechanisms map and synergism map were constructed as a function of electrode potentials and load.

2:50pm **E3-2-5 Microstructures and Mechanical Properties Evaluation of TiAlN/CrSiN Multilayered Thin Films with Different Bilayer Thickness**, ***J.-M. Kao***, Tungnan University, Taiwan, *J.-W. Lee (jefflee@mail.mcut.edu.tw), L.-C. Chang*, Mingchi University of Technology, Taiwan

Nanostructured TiAlN/CrSiN multilayer coatings were deposited periodically by a bipolar asymmetric pulsed DC reactive magnetron sputtering technique. The structures of multilayer coatings were characterized by an X-ray diffractometer. The surface and cross sectional morphologies of thin films were examined by a scanning electron microscopy (SEM) and transmission electron microscopy (TEM), respectively. The surface roughness of thin films was explored by an atomic force microscopy (AFM). The nanohardness and elastic modulus of multilayer coatings were investigated by means of a nanoindenter . The scratch and wear testers were used to evaluate the tribological properties of thin films. It is observed that coatings with bilayer thickness ranges from 5 nm to 40 nm were produced in this work. The surface roughness of the multilayered coating decreased with increasing bilayer thickness. An optimal hardness and tribological behaviors were found on the coating with a critical bilayer thickness of 12 nm.

3:10pm **E3-2-6 Nanostructured Hard Coatings Deposited by Cathodic Arc Evaporation: from Concepts to Applications**, ***F. Sanchette*** *(frederic.sanchette@cea.fr), C. Ducros,* CEA, France*, T. Schmitt,* Ecole Centrale de Lyon, France*, P. Steyer*, INSA de Lyon, France **INVITED**

The vacuum cathodic arc evaporation (CAE) process is now widely used on an industrial scale essentially to prepare protective hard coatings on cutting tools, metal molds etc… It has been recognized that high ionization levels of cathodic arc discharges and high ions energy can provide advantages as, for example, enhanced adhesion which is required for mechanical applications involving high loads. CAE allows deposition of a wide range of hard compounds as nitrides or carbonitrides. However, CAE generates macrodroplets that lead to degrade the surface roughness of coatings. The recent trend is to develop advanced nanostructured hard coatings in order to enhance properties as hardness, toughness, oxidation resistance etc…

This paper deals with the recent developments in both CAE technology and nanostructured thin films synthesis. Technological progresses on macrodroplets filtering or new cathodes are discussed. Elaboration and characterization of both nanocomposite and nanolayered hard coatings are described. Thus, relationships are established between deposition parameters, nanostructure and tribological behaviours of the coatings.

3:50pm **E3-2-8 High-Temperature Sliding-Wear Performance of Nanomultilayer PVD Coatings**, ***F. Kustas*** *(fkustas.eci@gmail.com), D. Falsone,* Engineered Coatings, Inc.*, R. Wei,* Southwest Research Institute*, A. Kustas, J. Williams*, Colorado State University

High performance turbine engines, aircraft-engine control components, and air-foil bearings are required to operate at increasing temperatures, which increases system efficiency. Liquid lubrication systems have limited temperature capability and reaction with steel surfaces can result in corrosion. Development of wide-temperature-range solid lubrication that offers low coefficient of friction (COF) and low wear factor (WF) is a key technology for future mechanical systems. Engineered Coatings and Southwest Research Institute deposited nanomultilayer coatings, adopted from the dry-machining industry, for tribological-property characterization at room temperature (RT), 260°C (M50 steel substrates vs. M50 balls), 485°C (Pyrowear substrates vs. Si_3N_4 balls), and 648°C (Pyrowear substrates vs. Si_3N_4 balls). From the sliding-wear tests conducted in air on coated Pyrowear substrates, nanomultilayer coatings consisting of TiAlCrN / (Ti-W-Ti)N exhibited the best combination of low COF (~0.4 at RT and ~0.37 at 485° C) and low ball WF at RT and 485° C, while a nanomultilayer coating of TiAlCrN / TiN exhibited the best performance at 648°C (COF ~0.37). A TiAlCrN / (Ti-W-Ti)N multilayer coating with a WS_2 cap layer exhibited lowest COF at RT on Pyrowear, but the low COF (~0.2) lasted for only about 50% of the test duration; at 485°C the COF was ~0.4. At lower temperatures on M50 steel substrates, the best performing coating was a monolayer of AlTiCrSiCN at RT, while at 260°C the best performer was the nanomultilayer coating TiAlCrN / TiN. However in both cases COF on coated M50 steel was higher than for coatings on Pyrowear. Photographs of the ball wear scars were taken to characterize the wear behavior.

4:10pm **E3-2-9 Application of Thick and Thin Film Coatings in Oil & Gas Drilling**, ***C. Lin*** *(chih.lin@bakerhughes.com)*, Baker Hughes**INVITED**

Oil and gas drilling represents a unique industry that demands innovation and efficiency and where many physical limitations and technological challenges exist. The materials used in drilling oil and gas wells have to balance between different opposing attributes and are usually pushed to their maximum mechanical capability. This presentation will discuss the applications of various thick and thin film coatings in drill bits that are used to make the well for extracting oil and gas. The drilling environment can be corrosive or abrasive or both. Thus, keeping a rock bit drilling in the hole for an extended period of time with a desirable penetration rate requires substantial protection on the exterior surface and sustaining wear resistance of the internal components. Functional coatings, such as tungsten carbide hardfacing, silver plating, thermally sprayed coating, and diamond-like carbon coating, have been attractive engineering solutions as they can be applied to almost any geometry without adding substantial dimensions. Careful material selection, testing, and application of the coating can not only enhance the performance but also extend the life of a rock bit. A comprehensive test program will be demonstrated to show how tungsten carbide hardfacing and diamond-like carbon coating were successfully brought to commercialization in oil and gas drilling.

4:50pm **E3-2-11 Comparative Analysis on Structure and Tribo-Mechanical Properties of Ti-B-C Nanocomposite Coatings Prepared by Magnetron Sputtering**, ***J.C. Sánchez-Lopéz****, M.D. Abad, A. Justo,* Instituto de Ciencia de Materiales de Sevilla (CSIC-US), Spain*, M. Brizuela, A. García-Luis*, Fundación Inasmet-Tecnalia, Spain

Protective coatings based on hard ceramic phases (TiC, TiB_2) combined with amorphous carbon (a-C) at a nanometric scale are of interest because of the adequate balance between mechanical and tribological properties. In this work, two series of Ti-B-C nanocomposite coatings were prepared by sputtering of a graphite target and a second one composed of either TiB_2:TiC (mixed) or pure TiB_2 (single). Varying the sputtering power ratio, the a-C content could be tuned inside the coatings as observed by means of Raman and X-ray photoelectron spectroscopy (XPS). The microstructural characterization demonstrated that the set of coatings differ significantly in the crystal size and its dependence with the carbon content. The analysis of the carbon bonding by XPS and Raman revealed the differences in terms of relative amount of a-C and carbide components (TiC and TiB_xC_y). The hardness values decreased by half when the carbon addition leads to the formation of an amorphous carbon matrix. However, in the case of the mixed-target series the carbon content can be increased maintaining almost invariable the hardness because it is incorporated in the form of non-stoichiometric TiB_xC_y compound. The friction properties are correlated with the detected phases displaying a sharp transition from 0.6-0.9 to <0.3 when the fraction of a-C is above 50 at. %. Raman observation of the wear tracks determined the presence of disordered sp^2-bonded carbon phase associated to the diminution of the friction level.

5:10pm **E3-2-12 Particle Erosion Characteristics of Super-Elastic Hard Ti-Si-C Films Prepared by PECVD**, ***S. Hassani****, J.-E. Klemberg-Sapieha (jsapieha@polymtl.ca), L. Martinu*, Ecole Polytechnique de Montreal, Canada

Titaniun carbide (TiC) thin films are widely used for tribological applications due to their high hardness (*H*) and wear resistance. TiC films prepared by low temperature Plasma Enhanced Chemical Vapor Deposition (PECVD) exhibit an unusual simultaneous combination of properties such as very high *H*, low Young's modulus (*E*), and low friction coefficient (μ). Tailoring such properties is well suited for a wide range of tribological applications, particularly for the protection against solid particle erosion in different components of aircraft and helicopters. In order to further improve the properties of TiC, in the present work, we incorporated silicon (Si) as an alloying element to obtain ternary nanostructured Ti-Si-C films. Si addition into the base Ti-C resulted in significant microstructural, mechanical and tribological modifications. By controlling the Si content in the films, we succeeded to obtain transition from films consisting of fine nano-sized TiC crystallites embedded in a an amorphous SiC/a-C:H matrix to a microstructure formed by nano-sized SiC crystallites encapsulated in a TiC/a-C:H matrix. This allowed one to control the main mechanical characteristics, namely *H*, *E*, and μ, in the range of 14-32 GPa, 140-240 GPa, and 0.16-0.6, respectively. For films prepared under optimized conditions, high resistance to elastic and plastic deformation of the Ti-Si-C films, expressed by high values of H/E and H^3/E^2 ratios, respectively, resulted in 8 times higher erosion resistance at 90° compared to bare steel substrate. At the same time, erosion resistance at 30° impact angle increased by a factor of 22 due to a simultaneous combination of high *H* and low μ. Taking into consideration the severe erosion test conditions and the Ti-Si-C film thickness of only 2.5 µm in this work, further improvement is expected for thicker films.

5:30pm **E3-2-13 Tribological Properties of Nanoporous Anodic Aluminum Oxide Film**, *H.S. Kim,* ***H.S. Ahn*** *(hsahn@snut.ac.kr), D.H. Kim,* Seoul National University of Technology, Korea*, J.H. Hahn, W. Lee, S.J. Cho*, Korea Research Institute of Standards and Science, Korea

Friction and wear properties of nanostructured anodic aluminum oxide (AAO) films were studied in relation to contact load and pore density (pore size and inter-pore distance). Uniformly arrayed nanoporous aluminum oxide films (pores of 28 nm, 45 nm and 200 nm dia. and 2 µm thick) were synthesized by mild anodization. Reciprocating wear tests using 1 mm diameter steel balls as counterpart were carried out for a wide range of load (from 1 mN to 1 N) at ambient environment. The friction coefficient significantly reduced with the increase of load. The pore density marginally affected the frictional properties of AAO films. The friction coefficient was decreased by approximately 10% when the pore density decreased 60 times. The worn surface of AAO films tested at low loads (1 mN and 10 mN) did not experience tribochemical reaction and exhibited only mild plastic deformation. Dispersed thick smooth films were formed on the worn surface of all samples at relatively high loads (100 mN and 1 N) whereas only extremely thin smooth film patches were rarely formed at low loads (1 mN and 10 mN). These thick smooth films were generated by combined influence of tribochenmical reaction at the contact interface and plastic deformation of compacted debris particles as evidenced by energy-dispersive spectroscopy and X-ray photoelectron spectroscopy analyses. We suggest that these thick films mainly contributed to the decrease of friction regardless of the pore density.

Surface Engineering for Thermal Transport, Storage, and Harvesting
Room: Sunrise - Session TS4

Surface Engineering for Thermal Transport, Storage, and Harvesting
Moderator: A.A. Voevodin, Air Force Research Laboratory, T. Fischer, Purdue University

1:30pm **TS4-1 Thermoelectric Energy Conversion in Multilayers and Embedded Nanoparticle Materials**, ***A. Shakouri*** *(ali@soe.ucsc.edu)*, University of California at Santa Cruz **INVITED**

In this talk we will review the trade offs between electrical conductivity, Seebeck coefficient and thermal conductivity. We describe how these parameters are related to the bandstructure and the transport of various phonon modes. Theoretical calculations show that superlattices, embedded nanoparticles and hot electron filtering can improve the thermoelectric energy conversion. Novel metal-semiconductor nanocomposites are developed to modify the transport of both electrons and phonons. Theory and experiment are compared for a series of samples based on rare-earth nanoparticles in III-V semiconductor matrix as well in nitride metal/semiconductor multilayer films. Potential to reach energy conversion efficiencies exceeding 15-20% is discussed. We also describe how similar principles can be used to make micro refrigerators on a chip and remove hot spots in integrated circuits. In this case the three dimensional heat and current spreading plays an important role.

2:10pm **TS4-3 Thermal Conductivity in Anisotropic Thin Film Materials**, ***C. Muratore*** *(christophermuratore@hotmail.com),* Air Force Research Laboratory, *J.J. Hu,* UDRI/Air Force Research Laboratory, *J. Gengler,* Spectral Energies/Air Force Research Laboratory, *R.C. McLaren,* University of Illinois Urbana-Champaign, *S.A. Putnam,* Air Force Research Labs/Universal Technology Corp., *W.P. King, D.G. Cahill,* University of Illinois Urbana-Champaign, *A.A. Voevodin*, Air Force Research Laboratory

Materials with hexagonal crystal structures, such as graphite, molybdenum disulfide and boron nitride are composed of atomic lamellae. Crystals comprised of these materials possess markedly different physical properties along these atomic planes compared to those measured across atomic layers due to the nature of the intra- versus inter planar chemical bonding. For example, in MoS_2, each layer consists of two planes of sulfur atoms and an intermediate plane of molybdenum atoms, all covalently bonded. The layers themselves, however, are held together by weaker Van der Waals bonds. Thus, the shear strength, surface energy and electrical conductivity all vary by orders of magnitude, depending on crystal orientation. Such crystallographically anisotropic compounds also offer an opportunity to study fundamentals of thermal conductivity in crystals, as well as applications for directing or spreading heat within a compositionally homogeneous material. To this end, plasma-based deposition methods to control the c-axis orientation of MoS_2 and BN films with thicknesses of 0.1 – 1 mm were identified. The orientation of MoS_2 films was dictated primarily by deposition rate during pulsed magnetron sputtering of a MoS_2 target. The intensity of (002) peaks increased with deposition rate and also ion energy. Boron nitride films were oriented by mixing hydrogen with the reactive nitrogen gas while dc sputtering a pure boron target. Increasing the hydrogen flow promoted (002) orientation of BN films, presumably by increasing the etch rate of (100) crystals during competitive growth of both orientations. Amorphous films and films with mixed orientations were also examined. Laser thermoreflectance-based techniques were used to measure the through-thickness thermal conductivity of the films. The thermal conductivity was dependent on the orientation and thickness of the films for both materials. In initial experiments, thermal conductivity was as low as 0.2 $W\ m^{-1}K^{-1}$ through (002) oriented MoS_2, and as high as 1.4 along the 100 planes. For 100 nm thick boron nitride films, thermal conductivity went from 0.7 for the 002 orientation to over 5 $W\ m^{-1}K^{-1}$ for the 001 films. The measured values of thermal conductivity were compared to values predicted by molecular dynamics models and models in the literature presented by Slack and others to gain insight with respect to mechanisms of phonon transport in anisotropic crystalline thin film materials.

2:30pm **TS4-4 Time Domain Thermoreflectance and 3-Omega Comparison Studies of Polymer-Metallic-Ceramic Nanolaminate Coatings**, ***A.R. Waite*** *(adam.waite@wpafb.af.mil),* Air Force Research Labs/Universal Technology Corp., *J. Gengler,* Spectral Energies, LLC, *J. Jones,* Air Force Research Labs, *C. Muratore, A.A. Voevodin*, Air Force Research Laboratory

Multilayered polymer-metal-ceramic nanolaminate coatings were grown by room temperature plasma enhanced chemical vapor deposition (PECVD) and magnetron sputtering processes in a dual chamber PVD-CVD system to examine optical coatings with tailored, through-thickness thermal conductivity. Highly cross-linked fluoropolymer films were grown by PECVD from an octafluorocyclobutane gas precursor. High refractive index ceramic layers were deposited by pulsed DC magnetron sputtering of a TiO_2 target. Thin (5-50 nm) silver interlayers with thicknesses on the order of phonon mean free paths were also integrated into the nanolaminate stack. The thickness and position of the layers with high and low refractive index layers could by adjusted to develop optical coatings with desired functionality for different wavelengths of incident light, while metal layers were integrated to distribute heat and eliminate decomposition of the polymer films during heating by incident light. The through-thickness thermal conductivity of the films with and without the integrated silver layers was compared by time domain thermoreflectance (TDTR) and 3-Omega techniques. The 3-Omega analysis provided the bulk thermal conductivity of the nanolaminate stack which was compared to the constructed thermal transport model from the TDTR analysis of each film material and their respective interfaces.

2:50pm **TS4-5 Effects of Combined Macro- and Nano-Scale Surface Structuring on Pool Boiling**, ***C.N. Hunter*** *(chad.hunter@wpafb.af.mil),* Air Force Research Laboratory, *S.A. Putnam, A.R. Waite,* Air Force Research Labs/Universal Technology Corp., *C. Muratore, J. Jones, L.J. Gschwender*, Air Force Research Laboratory

In cooling technologies that utilize the latent heat of vaporization (e.g. pool boiling, heat pipes, spray cooling, etc.), knowledge of the critical heat flux (CHF) is "critical", as it dictates the maximum safe operating temperature for the actively cooled system. Interactions between the liquid coolant and the heated surface largely dictate the magnitude of the CHF, however a combination of macro- and nano-scale surface engineering has only recently been applied to control boiling phenomena. For example, at superheats beyond the critical heat flux, a continuous vapor layer forms between the liquid coolant and the solid heater substrate that impedes heat transfer. The existence of this thermally-resistive vapor layer is well known and engineering systems are designed to operate below this CHF threshold, however a clear understanding of how multi-scale manipulation of surfaces can increase the CHF is only beginning to emerge. In this work we present results on how combined macro- and nano-scale surface structuring influences the onset of the Leidenfrost point and the magnitude of the CHF. The basic mechanisms controlling formation of the resistive vapor layer are linked to surface wetting by the liquid coolant, solid-liquid contact area, spacing between features and other physical characteristics of the surface. Examples demonstrating this effect include superheats (ΔT) greater than 100°C for unstable film boiling of water on macro-scale patterned MoS_2-Si thin films and macro-scale patterned PTFE on Cu and Si thin-film substrates of different surface energies and surface roughness. We also present CHF data for patterned Cu and Si nanowhisker substrates of different aspect ratios and packing densities

3:10pm **TS4-6 Chromium-Containing Amorphous Hydrogenated Carbon Thin Films as Solar Selective Absorber Coatings: Effects of Hydrogen Content and Metal-Concentration**, ***H.-H. Cheng***, *J.-M. Ting (jting@mail.ncku.edu.tw)*, National Cheng Kung University, Taiwan

Various chromium-containing amorphous hydrogenated carbon (a-C:H/Cr) thin films were prepared and investigated for use as solar absorber coatings. The films were deposited on oxygen-free copper substrates using a reactive co-sputter deposition technique. The obtained films were characterized using scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HR-TEM), secondary ion mass spectrometer (SIMS), X-ray absorption near edge spectroscopy (XANES), and valence-band photoemission spectroscopy (PES). The hydrogen content was measured by elastic recoil detection (ERD). The optical performance was examined using UV-Vis-NIR spectrophotometry and Fourier transform infrared spectrometry. Effects of hydrogen content and metal-concentration on the optical properties were studied. We show that a-C:H/Cr films having appropriate hydrogen contents and metal-concentrations exhibit high absorption greater than 96 % from 0.3 to 2.5 μm at room temperature and low emittance less than 1 % from 2.5 to 10 μm at 100℃.

Characterization: Linking Synthesis Properties and Microstructure
Room: Royal Palm 1-3 - Session F3

Application of Ion and Electron Microscopy
Moderator: M. Watanabe, Lehigh University

1:30pm **F3-1 Nano-Scale Characterization of Interfaces by Scanning Transmission Electron Microscopy**, ***V. Srot*** *(srot@mf.mpg.de),* Max Planck Institute for Metals Research, Germany, *C.. Scheu,* Ludwig-Maximilians-University of Munich, Germany, *M. Watanabe,* Lehigh University, *U. Wegst,* Drexel University, *M. Rühle, P.A. van Aken*, Max Planck Institute for Metals Research, Germany **INVITED**

There is a wide range of technologically advanced applications, where different material classes such as metals and oxides are combined. The properties of such systems can be strongly affected or even controlled by the occurring interfaces and may not be the same as the properties of their constituent compounds [1,2]. Therefore, interfaces can play a notable role and thus a basic understanding of their microstructure is required to improve the functionality of materials. Since interface phenomena (e.g., segregation, diffusion, formation of interphases) occur in a very narrow area [2], characterization methods with high spatial resolution are essential. Modern transmission electron microscopy (TEM) with a variety of imaging and analytical techniques represents a valuable experimental tool and can be used to study the atomic structure, chemical composition and bonding across interfaces [3]. Such information can be obtained in combination of high-angle annular dark field imaging with X-ray energy dispersive spectroscopy (XEDS) and electron energy-loss spectroscopy (EELS) in scanning TEM (STEM) and this will be demonstrated and discussed for interface studies of various materials systems (e.g., metal – ceramic interfaces, interfaces in biological systems). In particular results obtained on platinum (Pt) films deposited on yttria stabilized zirconia (YSZ) will be shown where the quantitative analysis of XEDS results was performed using the recently developed ζ-factor method [4] in order to detect any irregularities across the interfaces. The local electronic structure and different polymorphic modifications were analyzed by electron energy-loss near edge structures (ELNES) investigations. The measured O-K ELNES at the Pt/YSZ interface were studied in details and compared with the results of ab initio full multiple scattering FEFF [5] modeling. The effects of the TEM specimen preparation can be a limiting factor for the investigations of materials, especially when different materials co-exist or in the case of highly sensitive specimens (e.g., biological specimens). Therefore, several different preparation methods were applied in order to get quality specimens with reduced artifacts.

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2:10pm **F3-3 Application of Electron Microscopy and Spectroscopy Techniques to the Characterization of Nanostructured TiAlSiN Coatings**, *V. Godinho (godinho@icmse.csic.es), D. Philippon, T.C. Rojas,* Instituto de Ciencia de Materiales de Sevilla, Spain, *M.-P. Delplancke-Ogletree,* Université Libre de Bruxelles, Belgium, ***A. Fernandez***, Instituto de Ciencia de Materiales de Sevilla, Spain

In the last decades ternary and quaternary systems of metal-nitrides for hard coatings have been widely explored. The development of TiAlN coatings as an alternative to the traditional TiN thin films was presented as a solution with better cutting behaviour and resistance to oxidation at high temperatures. The introduction of silicon in this kind of coatings promoting the formation of the nanocomposite nc-TiAlN/a-Si3N4 allowed to increase the hardness to values ≥ 50GPa [1] .Much discussion is going on about the reproducibility of these results, the validation of the mechanical properties of superhard coatings and the influence of impurities and microstructure are important issues [2-4] .

Oxygen has been reported as an impurity playing an important role on the mechanical properties of superhard coatings [4] . Many authors have described the incorporation of contamination oxygen in their films [5-7] . The working pressure and substrate temperature during deposition seems to play an important role on controlling the introduction of oxygen [8,4] and also the microstructure of the films. The aim of this work is to localize oxygen (if it is in bulk or superficial layers) and to carry an exhaustive microstructural characterization in TiAlN and TiAlSiN thin films deposited by magnetron sputtering, using electron microscopy and spectroscopy techniques. Samples with different deposition conditions were investigated. The combination of different characterization techniques such as Scanning Electron Microscopy (SEM-FEG), Transmission Electron Microscopy (TEM), Selected Area electron diffraction (SAED), Electron Energy Loss Spectroscopy (EELS), energy filtered TEM images and X-Ray Photoelectron Spectroscopy are presented as a suitable methodology to characterize the microstructure and chemical composition in nanostrutured coatings.

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2:30pm **F3-4 A TEM Study on the Thermal Stability of Sputtered Al_2O_3 Coatings**, ***V. Edlmayr*** *(viktoria.edlmayr@unileoben.ac.at),* Montanuniversität Leoben, Austria, *D. Kiener, C.. Scheu,* Ludwig-Maximilians-University of Munich, Germany, *C. Mitterer*, Montanuniversität Leoben, Austria

Al_2O_3 as deposited by high-temperature chemical vapor deposition is widely used for wear and corrosion protection of cemented carbide cutting tools because of its chemical inertness, corrosion resistance and high hardness. Low-temperature deposition by physical vapor deposition usually results in formation of amorphous or metastable Al_2O_3 phases, where only limited information about their thermal stability is available. The aim of this work is to examine the microstructural changes of metastable Al_2O_3 phases formed in sputtered films during annealing.

Al_2O_3 thin films were deposited by a production-scale pulsed direct current magnetron sputtering system. The thermal stability was investigated during vacuum annealing at different temperatures up to 1000°C for 3h and 12h. The morphology of fracture cross-sections was investigated by scanning electron microscopy. Additionally, the microstructure was studied by transmission electron microscopy (TEM) using several techniques such as bright field imaging, selected area diffraction, high-angle annular dark field imaging, high-resolution TEM, and electron energy-loss spectroscopy (EELS). The EELS measurements were performed at an acceleration voltage of 80keV and were used to examine the distribution of alumina polymorphs via detailed analysis of the energy-loss near-edge structure (ELNES) of the Al-$L_{2/3}$ and O-K edge. ELNES clearly facilitates the differentiation between different alumina phases due to changes in peak positions and the overall shape.

For the coating deposited under low ion bombardment conditions, diffuse illumination in the central region of the SAD pattern implies the presence of amorphous material, while the diffraction spots on the concentric rings correspond to γ- and/or δ-Al_2O_3 grains. This indicates the co-existence of amorphous and crystalline phases. In contrast, for high-energetic growth conditions clear evidence for γ-Al_2O_3 formation was found. Annealing of the γ-Al_2O_3 structured film at 800°C for 3h results in the irreversible formation of α-Al_2O_3. For the predominantly amorphous film, growth of the γ-Al_2O_3 phase is promoted but no transformation to α-Al_2O_3 was detected, even during annealing at 1000°C for 12h. The obtained results contribute to the understanding of phase-transformations in metastable Al_2O_3 coatings at temperatures typical for cutting processes.

2:50pm **F3-5 Atomic Structure Characterization of Cu/MgO(001) Interfaces by C_S-Corrected HRTEM**, ***S. Cazottes*** *(sophie.cazottes@insa-lyon.fr), Z.L. Zhang,* Erich Schmid Institute of Material Science, Austria, *R. Daniel,* Montanuniversität Leoben, Austria, *D.G. Gall,* Rensselaer Polytechnic Institute, *G. Dehm*, Montanuniversität Leoben, Austria

The Cu/MgO interface is a model system for the study of metal ceramic systems used e.g. in microelectronic devices. Due to the difference in lattice parameter of those two *fcc* crystals with values of a=0.360 nm for Cu and a=0.4212 nm for MgO, there is a large mismatch of ~15% between the two crystals. This mismatch induces the presence of misfit dislocations at the interface in order to accommodate the mismatch strain. Two kinds of dislocation network are usually proposed for this type of interface, a dislocation network consisting of edge dislocation with 1/2 <110> Burgers vector and dislocation line direction along <110> Cu or another one with ½ < 100> Burgers vector and <010> line direction. Depending on the dislocation network present, the bonding of Cu on MgO at the interface will be different.The aim of the present study is to characterize the atomic structure of the interface, and particularly the dislocation network and the chemical bonding between the two crystals. The samples were prepared by magnetron sputtering. Cu exhibits a cube on cube orientation relationship with the MgO substrate, i.e. $(001)_{Cu}//(001)_{MgO}$ and $[001]_{Cu}//[001]_{MgO.}$ TEM samples were prepared using the Tripod polishing technique and finally Ar^+ ion milled using a Baltec RES 101 ion milling device. HRTEM was performed with an image-side C_s corrected Jeol 2100F operated at 200kV. In order to reveal the dislocation network, the interfaces were observed along <100> and <110> directions. Along the <100> orientation, some edge dislocations are visible on the Cu side, with a Burgers vector of ½ <100>. Along the <110> orientation, no edge dislocations were observed, but some dislocations are present in the Cu side, with a projected Burgers vector of ½ <110>. This information indicates that the dislocation network consists of edge dislocations with Burgers vector of ½ <100> with a <010> line direction. For this dislocation network it is expected by geometrical considerations that the atomic structure at the interface between Cu and MgO should alternate from Cu on top of Mg to Cu on top of O between the misfit dislocations. On the <110> micrographs, the C_s corrected HRTEM image recorded under a negative C_S value allows to directly discriminate between Mg and O atom columns, which gives information on the atomic structure and thus about the bonding at the interface. The mismatch between the two crystals also induces the presence of uncompensated strain in the Cu side, which was characterized using a Geometrical Phase Analysis of the HRTEM micrographs. This remaining strain creates some distortion of several Cu atomic planes close to the interface.

3:10pm **F3-6 On Overview of the TEAM Microscope and its Applications to Interface Problems**, ***U. Dahmen*** *(UDahmen@LBL.gov)*, National Center for Electron Microscopy, LBNL **INVITED**

The TEAM (Transmission Electron Aberration-corrected Microscope) project was driven by the need for improved resolution, sensitivity and precision in the analysis of atomic structure on the nanoscale. After five years of development and construction, the project came to a successful conclusion in the fall of 2009. The TEAM instrument offers half-Angstrom resolution in both scanning probe and broad beam modes of operation and is now available as a user facility at the National Center for Electron Microscopy.

Following an overview of the TEAM project, this talk will describe the instrument's performance and its initial applications with particular emphasis on atomic-scale analysis of interfaces in materials. The unique technical features of the instrument include a new piezoceramic stage based on AFM technology, a novel high-brightness electron gun, an electron optical corrector for spherical as well as chromatic aberrations and an active pixel sensor for direct electron detection. These new technologies will be explained briefly, and specific examples will be presented to highlight the microscope's unique capabilities and its capacity to adapt the electron optical environment to the experiment to the problem at hand. By operating between 80 and 300kV, the instrument can be tuned to maximize the experimental signal and minimize the beam damage to the sample. This will be illustrated with observations on Al-Li alloys, Au bicrystals, and atomic layer sheets of graphene and BN.

This presentation will give instances of recent work with the TEAM microscope, ranging from interfaces in metals and alloys to defect structures in metals, oxides and semiconductors. A particular focus will be the atomic structure and properties of an incommensurate grain boundary in gold. We have found that local relaxation of the boundary near the surface leads to a chevron-like defect of whose size and stability is related to the stacking fault energy. By compressing bicrystalline nanopillars of gold in-situ, it was possible to make a direct correlation between atomic interface structure and mechanical properties, providing insights into the effect of defects and surfaces during deformation.

Finally, based on the capabilities of the instrument, some opportunities for its future application in research on interfaces and coatings will be outlined. The National Center for Electron Microscopy is supported by the Director, Office of Science, Office of Basic Energy Sciences, Materials Sciences and Engineering Division of the U.S. Department of Energy under Contract No. DE-ACO3-76SFOOO98.

Applications, Manufacturing, and Equipment
Room: Sunset - Session G1-2

Innovations in Surface Coatings and Treatments
Moderator: M. Rodmar, Sandvik Tooling, A. Leyland, University of Sheffield

1:30pm **G1-2-1 Nano-Structured Multi-Functional Composite Coatings and their Applications**, ***X.T. Zeng*** *(xzeng@simtech.a-star.edu.sg)*, Singapore Institute of Manufacturing Technology, Singapore **INVITED**

Surface engineering for nanocomposite coatings is offering a significant impact on product performance and quality because of their unique material properties and integrated multiple functionalities through nano-structuring and engineering. Such coatings containing nano-sized multi-phases in composition and multi- or nano-layers in structure render substantially improved mechanical, chemical and tribological properties as well as additional functions such as anti-sticking, self-lubricating, easy-to-clean or self-cleaning, corrosion and oxidation resistance, and environment- and bio-compatibility.

In this paper, nano-phased hybrid multi-functional coating materials and deposition processes will be reviewed based on our research work in surface engineering using unbalanced magnetron sputtering and cathode arc, sol-gel and electro-chemical process technologies. Case studies in coating design, material selection and deposition processes will be shared and discussed for applications in precision engineering, aerospace and automotive as well as construction industries, with emphasis on PVD composite coatings for high temperature wear and oxidation protection and sol gel based composite coatings for corrosion protection and surface cleaning and maintenance.

2:10pm **G1-2-3 Influence of Interface and Multi Layer Structure on Corrosion and Erosion Resistance of Thin Films (PVD)**, ***J. Ellermeier*** *(ellermeier@mpa-ifw.tu-darmstadt.de), O. Durst, U. Depner, T. Trossmann, H. Scheerer, C. Berger*, TU Darmstadt, Zentrum für Konstruktionswerkstoffe, Germany

The research activities in the field of thin film PVD or CVD coatings are mainly focused on wear protection of tools or other machine parts. But these thin coatings are also relevant for applications where corrosion and erosion are present as single loading or as a superimposed loading. The main objective is to replace high alloyed and therefore expensive bulk materials with high corrosion resistance through low alloy steels thin film coated. That is the reason to investigate modern PVD multilayer structures with respect to the possibilities to protect against corrosion and erosion.

The focus of this research project was to develop multi layer coatings which exhibit as few as possible defects. So to be done with the PVD HPPMS process (CrN/a-C). It was necessary to investigate the influence of alternating hardness and the plasma-nitriding of the substrate material (42CrMo4) to the interface bonding. Also the influence of the coating parameters (e.g. bias voltage, gas flow, target power, HPPMS parameters) to the bonding of the layers was determined. An alternating layer structure of the multi layer coating should avoid the growing of defects to obtain a dense coating with high corrosion resistance. The top layer must have a high hardness and adequate toughness to realize a sufficient resistance against erosion. Depending on the particle flow (perpendicular or parallel to the surface) therefore the erosion loading changes and different properties of the thin film are essential. The bonding between the layers is of prominent importance for the perpendicular flow of the erosion particles. For the parallel flow the hardness of the top layer is a significant factor.

Besides the usual investigations like scratch test, Rockwell test, metallographic and SEM investigations for the characterization of the coatings, application orientated corrosion and erosion tests were carried out. With polarization curves of coated samples in artificial seawater the defects of the thin films can be detected. It was possible to produce thin films in multi layer structure which show a very low defect rate during the polarization test. For erosion-corrosion tests artificial seawater and demineralized water with additions of Al_2O_3 particles were used. The load of the thin films is quite higher with the superposition of corrosion and erosion than with erosion as dominant load. The resistance against erosion depends on the amount of defects in the thin films when the particle flow is nearly perpendicular to the surface.

2:30pm **G1-2-4 Novel Materials for Thermal Compensated Strain Gauges**, ***R. Bandorf*** *(ralf.bandorf@ist.fraunhofer.de), U. Heckmann, M. Luebke, M. Peters, G. Braeuer*, Fraunhofer IST, Germany

For the measurement of stress and strain e.g. used for detecting loads or applied forces strain gauges are commonly used. While conventional polymer based strain gauges glued to the substrate show swelling and creep due to temperature and humidity thin film strain gauges avoid this problems. For improvement of the sensing properties of the material an increase in the gauge factor is required. For reliable measurement also a compensated temperature coefficient of resistivity TCR is beneficial.

Investigations on the synthesis of new materials with compensated TCR, i.e. a TCR lower than 200 ppm/K were carried out on different material systems. It turned out that DLC based coatings using Ni as dopand are well suited to tailor the TCR and increase the gauge factor. A gauge factor exceeding 10 with a TCR close to zero was realised for films containing approximately 55 at% Ni. Another material class with high potential for high temperature use are the M-A-X coatings. For Ti-Si-C films sputtered from a stoichiometric Ti_3SiC_2 target also a TCR close to zero was found. The gauge factor of approximately 2.5 was close to conventional NiCr. In contrast to NiCr the Ti-Si-C films showed no modification of the properties with annealing up to 600°C.

2:50pm **G1-2-5 SiBNCO PVD Coatings for High Performance Applications**, *J. Vetter (joerg.vetter@sulzer.com),* Sulzer Metaplas GmbH, Germany, ***M. Isaka**, T. Ishikawa, K. Kubota,* Hitachi Tool Engineering, Japan, *G. Erkens, J. Mueller, J. Alami*, Sulzer Metaplas GmbH, Germany

PVD coatings for high performance applications require at least one selected outstanding property like low friction, high hardness, high temperature stability or high oxidation stability. In the last decade a lot of high impact coatings were new developed and successfully introduced in industrial production of tools and components. Such coatings comprise TiSi-based and AlCr- based types (TiSiN, AlCrSiN). These coatings are belonging to the group of crystalline coatings and show a limit in the oxidation temperature of about 1000°C. The SiBNC0 coatings deposited by magnetron sputtering are able to withstand higher temperatures without a significant oxidation rate. The paper describes coating properties in dependence from the used reactive gases nitrogen, oxygen and carbon. Coating properties are high lightened by SEM, hardness measurement, EDX, X-ray diffraction and XPS. Tribological properties were investigated by Pin-On-Disc. Oxidation experiments were carried out up to 1000°C.

3:10pm **G1-2-6 Ultra-Fast and Thick Boriding as a Novel Surface Treatment for Demanding Tribological Applications**, ***A. Erdemir** (erdemir@anl.gov),* Argonne National Laboratory, *G. Kartal,* Istanbul Technical University, Turkey, *O.L. Eryilmaz, V. Sista, G. Krumdick,* Argonne National Laboratory, *S. Timur*, Istanbul Technical University, Turkey

Increasingly more demanding and very stringent operating conditions of next-generation tribological systems will require much stronger and harder materials that can last for the duration of intended applications. Accordingly, there is an urgent need for the development of more robust surface engineering technologies that can meet such requirements for future tribological systems. In this study, we report an ultra-fast boriding technique that can results in very hard and thick boride layers in minutes. Specifically, the new technique produces 80-100 µm-thick boride layers on steel substrates in about 30 min., depending on the type of steel. Compared to conventional surface treatment methods (e.g., nitriding, carburizing, and pack-boriding which are used extensively by industry to achieve superior hardness and tribological properties in all types of steel components), novel ultra-fast boriding provides great advantages in terms of productivity, versatility, and environmental cleanliness. It is done in a molten salt electrolyte consisting of a mixture of natural borax and sodium carbonate at elevated temperatures. Work pieces to be borided are attached to a cathode, while the crucible that holds the electrolyte acts as an anode. The hardness of borided steel surfaces may range from 17 GPa to more than 20 GPa (depending on the steel type). The very thick boride layers produced on the surface has excellent resistance to wear, erosion, and corrosion. Under boundary lubricated sliding conditions, the boride layers provide low friction and extreme resistance to wear and scuffing. In addition to being ultra-fast, the new boriding technique is very cheap and produces no gaseous emissions and solid wastes. Overall, it may have significant positive impact on the heat treating and surface treatment fields.

3:30pm **G1-2-7 Using Electroless Plating Cu Technology for TFT-LCD Application**, ***Y.-T. Chou**, P.-T. Liu (ptliu@mail.nctu.edu.tw), C.-Y. Su,* National Chiao Tung University, Taiwan, *H.-M. Chen*, Liquide Laboratories, Japan

With the trend of increasing size for active matrix liquid crystal display (AMLCD) development, the requirement of low-resistivity metallization to release resistivity-capacity delay (RC delay) problems becomes more and more critical. Copper (Cu) interconnection architecture, for this reason, attracts lots of attention for its low resistivity below 3µΩ-cm. However the conventional copper deposition technology, such as sputtering, almost needs vacuum systems which need high maintaining and process cost. Other methods like electroplating methods still face poor uniformity issues, limiting its application in AMLCD. In this study, we applied a novel electro-less plating (ELP) method to form Cu film no need of any vacuum system. With the control of process temperatures, the highly uniform copper film on glass substrate can be easily achieved. Successful fabrication of amorphous silicon thin film transistors (a-TFTs) with ELP Cu electrodes also indicates the capacity of this proposed technology for AMLCD applications.

In this study, a layer of NiP film was first formed by ELP method to serve as a great adhesion layer between the subsequent copper film and glass substrate as well as to prevent copper diffusion. The chemical solution mixed with $NiSO_4$ and NaH_2PO_2 were served as precursors of Ni and P for the NiP film deposition. Also, the chemical $SnCl_2$, $PdCl_2$ and NaH_2PO_2 were used to catalyze and condition the base surface after pre-cleaning and macro-etching the glass substrate. After catalyzing the seed layer of NiP film, the copper film was deposited with self-alignment on the NiP surface by immersing the samples in $CuSO_4$ solution. All ELP processes were done in the ambient free of any vacuum system. The resistivity of ELP as-deposited Cu film is about 2.6µΩ-cm. XRD results indicated the ELP Cu film is of polycrystalline structure. The surface morphology was analyzed in this work as well. Following the conventional a-TFT manufacturing process with ELP Cu as gate electrode, the electrical characteristics were measured by Keithley 4200 semiconductor analyzer comprehensively. The threshold voltage (V_{th}) and mobility (µ) were extracted about 3.55V and 0.56, respectively, at V_D=7.67V. Besides, the electrical stability of the a-TFT with ELP Cu gate electrodes also was discussed by DC and AC bias stress under a variety of measurement temperatures for 10^4 sec. Compared to the typical a- TFT with MoW gate electrode, experimental results have shown the proposed ELP Cu-gate a-TFT possesses superior electrical performance and good stability for realistic AMLCD applications.

3:50pm **G1-2-8 Etching Properties of Si and HfO_2 in an Inductively Coupled Plasma Etcher**, ***S.H. Lee** (shlee@utdallas.edu), B. O'Shaughnessy,* University of Texas at Dallas, *K.J. Park, Y.H. Joh,* DMS, Korea, *K.J. Chung,* Hanyang University, Korea, *G.S. Lee, J.Y. Kim, M.J. Kim*, University of Texas at Dallas

The etch rate behaviors of Si and HfO_2 in an inductively coupled plasma etcher are studied. CHF_3(40 sccm)/Ar(10 sccm) gases are used at 10 mTorr chamber pressure. Ion flux and bombarding energy, which are two key factors of adjusting plasma-surface interactions and etch properties, are controlled by source power and bias power respectively. Source power and bias power are varied over a wide range (200 W ~ 900 W for source power and 10 W ~ 100 W for bias power) to investigate dry etching characteristics. Boron doped p-type (100) Si wafers and HfO_2 films deposited on the Si wafers using an atomic layer deposition system are utilized to investigate etching properties. While the attempt of etching for Si and HfO_2 resulted in the polymer deposition at low bias power, both materials are etched at higher bias power. While both source power and bias power affect etch rate of Si, the etch rate of HfO_2 mainly depends on bias power for all etch conditions in this study. Different behaviors of HfO_2 films are attributed to higher bombarding energy required to trigger the etching process, which is consistent with the slow etch rate. In the case of Si etching, the amount of polymer deposition decreases and etch rate continuously increases with bias power. Nonetheless, HfO_2 shows step-like etch rates as bias power increases: first the amount of polymer deposition on the HfO2 surface decreases, then its etch rate is kept nearly constant, until the bias power reaches 50W where the etch rate starts increasing. The step-like behavior is a result of the competition between polymer deposition and etching. The effect of the distance of the sample from the plasma source is also investigated. As the distance increases from 4 mm to 14 mm, ions experience more collisions which results in lower ion flux near the sample surface. The ion flux decreases to 15~28% at longer distance (14 mm) from that at a shorter distance (4 mm) which is measured with an in-situ measurement. The etch rate is expected to be lower at the same source power and bias power with a longer distance from plasma source due to the smaller ion flux. In case of Si, the etch rate decreases to ~16 % at longer distance compared to shorter distance at lower source power (where the source power dominantly affects the etch rate) while little change is observed at high source power (where bombarding energy dominates etch rate). However, the etch rate of HfO_2 does not change much at longer distance because that of HfO_2 is mainly affected by bombarding energy, which is controlled by bias power, rather than ion flux controlled by source power.

Coatings for Fuel Cells and Batteries
Room: Royal Palm 4-6 - Session TS2

Moderator: E. Yu, Newcastle University, Adrian Bude, Mercedes Benz Research and Development North America

1:30pm **TS2-3 Recent Progress in Development of Protective Coatings for SOFC Interconnect at PNNL**, *G.X. Xia (guan-guang.xia@pnl.gov), J.D. Templeton, Z.M. Nie, Z.G. Yang, J.W. Stevenson,* ***Li***, Pacific Northwest National Laboratory

Due to their good oxidation resistance and excellent thermal expansion match to the other stack components, ferritic stainless steels are among the most promising candidate materials for interconnect applications in intermediate-temperature planar SOFC stacks. In particular, newly developed compositions demonstrate improved properties relevant to the interconnect applications over traditional ones. However, to help accelerate commercialization of SOFC technology, it is desirable to find more cost-effective alternatives for the applications. Thus, efforts have been initiated to identify and develop ferritic stainless steels that demonstrate comparable performance to the newly developed alloys, but are more cost-effective. This paper will present details of recent progress on this work, including evaluation of the effectiveness of protective coatings on the inexpensive candidate steels.

1:50pm **TS2-4 Effect of Substrate Alloy Composition on Oxidation and Electrical Conductivity Behavior of Co-plated Interconnect Steels**, ***J.H. Zhu*** *(jzhu@tntech.edu), Z.H. Bi*, Tennessee Technological University

In the planar design of a solid oxide fuel cell (SOFC) stack, the interconnect acts not only as electrical connection between the various cells but also as the mechanical support for the thin electroactive ceramic parts and as gas-proof separation of air and fuel gas. With the reduction of the SOFC operating temperatures to 600-800°C, chromia-forming ferritic steels are widely used as interconnect materials in the planar-type SOFC stacks currently under development. One of the most serious problems for these ferritic steels such as Crofer 22 APU is the Cr volatility and associated “poisoning” of the cathode under the operating environments of SOFC. Co plating is widely used for protecting these interconnect alloys, with the Co layer subsequently thermally converted into a Co-containing spinel coating at the SOFC operating temperatures; however, the effect of the substrate alloy composition on the microstructure, composition and the electrical conductivity of the converted spinel coating has not been systematically evaluated. In this presentation, six Fe-Cr alloy substrates with different compositions including three relatively simple model alloys and three commercial alloys were electrodeposited with a 5-mm Co layer, followed by thermal oxidization at 800°C in air for 100 h. The surface morphology and scale microstructure of the oxide layer formed on different substrates were studied with X-ray diffraction, scanning electron microscopy and energy dispersive spectroscopy. It was demonstrated that the addition of La and Mn into the alloys appeared to alter scale growth behavior of the plated Co layer, with La leading to a more adherent scale/metal interface and Mn leading to a thinner Cr_2O_3 layer. In addition, diffusion of Co into the substrates was observed except for the SS430 substrate. Outward diffusion of Mn was restricted to the Cr-rich scale layer, leading to formation of a Co_3O_4 spinel outer layer essentially free of Mn. For the three commercial alloy substrates (Crofer 22 APU, SS430, and ZMG 232), the thickness of the Cr-rich oxide scale was much thinner and their area-specific resistance (ASR) was lower than that of three home-made alloys. The scale ASR of the different alloys could be correlated with the thickness of the Cr-rich oxide scale formed on them.

2:10pm **TS2-6 Constitution, Microstructure, and Battery Performance of Magnetron Sputtered Li-Co-O Thin Film Cathodes for Lithium-Ion Batteries as a Function of the Working Gas Pressure**, ***C. Ziebert*** *(Carlos.Ziebert@imf.fzk.de), B. Ketterer, M. Rinke, C. Adelhelm, S. Ulrich, K.-H. Zum Gahr, S. Indris, Th. Schimmel*, Karlsruhe Institute of Technology, Germany

Despite of their widely use in mobile communication and portable electronic equipment there is a strong need for further development and optimization of the components for lithium-ion batteries, especially for the positive electrode (cathode). Nanocrystalline thin film cathode materials are of increasing interest due to their potential to provide both high power and high energy density.

Li-Co-O thin film cathodes have been deposited onto Si and stainless steel substrates by RF magnetron sputtering from a ceramic $LiCoO_2$ target at various working gas pressures ranging from 0.15 to 25 Pa. The composition, crystal structure and thin film morphology were examined using inductive coupled plasma optical emission spectroscopy (ICP-OES), carrier gas hot extraction (CGHE), X-ray diffraction (XRD), Raman spectroscopy (RS), atomic force microscopy (AFM) and scanning electron microscopy (SEM). Thin film properties such as intrinsic stress, conductivity and film density were determined. As deposited films at 0.15 Pa as well as in the range between 5 Pa and 10 Pa working gas pressure showed a nanocrystalline metastable rocksalt structure with an unordered cation arrangement and were nearly stoichiometric.

With increasing annealing temperature a cation ordering process was observed by XRD. Heat treatment of the films deposited at 10 Pa Argon gas pressure at 600 °C leads to the formation of the hexagonal high temperature phase HT-$LiCoO_2$ with a layered structure. The Raman spectrum of the films deposited at 0.15 Pa and annealed at 400°C indicates the formation of the low temperature phase LT-$LiCoO_2$ with a cubic spinel-related structure, which is assumed to be stabilized due to high compressive stress in the film.

The battery performance of the as grown and the annealed thin film cathodes was studied and it was revealed that the discharge capacity strongly depends on the crystal structure of the films. Thin Li-Co-O films with a perfect layered HT-$LiCoO_2$ structure showed the highest discharge capacities.

2:30pm **TS2-7 Anode Coatings for a Direct Glucose Fuel Cell Application**, ***T. Vidakovic*** *(vidakovi@mpi-magdeburg.mpg.de),* Otto-von-Guericke-Unversity, Germany, *I. Ivanov,* Max-Planck-Insittue, Germany, *K. Sundmacher*, Otto-von-Guericke-Unversity & Max-Planck-Institute, Germany **INVITED**

In this presentation some of our efforts to date on different anode coatings for application in a direct glucose fuel cell will be reviewed. Our initial research in this area focused on gold and gold surfaces coated by self-assembled monolayer (SAM) [1]. We have shown that the activity of gold for glucose oxidation is strongly influenced by temperature and an applied potential window. The rough gold undergoes structural changes at elevated temperature, which leads to loss of activity for glucose oxidation and lower affinity for the self-assembly. The transformation of "active" into "inactive" surface can be prevented by SAM formation. The SAM modified gold exhibits high activity for glucose oxidation.

The SAM modified gold surface was further used for enzyme (glucose-oxidase (GOx)) immobilization. For this purpose the pyrroloquinoline quinine (PQQ) mediator was covalently attached, followed by an attachment of a modified enzyme cofactor flavin adenine dinucleotide (FAD) and a reconstitution of an apo-GOx. Our results showed that the activity for glucose oxidation decreases with an increase of number of layers and the activity of enzyme modified gold electrode can not be assigned to enzyme itself.

Our recent approach concentrates on use of conductive organic salts (charge transfer complexes (CTC)) as an active surface for enzyme immobilization [2]. This enzymatic electrode exhibits high stability and activity for glucose oxidation and significant oxygen tolerance. The influence of different parameters, including CTC loading and morphology, GOx loading, membrane thickness, etc. on the activity of the bioanode has been investigated.

[1] Ivanov, I.; Vidaković, T.; Sundmacher, K. The influence of a self-assembled monolayer on the activity of rough gold for glucose oxidation, Electrochemistry Communications 2008, 10, 1307

[2] Ivanov, I.; Vidaković, T.; Sundmacher, K. Glucose Electrooxidation for Biofuel Cell Applications. Chemical and Biochemical Engineering Quarterly 2009, 23, 77.

3:10pm **TS2-9 Pseudocapacitive Performance of Hybrid Manganese Oxide Films with Multiwalled-CNTs Additions**, ***C.-K. Lin*** *(cklin@fcu.edu.tw), C.-Y. Tsay, C.-H. Wu, C.-Y. Chen,* Feng Chia University, Taiwan, *S.-C. Wang*, Southern Taiwan University, Taiwan

In the present study, hybrid manganese oxide films with additions of multiwalled carbon nanotubes (MWCNTs) were prepared by sol-gel process. Manganese acetate was used as the precursors and MWCNTs were added during the process. The effects of MWCNTs addition and post heat treatment on the material characteristics and pseudocapacitive performance of the hybrid MWCNTs/MnOx films were investigated. These films were characterized by X-ray diffraction and scanning electron microscopy. Pseudocapacitive performance of the films was evaluated by cyclic voltammetry (CV). In addition, synchrotron X-ray absorption spectroscopy was used to reveal the difference before and after CV test. Experimental results showed that manganese oxide composed of Mn_3O_4 and Mn_2O_3 phase. MWCNTs served as the template for the growth of manganese oxide films. With the addition of MWCNTs, not only the specific capacitance increased but also the reliability improved. Among the hybrid films prepared in the present study, manganese oxide films with 0.05 wt.% MWCNTs addition heat treated at 350 ^{o}C exhibited the best electrochemical performance.

3:30pm **TS2-10 Conductive Coatings for Stainless Steel Bipolar Plates for PEM Fuel Cells**, ***G.V. Dadheech*** *(gayatri.dadheech@gm.com), M. Abd Elhamid*, General Motors

Stainless steel is a candidate for use as a metallic bipolar plate material in proton exchange membrane fuel cells (PEMFCs). It offers many advantages over conventional graphite plates, yet stainless steel has a passive resistive oxide which reduces the overall power output of the PEMFC. It is therefore necessary to reduce the contact resistance across the interface between metallic bipolar plate and porous gas diffusion medium (GDM) to improve the fuel cell performance. An electrochemically stable and electrically conducting coating has been developed to reduce the interfacial contact resistance at the GDM and stainless steel bipolar plates for its use in PEM fuel cells. The approach relies on coating the bipolar plates with a nano-thin layer of gold using a physical vapor deposition technique or by other similar methods. The results show that the interfacial contact resistance is decreased by as much as a factor of four when these coatings are applied on stainless steel bipolar plates. Data from ex-situ and in-situ fuel cell testing demonstrate the impact on overall fuel cell performance of the nano-thin gold coatings.

3:50pm **TS2-12 Deposition of Hydrothermally Synthesized Pt on Carbon Nanofibers for Use as Direct Methanol Fuel Cell Electrodes**, ***C.Y. Huang****, C.M. Chung, J.-M. Ting (jting@mail.ncku.edu.tw)*, National Cheng Kung University, Taiwan

Deposition of Pt particles on carboneous materials using wet impregnation, physicalevaporation, electrodeposition, microwave-assisted polyol strategy, supercritical fluid method, and microemulsion have been reported. These methods, however, are often complex and not environmentally friendly, and often require expensive equipments. In this paper, we report the dposition of Pt particles on carbon nanofibers (CNFs) using a convenient hydrothermal method. The sizes and the distribution of the resulting Pt particles can be effectively controlled using this method. The obtained Pt modified CNFs were characterized using transmission electron microscopy, X-ray diffractometry, and X-ray photoelectron spectroscopy. Electrodes were also fabricated using selected Pt modified CNFs for using in direct methanol fuel cells. The electrodes were examined for the methanol electro-oxidation using cyclic voltammetry.

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

Coatings to Resist High Temperature Oxidation
Moderator: Y. Zhang, Tennessee Technological University, D. Naumenko, Forschungszentrum Jülich GmbH

8:00am **A1-1-1 Oxidation and Hot Corrosion of MCrAlY Alloys**, ***G.H. Meier*** *(ghmeier@pitt.edu)*, *F.S. Pettit*, University of Pittsburgh **INVITED**

The MCrAlY (M= Ni and/or Co) coatings have been used for many years to protect superalloys from oxidation and corrosion. Nevertheless, there is still considerable research activity relative to the oxidation and hot corrosion mechanisms of these coatings. This presentation will describe recent results from the authors and others regarding the effects of composition, microstructure and surface preparation on the oxidation and hot corrosion behavior of MCrAlY coatings and bulk alloys. Particular attention will be given to the concentration and distribution of Y in the alloys with regard to cyclic oxidation resistance. The effect of composition and heat treatment (and the resultant phase constitution) on Type I and Type II hot corrosion will be described. Finally, the effect of intermittent exposure to hot corrosion conditions on cyclic oxidation behavior will be discussed.

8:40am **A1-1-3 Characterization of the Alumina Scale Formed on a Commercial MCrAlY Coating**, ***K.A. Unocic*** *(unocicka@ornl.gov)*, *B.A. Pint*, Oak Ridge National Laboratory

A commercial MCrAlY (M = Ni,Co) coating deposited on a Ni-base superalloy 1484 substrate was characterized before and after high temperature oxidation. The coating contained small additions of Hf and Si that are reported to improve its high temperature oxidation performance. High resolution characterization techniques including scanning transmission electron microscopy will be used to study the segregation behavior of Y and Hf to the alumina grain boundaries after isothermal exposure at 1100°C. Comparisons will be made to prior observations of the alumina scale formed on model NiCrAl+(Y,Hf) alloys.

9:00am **A1-1-4 Thermodynamic Investigation into the Equilibrium Phase Fractions, Phase Compositions and Phase Transformation in the NiCoCrAl System at Elevated Temperatures**, ***K. Ma***, *J.M. Schoenung (jmschoenung@ucdavis.edu)*, University of California, Davis

NiCoCrAlY alloys have been widely applied as the bond coat layer in thermal barrier coatings. Extensive microstructural characterization has been carried out experimentally on NiCoCrAlY bond coat by various researchers. It is generally agreed that the major phases in the NiCoCrAlY are γ phase and β phase. Additionally, γ' precipitates, Cr- and Co-rich σ precipitates, and α-Cr precipitates have been reported to be present in the NiCoCrAlY bond coat. It must be noted, however, that the chemical compositions of the NiCoCrAlY alloys vary from one study to another. Thermodynamic calculations have demonstrated that even minor changes in composition and in temperature can lead to major changes in the resulting phases. The present work reviews the literature on the experimental descriptions of the phases present in NiCoCrAlY alloys and the corresponding phase transformations. To complement this literature review, the computational tool, Thermo-calc$^{®}$ is applied to investigate, as a function of temperature, the equilibrium phase fractions, phase compositions and phase transformations in the NiCoCrAl system, allowing for a wider and continuous variation in composition (Co, Cr or Al content). Comparisons between the experimental and computational findings are provided.

9:20am **A1-1-5 Modeling Aluminum Depletion Kinetics in MCrAlY Coatings**, ***M. Rudolphi*** *(rudolphi@dechema.de)*, *D. Renusch*, *M. Schütze*, Karl-Winnacker-Institut der DECHEMA e.V., Germany

MCrAlY coatings are widely used in high temperature applications due to their ability to form a dense protective alumina layer during high temperature exposure. By doing so, the underlying superalloy material is protected from corrosive attack and the component life-lime is extended. However, as a result of the alumina growth, aluminum is consumed from the coating reservoir and eventually the coating may become depleted from aluminum. This finally leads to a change in oxidation mechanisms and the growth of voluminous and non-protective spinels and consequently a breakdown of the protective behavior of the coating.

Life-time prediction is therefore of high interest to ensure safe service inspection intervals of component parts. This leads to the demand of a detailed understanding of the complex depletion kinetics in a coating/substrate system. In the course of this project, modeling equations have been developed to calculate the aluminum profile of a coating/substrate system as a function of exposure time and temperature. The equations take the most important aspects of Al depletion into account: (i) Al outward diffusion due to alumina scale growth and (ii) Al interdiffusion between the coating and the substrate material. The calculated aluminum profiles have been validated with experimental EPMA line scan data from several different systems with varying aluminum content. Finally, the developed equations have been built into a software tool to allow user friendly comparison of modeled and measured Al profiles. Furthermore, the software calculates the average Al concentration of the coating as a function of exposure time and temperature to provide information about coating lifetime.

9:40am **A1-1-6 Reactivity and Microstructure Evolution of SPS Prepared CoNiCrAlY/Talc Cermet**, *N. Ratel (nicolas.ratel@ensiacet.fr)*, *D. Monceau*, ***D. Oquab***, *C. Estournès*, CIRIMAT, France

A mixture of CoNiCrAlY and talc powders is considered as a new candidate composition for abradable seal coatings applications. Dense specimen having the composition of 1:20 weight ratio of talc with respect to CoNiCrAlY was prepared using the Spark Plasma Sintering (SPS) technique. The aim of the present investigation is the determination of the reactivity and microstructure evolution of the β/γ-CoNiCrAlY based cermet. The resulting microstructures were analysed and their compositions determined using standard analytical techniques such as SEM, TEM and X-Ray diffraction. After fabrication, the bulk of the material is shown to contain a continuous oxide layer of $MgAl_2O_4$ at the periphery of metallic particles, resulting from the reaction between aluminium, which has diffused from the bulk of CoNiCrAlY grains, with magnesium and oxygen delivered during the high temperature decomposition of the talc phase. Thermodynamic calculations were conducted to support the experimental observations.

10:00am **A1-1-8 The Effects of Chemical Composition on the Oxidation Behavior of Platinum-Modified Aluminide Coatings**, ***K. Tolpygo*** *(vladimir.tolpygo@honeywell.com)*, Honeywell Aerospace **INVITED**

The effects of chemical composition on the cyclic oxidation behavior of platinum-modified nickel-aluminide CVD coatings are described. While these coatings typically demonstrate excellent oxide adhesion, they are prone to plastic deformation during thermal cycling, also known as surface rumpling. Another form of microstructural degradation that occurs in the course of high temperature exposure is the development of pores or cavities within the coating. Both phenomena are shown to be influenced by chemical composition of the coating and superalloy substrate. This paper summarizes various observations and measurements of rumpling and pore formation and provides comparison of the extent of degradation between different coatings. The significance of bond coat rumpling in the thermal barrier coating systems is also discussed.

10:40am **A1-1-10 Early Stages of Oxidation of NiPtAl Coatings in Low and High pO_2 Gases**, ***P. Song***, *D. Naumenko (d.naumenko@fz-juelich.de)*, Forschungszentrum Jülich GmbH, Germany, *W. Braue*, German Aerospace Center (DLR), Germany, *L. Singheiser*, *W. Quadakkers*, Forschungszentrum Jülich GmbH, Germany

NiPtAl-coatings produced by low Al-activity pack cementation process on CMSX-4 were studied. Isothermal oxidation experiments were performed in Ar-20%O_2 and Ar-4%H_2-2%H_2O for durations up to 100 hours at 1150°C. The specimens after oxidation were analyzed by optical metallography, laser-induced fluorescence spectroscopy and scanning electron microscopy (SEM). From selected areas of the oxidized surfaces thin lamella were prepared using a focused ion beam (FIB) facility, which were analyzed in a transmission electron microscope (TEM). The analytical studies revealed that in both oxidizing environments alumina scales were formed, whereas transformation of the metastable theta alumina into thermodynamically stable alpha alumina was accelerated in the low pO_2, Ar-H_2-H_2O gas as compared to the high pO_2, Ar-O_2 atmosphere. Furthermore, indications were found that the rate of theta to alpha alumina transformation has a relationship with the grain orientation of the NiPtAl-coatings.

Hard Coatings and Vapor Deposition Technology
Room: Pacific Salon 3 - Session B1-3

Sputtering Coatings and Technologies

Moderator: P. Eklund, Linköping University, M.-S. Wong, National Dong Hwa University

8:00am **B1-3-1 Sputter-Deposited Thin-Film AlN-Based Electro-Acoustic Devices for Biosensor Applications**, ***G. Wingqvist*** *(gunwi@ifm.liu.se)*, Linköping University, Sweden **INVITED**

Biosensors, using biological recognition elements for specific detection on a molecular level, are today important devices for applications ranging from medical, environmental to safety areas.

A new type of label-free biosensor device has been developed and studied, which is fabricated using the same processes used for the fabrication of integrated circuits. This enables tighter integration and further sensor/biosensor miniaturization. The device is a so-called Thin Film Bulk Acoustic Resonator (FBAR). Developments are here reported of a low temperature reactive sputtering process for growing wurtzite-AlN thin films with a c-axis inclination of 20-30 degrees. This process enabled shear mode FBAR fabrication suitable for in-liquid operation, essential for biosensor applications. Shear mode FBARs were fabricated, operating at frequencies above 1GHz, exhibiting Q values of 100-200 in contact with water and electromechanical coupling factors k_t^2 of about 1.8%. This made it possible to move the thickness excited shear mode sensing of biological layers into a new sensing regime using substantially higher operation frequencies than the conventionally used quartz crystal microbalance (QCM) operating at 5-20 MHz. Measured noise levels of shear mode FBARs in contact with water showed the resolution to be in the range 0.3ng/cm^2 to 7.5ng/cm^2. This demonstrated the FBAR resolution without any averaging or additional stabilization measures already to be in the same range as the conventional QCM (5ng/cm^2), suggesting that FBARs may be a competitive and low cost alternative to QCM. The linear thickness limit for sensing of biomolecular layers was concluded to be larger than the thickness of the majority of the molecular systems envisaged for FBAR biosensor applications. A temperature compensated shear mode FBAR composite structure was demonstrated with retained coupling factor and Qvalue by utilizing the second harmonic mode of operation. Understanding has been gained on the sensor operation as well as on how the design parameters influence its performance. Specifically, sensitivity amplification utilizing low acoustic impedance layers in the FBAR structure has been demonstrated and explained.

8:40am **B1-3-3 Enhancement of Bottom Electrode on Ferroelectric Properties and Fatigue Properties of BFO/STO Symmetrical Structure**, ***S.J. Chiu***, National Tsing Hua University, Taiwan, *H.-Y. Lee (hylee@nsrrc.org.tw),* National Synchrotron Radiation Research Center, Taiwan, *G.-P. Yu, J.-H. Huang*, National Tsing Hua University, Taiwan

Superlattice structures consisting of symmetric multiferroic BiFeO$_3$ (BFO) and paraelectric SrTiO$_3$ (STO) sublayers were successfully deposited with a RF magnetron sputtering system. Two popular electrode materials, (001) Nb-doped STO electrode and LaNiO$_3$ (LNO) electrode, were chosen to investigate the effect of bottom electrode on BFO/STO superlattice structure. J-V characteristics of BFO/STO superlattice films would be measured. Synchrotron X-ray study including azimuthal scan and Crystal truncation-rod (CTR) spectra confirmed the epitaxial growth of the superlattice films. CTR spectra along [2 0 0] direction also showed well strained effect of Nb-doped STO electrode and LNO electrode on BFO/STO superlattice films. BFO/STO superlattice films showed saturated P-E hysteresis loop, and the LNO bottom electrode which deposited on the single crystal STO (002) substrate showed better enhancement of ferroelectric properties and fatigue properties on BFO/STO superlattice structure than Nb-doped STO electrode.

9:00am **B1-3-5 Optical Emission Spectroscopy of Radio Frequency PVD Process Related to the AlN Film Stechiometry and Deposition Rate**, ***J. Acosta*** *(jorge.acosta@itesm.mx)*, ITESM-CEM, Mexico, *E. Bauer-Grosse,* Institut Jean Lamour, France, *V. Brien, P. Pigeat, R. Hugon*, lpmi.uhp-nancy, France

Spectra of the mixture Ar-N2 plasma have been obtained for different N2 flows, maintaining Ar flow constant. Evolutions of Al, NI and Ar peaks have been analyzed in terms of species density finding three different regions. Peak ratios IAl/IAr; INI/IAr and IAr 750nm /IAr 811 nm have been computed in order to explain the plasma conditions for the three regions in terms of the species densities ratio and electron temperature. Seven AlN films have been prepared for different N2 flows, correlating the stechiometry films and deposition rate to the three regions I, II and III of the Ar peak 811 nm of the spectra from Ar-N2 mixture plasma. Region I was found a sub-stechiometric AlN film, regions II and III correspond to the reactive process. Region III presents a decrement of the deposition rate.

Hard Coatings and Vapor Deposition Technology
Room: Town & Country - Session B6-2

Hard and Multifunctional Nano-Structured Coatings

Moderator: C.P. Mulligan, U.S. Army ARDEC, Benét Laboratories, R. Sanjines, EPFL, P. Zeman, University of West Bohemia

8:00am **B6-2-1 The Role of Interfaces in the Strengthening and Stability of Superhard Nanocomposites**, ***S. Veprek*** *(stan.veprek@lrz.tum.de), R.F. Zhang, S.H. Sheng,* Technical University Munich, Germany*, A.S. Argon,* Massachusetts Institute of Technology*, M. Jilek,* SHM s.r.o*, A. Bergmaier*, Universität der Bundeswehr, Germany

Superhard nanocomposites of -TiN/a-Si$_3$N$_4$ can reach hardness of more than 100 GPa when prepared under conditions which allow the formation of fully segregated phases with about 1 monolayer (ML) thick Si$_3$N$_4$-like interface, free of impurities, which is significally strengthened by valence charge transfer from surounding TiN nanocrystals [1,2]. In the present paper we shall show, that such strengthening results in weakening of the neigbour TiN by Friedel oscillations of the valence charge density [3]. The 1 ML SiN$_x$ interface is the strongest configuration because when its thicknes increases, the Friedel oscillations cause further weakening of the neighbor TiN. The Ti-Si-N system will then be compared with several others consisting of different transition metal and covalent nitrides in order to elucidate the possibility of finding a better one with reduced amplitude of the weakening Friedel oscillations.

It has been shown earlier, that impurities, in particular oxygen, strongly degrade the mechanical properties of these materials by embrittling the SiN$_x$ interfaces [4]. We shall briefly discuss the recent progress in the understanding of this detrimental effect on the atomic scale, and compare it with several examples from other disciplines to show, that this effect is not uncommon. The final part of our paper deals with the control of the impurities in industrial-size coating applications.We shall show how an impurity content of ≤ 0.1 at.% is achieved today in industrial production, and outline possibilities of its further decrease down to a few 100 ppm.

[1] S. Veprek et al., Phil. Mag. Lett. **87**(2007)955.

[2] M. Veprek-Heijman et al., Surf. Coat. Technol. **203**(2009)3385. [3] R. F. Zhang et al., Phys. Rev. Lett. **102**(2009)015503; Phys. Rev. B **79**(2009)245426. [4] S. Veprek et al., J. Vac. Sci. Technol. B **22**(2004)L5; B **23**(2005)L17

8:20am **B6-2-2 Durability of CrSiN Nanocomposite Coatings: Key-Role of Grain Boundaries and Interfaces**, ***T. Schmitt*** *(Thomas.Schmitt@ec-lyon.fr),* Ecole Centrale de Lyon, France*, P. Steyer,* INSA de Lyon, France*, J. Fontaine,* Ecole Centrale de Lyon, France*, N. Mary,* INSA Lyon, France*, F. Sanchette,* CEA, France*, C. Esnouf*, INSA Lyon, France

The recent developments in sputtering processes have allowed the achievement of complex ceramic hard coatings. The motivation of such research efforts is to provide multifunctional coatings in order to meet industrial needs, for instance in severe machining applications.

In this study, we are focusing on ternary nanocomposite CrSiN coatings deposited by arc evaporation PVD, process which is increasingly used in industry. Our objective is to improve CrN-based coatings durability by modifying, on the one hand, their chemistry (addition from 0 to 20 at.% Si) and, on the other hand, their architecture (single- and multi-layered films). Special attention will be paid to mechanisms involved in the formation of the nanocomposite CrSiN structure, and to their consequences on oxidation and wear behaviours. Microstructure was investigated by XRD analyses, SEM and TEM observations. Mechanical properties were measured by nanoindentation and SEM *in situ* tensile tests. Silicon enrichment leads to a drastic improvement of the oxidation resistance, whereas it appears to be detrimental to the wear resistance in the case of single-layered films. Nevertheless, the use of a multi-layered architecture leads to the best functional properties. These results will be discussed in light of films microstructure, especially regarding grain boundaries and interfaces.

8:40am **B6-2-3 Advanced Modelling of Structures and Properties of Crystalline, Nanocrystalline and Amorphous Nitrogen-Based Materials**, ***J. Houska*** *(jhouska@kfy.zcu.cz)*, University of West Bohemia, Czech Republic **INVITED**

The combination of experiment with advances in computer simulation techniques and growing computing capacities constitute a powerful approach for explaining the complex relationships between deposition conditions, structure and properties of functional materials. Different levels of theory can be used to describe the interatomic interactions, ranging from ab-initio density-functional theory to classical molecular dynamics (MD) using empirical potentials. We review usefulness of individual simulation approaches using examples of novel high-performance nitrogen-based materials that have important applications. A special attention is paid to the comparison of calculated and experimental results. Amorphous Si-B-C-N materials provide outstanding thermal stability in inert atmosphere up to the 1700 °C substrate limit and oxidation resistance in air up to 1600 °C in connection with controllable mechanical, electronic and optical properties. We investigate in detail how the Si/C ratio, N/(Si+B+C) ratio and the B content affect structure and characteristics of Si-B-C-N materials. Observing the formation of N_2 molecules and the dynamics of bond-breaking events in simulations of heated Si-B-C-N materials allows understanding of their thermal stability. Fcc metal nitrides exhibit superior but mutually different properties, including a qualitative difference between nonmagnetic hard cubic TiN, and magnetic oxidation-resistant CrN which may exhibit a cubic/orthorhombic structural transformation. Calculations of energies and electronic structures of Ti(Si)N(C) and Cr(Si)N(C) lead to complete understanding of evolutions of the lattice constant, elastic moduli, Poisson's ratio, magnetization and the structural preference. Depending on composition and deposition conditions, ternary metal nitrides may form superhard nanocomposite structures. We predict thermodynamically preferred structures of $Ti_{(50-x)}Si_xN_{50}$ nanocomposites of various compositions. We focus on formation and growth of TiN nanocrystals, and investigate how the Si content affects their number, size distribution, quality in terms of deformation and Si impurities, and thickness of the amorphous phase between them. Amorphous SiNH materials prepared by plasma-enhanced chemical vapor deposition are suitable for diverse applications including systems with a graded refractive index. We reproduce the deposition process of SiNH films from SiH_x and N radicals. We investigate the effect of particle flux composition and ion bombardment characteristics on vertical profiles of the films, deposition characteristics such as sticking coefficients, and material characteristics such as dimension of nanopores formed.

9:20am **B6-2-5 Electrical Conductivity in Si-Based Transition Metal Nanocomposite Nitrides**, ***R. Sanjines*** *(rosendo.sanjines@epfl.ch), D. Oezer, C. Sandu,* EPFL, Switzerland, *J. Patscheider*, Empa, Switzerland

In Me-S-iN (Me= Ti, Cr, Zr, Nb, Cr) nanocomposite materials composed of small MeN crystallites (5-10 nm size) surrounded by thin SiN_x layers (1-2 molecular layers), the electrical conductivity exhibits metallic or non-metallic behaviour depending on the Si content, the MeN crystallite size and the thickness of the SiN_x tissue phase. Resistivity measurements are therefore considered as a practical method to characterize the formation of nanocomposite films. By modelling the electron scattering mechanism, pertinent information can be obtained on the film morphology. However, as the Me-Si-N films deposited by magnetron scattering often exhibit columnar morphology, another parameter influencing the electrical conductivity is the film texture. In the present paper, we report on the electrical properties of Zr_xSi_yN thin films (from 10 nm to 200 nm) whose resistivity has been investigated as a function of the Si content, grain shape and size, and film thickness. Zr_xSi_yN films with selected Si content and film thickness have been deposited by reactive magnetron sputtering in UHV reactor chamber at 900 K. The grain size and shape were characterized by *in situ* STM and HRTEM , and the electrical conductivity of films was measured by the van der Pauw method in the temperature range of 20-350 K. The dependence of the electrical conductivity from grain boundary and grain size scattering effects is discussed.

9:40am **B6-2-6 Microstructure and Mechanical Properties of Nanocomposite Ti-B-C, Ti-B-C-N, and Ti-B-C-N-Si Films Deposited by Unbalanced Magnetron Sputtering**, ***I.-W. Park****, J.J. Moore (jjmoore@mines.edu), B. Mishra,* Colorado School of Mines, *A.A. Voevodin,* Air Force Research Laboratory, *K.H. Kim,* NCRC-HyMAS, Korea, *E.A. Levashov*, Moscow State Institute for Steels and Alloys, Russia

Multifunctional nanocomposite, based on nanocrystalline (nc-) and amorphous (*a*-) phases, films attract considerable interest to extend the lifetime of cutting tools, press-forming tools and various other mechanical components. Films for most tribological applications require combinations of properties such as a relatively high hardness, high fracture toughness, wear- and oxidation-resistance, and a low friction coefficient. The present work investigates the co-deposition of Ti-B-C, Ti-B-C-N, and Ti-B-C-N-Si nanocomposite films from a composite target of TiB_2-TiC and a pure boron doped Si target using DC unbalanced magnetron sputtering in Ar/N_2 gas mixtures. The microstructures and mechanical properties for the films were investigated in various N and Si contents. The microstructures of the synthesized films were characterized by X-ray diffractometer (XRD), scanning electron microscope (SEM), X-ray photoelectron spectroscope (XPS), high-resolution transmission electron microscope (HRTEM), respectively. Nano-indentation was conducted to assess the hardness and Young's modulus of the films. In the present work, the comprehensive microstructures and various mechanical properties of the films were investigated and correlated with deposition parameters.

10:00am **B6-2-7 Combinatorial Approach to the Growth of Al-Cr-O-N Thin Films by Reactive r.f. Magnetron Sputtering**, ***D. Diechle****, M. Stüber (michael.stueber@imf.fzk.de), H. Leiste, S. Ulrich*, Forschungszentrum Karlsruhe, Germany

The PVD synthesis of wear and oxidation resistant aluminum oxide and derivative coatings is currently attracting large scientific and technical interest. Ternary Al-Cr-O thin films with mechanical properties comparable or superior to binary Al-O thin films can be deposited at moderate deposition temperatures. New coatings from the quaternary Al-Cr-O-N system could even offer increased strength, hardness and toughness. A combinatorial approach to the growth of Al-Cr-O-N thin films by means of reactive r.f. magnetron sputtering will be presented. For specific deposition conditions well adherent, nanocrystalline Al-Cr-O-N thin films with high Vickers hardness and elastic modulus values were grown at non-equilibrium conditions on cemented carbide and silicon substrates. Detailed results on the coatings composition, constitution, microstructure and properties will be presented and discussed in comparison to ternary Al-Cr-O thin films deposited under identical conditions.

10:20am **B6-2-8 Design of Hard Ti-Based Nitride Coatings and Multilayer Structuring**, ***T. Suzuki*** *(tsuzuki@mech.keio.ac.jp), N. Fukumoto,* Keio University, Japan, *H. Hasegawa,* Okayama University, Japan, *T. Watanabe,* Kanagawa Academy of Science and Technology, Japan, *S. Kinoshita*, Tungaloy Corporation, Japan **INVITED**

In this talk, we present and summarize the effect of the coating properties by adding other elements such as Cr and (or) Si to this conventional TiAlN coating deposited by arc ion plating system, especially because of its tendency to form nanocomposite structure.

Quaternary TiCrAlSiN coatings with varying (Al+Si) content formed a nanocomposite structure and showed superior properties with high hardness, good oxidation resistance and thermal stability [1, 2]. The addition of Cr and Si to TiAlN resulted in a mixed-phase coating at some compositions, which degraded the coating properties. Therefore, a ternary TiAlSiN coating was introduced to clarify the effect of Si addition and to inquire a new hard and tough coating. The structural transformation easily occurs by adding other elements and the choice of the right composition is an essential factor. The addition of Y to TiAlN can induce the growth of protective oxide scales at high temperatures, which prompts the good oxidation resistance [3]. Another trend in hard coatings for wear-protection is the development of multilayer coatings with small multilayer periods (nanometer thick layers). The multilayer coating show peculiar characteristic of hardness at small periods and new multilayer coating can be designed not only to increase the hardness, but also to compensate the degrading properties of each layer. The TiAlSiN coating with low Al content was layered with high Al content CrAlN coating to develop a new multilayer coating that could have a high Al content with a single cubic structure [4]. This multilayer coating showed a superior property with good oxidation resistance compared to monolayer coatings.

[1] K. Ichijo, H. Hasegawa, T. Suzuki, Surf. Coat. Technol., 201, (2007) 5477.

[2] H. Ezura, K. Ichijo, H. Hasegawa, K. Yamamoto, A. Hotta, T. Suzuki, Vacuum, 82, (2008) 476.

[3] T. Urakawa, N. Fukumoto, T. Suzuki, PSE 2009 in press.

[4] N. Fukumoto, H. Ezura, T. Suzuki, Surf. Coat. Technol., (in press).

11:00am **B6-2-11 Multifunctional NbC-Based Nanocomposite Thin Films**, ***N. Nedfors*** *(nils.nedfors@mkem.uu.se),* Uppsala University, Sweden, *O. Tengstrand,* Linköping University, Sweden, *E. Lewin, A. Furlan,* Uppsala University, Sweden, *P. Eklund, L. Hultman,* Linköping University, Sweden, *U. Jansson*, Uppsala University, Sweden

Earlier studies have shown that magnetron sputtered nc-TiC/a-C nanocomposite coatings have excellent electrical contact properties [1]. Consequently, this type of material has a potential use in, e.g., sliding contacts where low contact resistance and high wear resistance combined with low friction are required. We propose that the performance of the nanocomposite coating can be further improved by exchanging Ti towards another carbide-forming transition metal. In this study we have investigated sputtered nanocomposite films in the Nb-C system for multifunctional applications with a focus on electrical and mechanical properties. Thin films of nc-NbC/a-C were deposited by nonreactive, unbalanced dc-magnetron sputtering from two separate Nb and C targets. Samples with relative carbon content between 49 and 64 at. % were deposited through tuning of magnetron currents. The structure of the films was characterized with X-ray diffraction (XRD) and scanning and transmission electron microscopy (SEM and TEM). X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy were used to characterize the relative composition and chemical bonding. The mechanical properties of the films was determined with nano-indentation and pin-on-disc measurements. Contact resistance measurements were carried out in a custom-built set-up with crossed cylinder geometry.

The results show that both the grain size of the NbC nanocrystallites as well as the relative amount of carbide and amorphous carbon matrix can be controlled by the process parameters. The electrical and mechanical properties are strongly dependent on the amount of matrix and carbide grain size. Optimum conditions are found with amorphous tissue phase between the carbide grains. The contact resistance for nc-NbC/a-C was about 50-90 μΩ at 100 N compared to 60-110 μΩ for nc-TiC/a-C at similar conditions. Possible mechanisms for this behaviour will be discussed.

[1] E. Lewin, O. Wilhelmsson, U. Jansson, Journal of Applied Physics **100**, 054303 (2006)

Tribology and Mechanical Behavior of Coatings and Thin Films
Room: Pacific Salon 1 - Session E2-1

Mechanical Properties and Adhesion
Moderator: R. Chromik, McGill University, L. Davies, Caterpillar, J. Michler, Empa

8:00am **E2-1-1 Strength: Size Matters in 1, 2 and 3 D**, ***W.W. Gerberich*** *(wgerb@umn.edu), A.R. Beaber, L.M. Hale, D.D. Stauffer*, University of Minnesota **INVITED**

The fact that size matters for the strength of films, wires or pillars, and spheres is now well documented. Due to crystallography, microstructure or confinement, the reasons may vary. Confinement models may depend upon grain size or second effects which limits exhaustion of nucleation sites and the crystallography of BCC or FCC may be factors as well. Here, we consider mainly one system, silicon single crystals, and focus on the confinement issue. Considering contact mechanics, such as nanoindentation of thin films, the constraint between hard contacts and hard substrates leads to Taylor (forest dislocation) hardening of thin soft Au films. This gives a (1/h)1/2 length scale dependency for films in the 100 to 400nm thickness (h) range. For silicon pillars small in 2D, Taylor hardening is clearly inappropriate and the competition between exhaustion hardening and linear hardening remains unclear. Most work has considered silicon single crystal nanospheres in the 40 nm to 400 nm diameter (d) range. These spheres small in 3D follow a linear hardening model with strength proportional to (1/d). Regarding the controlling mechanism, this is dislocation nucleation with small activation volumes in the 2 to 10 b3 range. Resulting contact flow stresses approach 50 Gpa.

8:40am **E2-1-3 Some Unpleasant Truth About Dynamic/Oscillatory Indentation Measurement Procedures**, ***N. Schwarzer*** *(n.schwarzer@siomec.de)*, Saxonian Institute of Surface Mechanics, Germany

The dynamic / oscillatory indentation method, where a supposedly small oscillation is superposed to the ordinary loading circle of an indentation experiment, is a widely used tool for the detection of internal surface respectively coating structures. Meaning, wherever there is suspicion that a coating is not homogeneous it was suggested to apply this method in order to find and analyze such an internal structure.

However, little is known about the many flaws of this method leading to virtual structures where there was homogeneity in reality or giving completely wrong structural information where there is an internal structure. Depending on the example in question the deviation from the truth can be rather dramatic. The author will not only present and discuss these flaws but also show a few “every day examples” where the dynamic / oscillatory indentation method leads to severe misinterpretation.

9:00am **E2-1-4 On Hall-Petch Strengthening Below 10 nm Grain Size**, ***A.F. Jankowski*** *(alan.jankowski@ttu.edu)*, Texas Tech University

The activity of dislocations provides the basis for the Hall-Petch mechanism of strengthening in crystalline materials. The loss of dislocation activity is routinely suggested as the domain size decreases below 10 nm wherein a transition occurs from an intra-granular dislocation-based behavior to an inter-granular boundary motion. A consequence is that Hall-Petch strengthening will be lost with further decrease in grain size. This transition in deformation behavior is dependent on the disorder found in the inter-granular boundaries as seen in the increasing role of triple junctions. However, the nature of the structural disorder in the boundary influences the deformation mechanism that results, and the change in strength that occurs with further decrease in domain size below 10 nm. We now examine the interplay between Hall-Petch type behavior for grain sizes below 10 nm, and those changes related to the activation volume for deformation. It can be derived from the consideration of plastic deformation as a thermally activated process, that a linear relationship should exist between the experimentally determined parameters of “d^n/m” and “v*”. In the first parameter, the domain (i.e. grain) size (d) is raised to an exponent (n) and divided by the strain-rate sensitivity exponent (m). The n represents the power law fit of strength with domain size. For the case of Hall-Petch behavior, n equals negative one-half. The exponent (m) to the power law fit between the strength and strain rate represents the strain-rate sensitivity. The second parameter “v*” is the activation volume for deformation that can be determined by a linear fit to the logarithmic change in strain rate with linear change in stress as the activation energy is a strong function of stress. Since these individual parametric components can be experimentally measured without an a priori assumption to value of the exponent n, an evaluation of Hall-Petch strengthening can be independently made for material behavior as it extends for grain sizes down to a few nanometers. The mechanical properties of electrodeposited nanocrystalline alloys are now assessed with regards to the behavior of the experimentally measured strain-rate sensitivity exponent (m) and activation volume (v*) for grain sizes (d) as small as 4 nm – a nanoscale regime that has here-to-fore gone without detailed examination. It is found from micro-scratch measurements that hardness (hence strength) approaches ideal values as the grain size decreases to 7 nm. Thereafter, softening in strength and departure from Hall-Petch behavior can be related to an increase in the activation volume for deformation as grain size decreases further.

9:20am **E2-1-5 The Effect of Microstructure on the Mechanical Properties of Submicron Thin Films and Nanostructured Devices**, ***S.J. Bull*** *(s.j.bull@ncl.ac.uk)*, Newcastle University, United Kingdom

The manufacture of mechanical devices such as MEMS from thin films can lead to circumstances where the scale of the mechanical deformation induced by device operation is comparable to the scale of the microstructure of the materials from which they are made. A similar observation occurs when using indentation tests to assess the properties of thin films where the plastic zone dimensions may be comparable to the grain size. For the purposes of design based on continuum mechanics approaches it is usually required that the grain size is very much smaller than the deforming volume which is not always observed in practice. Considerable differences between predicted and observed performance can be seen depending on the material tested and its grain size. This presentation will highlight the effect of grain size, shape and orientation on the mechanical response of metallic thin films used as protective coatings and for semiconductor metallisation. The conditions under which continuum mechanics may be used successfully will be discussed and the effect of crystallographic anisotropy on the choice of appropriate design data will be highlighted for copper and zinc coatings.

9:40am **E2-1-6 The Effect of Surface Roughness on Nanoindentation of Hard Coatings: Simulation and Experiment**, ***C. Walter*** *(claudia.walter@unileoben.ac.at), C. Mitterer*, Montanuniversität Leoben, Austria

In this work finite element modeling (FEM) is applied to investigate the influence of surface roughness on nanoindentation results. Surface roughness may pose a problem when indentation depth is limited e.g. for the indentation of thin films. It causes scatter of the measured data and makes it difficult to evaluate reliable mechanical properties from the measured load-displacement data.

Indentation with spherical indenter tips of CrN thin films with an arithmetic surface roughness Ra measured by atomic force microscopy of 3, 5, and 11 nm is investigated. Here, the different Ra values arise from differences in asperity height as well as different lateral extensions of the asperities. Additionally, artificial surface topographies are investigated by simulation, where only the vertical dimension of the asperities has been changed. Load-displacement curves have been generated for these samples by experimental measurement, 2-D FEM simulations and 3-D FEM simulations. The Oliver and Pharr method is then applied to analyse the load-displacement curves from all three methods. This allows for a critical discussion of the evaluated elastic modulus and its scatter as a function of the surface roughness. A comparison for different indenter radii is also shown.

The general trend of lower measured elastic modulus and larger data scatter with increasing surface roughness can be observed by all three methods. This can be explained by the fact that the surface area for the rough coatings can be a factor 2 smaller compared to the case of smooth surfaces in contact under the applied conditions. This will lead to a significant underestimation of the elastic modulus evaluated from the load-displacement data applying the assumption of smooth surfaces in contact. The FEM simulations visualise nicely the real contact area under maximum load. The deviation from the true elastic modulus increases with increasing roughness values.

It is also shown that a full 3-D simulation is needed, while a 2-D axisymmetric approach is not sufficient to capture the contact conditions adequately. Surface profiles will be represented as an assembly of concentric rings in the 2-D model, while the 3-D model captures the complete topography resulting in a large number of randomly distributed asperity tips in contact with the indenter. Visualized with FEM it becomes intuitive to understand that the concentric-ring setup will give artificial stiffness and scatter.

10:00am **E2-1-7 Size Effects in Ceramics - The influence of Yield Stress on the Effect of Size**, ***S. Korte*** *(sk511@cam.ac.uk), R.J. Stearn, W.J. Clegg*, University of Cambridge, United Kingdom

Size effects are commonly observed in mechanical tests at the micrometer scale. Extensive experimental work has been reported in the literature describing size effects in soft metals where the yield or flow stress at the micron scale is related to the specimen dimensions by a relation of the form $\tau{\sim}d^{-0.6}$. Experiments on harder materials such as bcc metals or semiconductors have shown that the size effect is less pronounced in these materials, but in contrast to fcc metals little data is available in the literature.

This paper presents experimental data obtained on a wide range of materials in order to identify the relationship between bulk yield stress and magnitude of the size effect. A direct relationship is found implicating that a simple description of the size effect of the form $\tau=\tau_0+Bd^{-x}$ is not sufficient and different mechanisms need to be considered if the origin of the effect of size is to be studied for materials other than soft metals.

10:20am **E2-1-9 Dimensionality of Plasticity Size Effects- the 'Thinness' Effect**, ***N.M. Jennett*** *(nigel.jennett@npl.co.uk), X.D. Hou,* National Physical Laboratory, United Kingdom*, R. Ghisleni, J. Michler,* Empa, Switzerland*, A.J. Bushby*, Queen Mary University of London, United Kingdom **INVITED**

The indentation size effect is now well-established, with many examples in the literature of "smaller being harder." Strain gradient plasticity has often been used to explain the size effect in indentation and in other loading geometries involving non-uniform deformation. However, it is now clear that a strain gradient is not a necessary condition for size effects. This paper reports spherical nanoindentation data and circular cross-section micro-pillar compression data from the same crystal. Taking the contact pressure in the indentation tests to be 3 times the stress, the magnitude of the size effect is found to be exactly the same in both cases, i.e. with and without a plastic strain gradient. These two results can, however, be fitted by a slip distance model using the same set of material parameters and very few assumptions. In both cases the slip distance can be represented by a single value due to axisymmetry. The slip distance model is based on the principle that plasticity in small structures requires small radius indentation loops, which take more strain energy to form; resulting in higher yield stresses. One way to investigate this theory further is to determine the dimensionality of plasticity size effects by looking at non-axisymmetric structures. Therefore, a series of tungsten micro-pillars with different geometries, ranging from square pillars to rectangular 'walls,' were compressed in a Nanoindenter and dimensionally characterised in an SEM. This clearly showed that the shortest dimension dominated the strength of the pillars, ruling out a surface area to volume effect (suggested by dislocation starvation models) and reinforcing the hypothesis that a minimum source size or slip distance is governing behaviour. Yield stress is determined by wall width; the length of the wall making little or no difference. The implication of this is that thin structures exhibit the same enhanced yield strength regardless of total size (volume) or surface to volume ratio; nano-layers are as strong as nanoparticles. This is good news for the surface engineering and coatings communities as it means that thin layers and multilayers may be the most cost effective solution, especially where 3-D dispersion of nano-particles to separate a matrix material into small elements is difficult, or there is resistance, using the precautionary principle, to the use of nano-particles at all.

11:00am **E2-1-11 Mechanical Properties Extraction of Bulk Materials and Thin Films Based on Vickers Instrumented Indentation Tests**, ***S.A. Rodriguez*** *(sararopu@gmail.com), M.C.M. Farias, R.M. Souza*, University of São Paulo, Brazil

In this work, the applicability of a new algorithm for the calculation of mechanical properties from instrumented indentation test was studied for thin films with different architectures. The proposed algorithm was based on one previously suggested by Rodríguez *et al* for Berkovich indentation. In this work, the algorithm coefficients for Vickers indentations on bulk materials were obtained and the proposed algorithm considers the effect of friction at the indenter-specimen contact. The feasibility of the algorithm for thin films was analyzed with the aid of both three-dimensional finite elements simulations and the analysis of experimental indentation tests. The equation coefficients for mechanical properties calculations correspond to the best fit to the simulated data, obtained from the numerical procedure. The numerical approach was also selected to analyze how the calculated mechanical properties of the film were affected by the mechanical properties of the substrate and by the ratio between film thickness and maximum indentation depth l/h_{max}. The experimental indentation tests were conducted on AISI H13 tool steel specimens, plasma nitrated and coated with thin films of TiN, TiC or TiC-TiN-TiC multi-layers. Although experimental variations, residual stresses and substrate effect limited the capability of mechanical properties estimation, the proposed algorithm allow more accurate calculation of mechanical properties when the value of the ratio of the residual indentation depth to maximum indentation depth h_r/h_{max} is low and when the strain hardening exponent n is high.

11:20am **E2-1-12 Effects of Mechanical Properties, Residual Stress and Indenter Tip Geometry on Instrumented Indentation Data in Thin Films***,* ***C.E.K. Mady****, S.A. Rodriguez, A.G. Gómez, R.M. Souza (roberto.souza@poli.usp.br)*, University of São Paulo, Brazil

In this work, an axisymmetric two dimensional finite element model was developed to simulate instrumented indentation testing of thin ceramic films deposited onto hard steel substrate. The indenter was modeled as a rigid cone (half angle of 70.3°) and two ratios between indenter tip radius and maximum penetration depth (R/h_{max}) were considered. The level of film residual stress (σ_r), the film elastic modulus (E) and the film work hardening exponent (n) were varied to analyze their effects on instrumented indentation data. Results indicated that all variables (R, σ_r, E, n) have effects on indentation morphology (pile-up and sink-in), on the maximum load necessary to achieve a given penetration depth and on the proportional curvature constant during loading. On the other hand, the load curve exponent was only affected by the indenter tip radius. These numerical results were used to analyze experimental data that were obtained with titanium nitride coated specimens, in which the substrate bias applied during deposition was modified to obtain films with different levels of residual stress. Good qualitative correlation was obtained when numerical and experimental results are compared, as long as all film properties are considered in the analyses, and not only the film residual stress level, due to the influence of all mechanical properties on the results.

Characterization: Linking Synthesis Properties and Microstructure
Room: Royal Palm 1-3 - Session F1-1

Advances in Characterization of Coatings and Thin Films
Moderator: P. Schaaf, Ilmenau University of Technology

8:00am **F1-1-1 GDOES for Accurate Well Resolved Coatings and Thin Film Analysis**, ***M. Wilke*** *(marcus.wilke@tu-ilmenau.de), G. Teichert*, Bauhaus-University Weimar, Germany, *P. Schaaf*, Ilmenau University of Technology, Germany **INVITED**

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 non-conductive layers and easy quantification even for light elements such as C, N and O. Starting with the fundamentals of GDOES, requirements for high depth resolution and low detection limits regarding parameter optimization and sample quality will be discussed. Furthermore, an overview of new developments in instrument design, aspects for accurate and well resolved thin film analyses and limitations for GDOES measurements as well as quantification will be presented. 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 the interface will be demonstrated by measurements of metallurgical coatings and films for industrial applications: Multilayer systems, hard coatings for wear applications, photovoltaic coating systems, implantation profiles and coatings for corrosion resistance. A discussion of the results in comparison to other analysis techniques is presented.

8:40am **F1-1-3 Effect of Process Conditions on Microscopic Structure and Macroscopic Properties of Zinc-Based Coatings**, ***J. Baier*** *(jennifa.baier@bam.de), U. Beck, T. Lange*, BAM, Germany, *G. Mollath*, Fraunhofer-Institute IPK, Germany, *M. Sahre*, BAM, Germany, *A. Spille-Kohoff*, CFX Berlin Software GmbH, Germany

Electro chemical deposition (ECD) is of great importance in particular for long-term and highly durable corrosion protection in various areas such as automotive bodywork, construction industry and several outdoor and off-shore applications under harsh environments. In addition to corrosion protection, other functional properties such as decorative (e.g. color or brightening) and functional (resistance to mechanical use) features are of interest.

Zinc-based coatings represent the huge majority of applications for the protection of steel against corrosion. As number, shape and size of components to be coated are varying, rack loading and bath parameters (hydrodynamics, current density, electrolyte composition and state, pH-value, temperature) have to be considered. In contrast to plasma deposition, the correlation of process parameters and coating properties and the model-based simulation of this interdependence on an industrial scale is not yet satisfactorily understood. This issue is addressed in this work in which zinc electrolytes serve as model system.

Zinc was electro-deposited on steel sheets out of an alkaline non-cyanic bath with different additives. Layer thickness in terms of intra- and inter-sample homogeneity was measured by X-ray fluorescence spectroscopy (XRF). The distribution of layer thickness was related to current density and hydrodynamics and verified by means of global (of the entire electrolyte vessel) and local (in front of the substrates) simulations. The crystal orientation and the morphology were investigated by means of X-ray diffraction (XRD) and scanning electron microscopy (SEM). As shown, microstructure mainly depends on the current density and the additives (inhibitors, alkali salt, Ni) of the electrolyte bath. According to the crystal orientation, different types of deposit structures (adapted from Fischer) were observed. The mechanical properties such as hardness, modulus and creep as measured by instrumented indentation testing (IIT) are related to the deposit structure and the composition of the zinc layer.

For reference electrolytes in a plating pilot plant, it could be shown that the simulation of the hydrodynamics is strongly correlated to the thickness distribution. In general, the surface of the zinc coating consists of crystal plates with a thickness of less than 50 nm. The roughness increases at lower current densities and for lower amounts of inhibitors whereas the current efficiency decreases at higher current densities and therefore at higher deposition rates.

This work was supported by the BMBF (FKZ 01RI0711B) in the project AnSim (www.ansim-online.de).

9:00am **F1-1-4 Thorough XPS Analyses to Investigate Thin Films Components and Improve Performances of All-Solid-State Thin Films Batteries**, ***B. Fleutot***, ICMCB and STMicroelectronics, France, *B. Pecquenard (pecquen@icmcb-bordeaux.cnrs.fr)*, ICMCB, France, *H. Martinez*, IPREM, France, *A. Levasseur*, ICMCB, France

Energy storage is vital for mobile system (mobiles phones, laptop,…) because it defines the system autonomy. In addition to the main power source (lithium-ion battery), these systems need a small embedded one mainly used to power the internal clock. This source is currently a primary button cell added on the printed circuit board. The aim is to replace this source by a microbattery, that need to be compatible with solder-reflow process. In addition, a microbattery may be relevant for a wide range of applications such as RFID tag and smart packaging, sensors, smartcards…

A microbattery is a monolithic system constituted by more than 10 layers including the active part (both electrodes and the electrolyte), protective layers, current collectors and barriers thin films, with a total thickness not exceeding 15 µm. In order to improve performances of such microbatteries, especially at low temperature, it is essential to optimize electrolyte thin films that ensure the transport of Li ions between the two electrodes. Among all solid electrolyte thin films, LiPON is the most used in lithium microbatteries. Nevertheless, despite its good ionic conductivity (3.10^{-6} S/cm), it suffers from a low thermal stability inducing a great increase of its activation energy after solder-reflow process, which is detrimental for the functioning of the microbattery at low temperature.

In order to better understand the role of nitrogen on its ionic conductivity as well as its evolution over thermal treatment, we have prepared various LiPON-type thin films with different compositions by radio-frequency sputtering from a Li_3PO_4 target by varying deposition conditions, in particular nitrogen flow rate. As these thin films are amorphous, we have used the complementarity of XPS, Raman spectroscopy and Nuclear Magnetic Resonance (NMR) to investigate the local structure and its evolution with nitrogen content and after solder reflow treatment. Some correlations have been established between deposition conditions, composition, local structure, ionic conductivity and activation energy. On the basis of these results, we have doped the LiPON thin films and succeeded to greatly enhance its thermal stability as well as its performances at low temperature (patent pending).

In some conditions, impedance spectroscopy measurements achieved on the all-solid-state thin films battery have evidenced a second semi-circle in addition to the one characteristic of the electrolyte, suggesting the formation of an interface between the electrolyte and one electrode, responsible for a capacity fading over cycles. XPS analyses have been achieved to investigate this interface after cycling or thermal treatment.

9:20am **F1-1-5 Chemical States in Al-Si-N Nanocomposite Thin Films as Evidenced by XPS**, *A. Pélisson-Schecker, H.J. Hug*, ***J. Patscheider*** *(joerg.patscheider@empa.ch)*, Empa, Switzerland

Ternary Al-Si-N films, as well as pure AlN and SiN_y films, were deposited by DC reactive magnetron co-sputtering from pure Al and Si targets in an Ar/N_2 atmosphere at 200°C and 500°C. Overall composition and bonding states were investigated by X-ray photoelectron spectroscopy (XPS). Photoelectron line positions, broadening and chemical shifts are reported, as well as the nitrogen Auger parameter and its Wagner plot. The results are compared to XRD data that indicate a transition upon increasing silicon content from a single phase $Al_{1-x}Si_xN$ solid solution to a two-phase composite – $Al_{1-x}Si_xN$ crystallites surrounded by an amorphous SiN_y phase – at about 6 at.% of Si. Two different compositional regimes were identified from XPS data that are characterized by a distinct change in the evolution of chemical shifts and of the photoelectron line broadening at about 10-15 at.% of Si. This concentration regime repesents the onset of formation of a SiN_y tissue phase thicker than two monolayers on an average. Under these conditions the chemical bonding in the tissue phase is similar to that in bulk SiN_y. The observed changes in the XPS data coincide well with the structural changes in the material at different silicon contents as deduced from XRD and optical measurements, It is shown that a consistent image of the material's constitution requires the combined use of several different characterization techniques, with XPS just being one of them.

9:40am **F1-1-6 Recent Advances in XPS for Thin Film Analysis**, *C. Blomfield (chris.blomfield@kratos.co.uk)*, Kratos Analytical Ltd., Manchester, United Kingdom, ***D. Surman***, Kratos Analytical Inc., New York **INVITED**

X-ray photoelectron spectroscopy is the most widely applied of a range of surface analysis techniques. Small area analysis from an area of a few microns and imaging XPS with spatial resolution of a few microns is now common place.[1] The advent of small analysis area XPS heralded an era for XPS depth profiling where a sputter crater is formed by an ion beam (typically Ar) and then XPS analysis formed in the crater. In such a way thin films of up to 1-2 microns in thickness can be analysed. XPS depth profiles can therefore elucidate the chemical composition of a thin film with a depth resolution of a few nanometers . XPS can analyse films and substrate materials which are either insulating or conductive.

Recent developments have focussed on improved ion gun design, by lowering the Ar ion energy, improved interface resolution is possible. To date, XPS depth profiling has been principally applied to inorganic materials but the recent development of polyatomic ion guns using large carbon based molecules such as Fullerene or Coronene has expanded XPS depth profiling into organic materials[2].

Examples will be given here which describe the state of the art in XPS depth profiling on both organic and inorganic materials. Examples of nanometer depth resolution and quantitative chemical composition of films of several hundred nanometers in thickness from a range of applications will be given.

[1] C.J. Blomfield, Journal of Electron Spectroscopy and Related Phenomena 143 (2005) 41-249

[2] G.X. Biddulph, A. M. Piwowar, J.S. Fletcher, N.P. Lockyer, J. C. Vickerman, Anal, Chem, 79, (2007), 7259-7266.

10:20am **F1-1-8 Formation of CoSi$_2$/Si$_x$N$_y$ Nanocrystals for Nonvolatile Memory Application**, ***J.-J. Huang*** *(m952030007@student.nsysu.edu.tw), T.-C. Chang*, National Sun Yat-sen University, Taiwan

Nonvolatile nanocrystal memories recently have been one of the promising candidates to replace traditional floating gate nonvolatile memory because the discrete nanocrystal as the charge storage media have effectively improved data retention under endurance test for the device scaling down. In this study, CoSi$_2$ nanocrystal surrounded with Si$_x$N$_y$ shell structure was proposed by rapid thermal annealing a nitrogen incorporated CoSi layer, which was deposited by sputtering CoSi target in the mixture gas of Ar+N$_2$ or Ar+NH$_3$, to improve data retention. The structures and elements composition of nanocrystal were analyzed by transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS), and the electrical characteristics of nanocrystals memories were defined by C-V curves. Because of the extra SixNy shell, the proposed memory can exhibit good data retention to 10 years.

10:40am **F1-1-9 Microstructure of Cr/ta-C Multilayers as Studied by SAXS, TEM and EELS**, ***U. Ratayski*** *(Ulrike.Ratayski@iww.tu-freiberg.de), D. Rafaja, V. Klemm, U. Mühle,* TU Bergakademie Freiberg, Germany*, H.-J. Scheibe, M. Leonhardt*, Fraunhofer Institute for Materials and Beam Technology IWS, Germany

The adhesion between the diamond-like carbon coatings (DLC) and the substrate is a limiting parameter for many applications of these coatings. One possibility, how to improve the adhesion, is the use of a buffer layer. As possible candidates for the buffer layers, transition metals forming carbides are discussed. We intended to employ chromium as a buffer between the steel substrate and the tetrahedral bonded amorphous carbon (ta-C) coating not only to improve the adhesion between both counterparts of the system, but also to hinder the diffusion of carbon into the steel substrate. The advantage of chromium is that it forms carbides with narrow homogeneity ranges, which serve like diffusion barriers for a further carbon diffusion.

The main goal of this work was the description of the interface formation between Cr and ta-C during the deposition and after the thermal treatment. For this reason, various Cr/ta-C multilayers with different thicknesses of the Cr layers (10 nm and 20 nm) were deposited on silicon substrates. Furthermore, the film deposition was carried out with different energies of the carbon ions. The Cr/ta-C multilayers were investigated using the small angle X-ray scattering (SAXS), the high resolution transmission electron microscopy (HRTEM) and the electron energy loss spectroscopy (EELS). SAXS yielded information about the electron density and thickness of individual layers and about the interface roughness and morphology. The electron density obtained from the SAXS experiments was employed for the estimation of the sp^3/sp^2 ratio in individual samples, which was verified by EELS. The interface roughness and the morphology of the interfaces were verified by HRTEM.

The thickness of the Cr layers in the Cr/ta-C multilayers influenced predominantly the interface roughness. The rms interface roughness was about 1.2 nm and 2.0 nm for the Cr layers having the thickness of 10 and 20 nm, respectively. The reason for the different roughness was a different degree of crystallinity of the Cr layers. Narrow Cr layers were nearly amorphous; thicker Cr layers grew crystalline and built facets, which contributed to the observed increase of the interface roughness. The crystallinity of Cr layers could also be controlled by the energy of the carbon ions. Moreover, this ion energy affected the ratio of the sp^3/sp^2 bonds in the ta-C films.

11:00am **F1-1-10 Hydrogen Incorporation on the Improvement of Electrical Characteristics for IGZO TFT**, ***S.-Y. Huang*** *(d982030008@student.nsysu.edu.tw), T.-C. Chang, M.-C. Chen, S.-C. Chen, S.-W. Tsao*, National Sun Yat-sen University, Taiwan

In this paper, the hydrogen incorporated InGaZnO (IGZO) thin-film transistors (TFTs) was investigated. The hydrogen was introduced during sputtering IGZO process. The experimental results indicated that the subthreshold swing of the device was greatly improved from 2.34 V/decade to 0.89 V/decade, and the hysteresis phenomenon was reduced. According to X-ray photoelectron spectroscopy (XPS) analyses, the improvements were attributed to that the dangling bonds (or traps) at interface of IGZO film and gate dielectric, and within the IGZO film were passivated by forming O-H bonds. In addition, optical properties were analyzed by using photoluminescence (PL) spectroscopy, with a He–Cd laser as the excitation source. Finally, the secondary ion mass spectrometry (SIMS) measurements were also used to obtain the hydrogen profiles in the IGZO films.

11:20am **F1-1-11 Resistance Switching of MnO$_2$ Thin Film of Nonvolatile Memory Application**, ***Y.-T. Tsai***, National Chiao-Tung University, Taiwan*, T.-C. Chang (tcchang@mail.phys.nsysu.edu.tw),* National Sun Yat-Sen University, Taiwan*, C.-C. Lin, L.-S. Chiang, S.M. Sze, T.-Y. Tseng*, National Chiao-Tung University, Taiwan

Electrical properties and switching mechanism of electron-beam evaporated MnO$_2$ thin films as transition layer of resistive random access memory was investigated in this study. The device with structure Ti/MnO$_2$/Pt shows reproducible and stable resistive switching behavior traced over 2000 times at room temperature. Transmission electron microscopy analyses are used to confirm the crystalline structure of MnO$_2$ on Pt bottom electrode. Secondary ion mass spectrometry reveals a change of oxygen distribution in MnO$_2$ thin film due to material characteristic of variant top electrodes. The current-voltage characteristics of MnO$_2$ with various top electrodes are presented. We suggest that the interface between MnO$_2$ and electrodes play an important role on the resistive switching behavior.

New Horizons in Coatings and Thin Films
Room: Royal Palm 4-6 - Session H1-1

Nanoparticle, Nanowire, Nanotube, and Graphene Thin-Films and Coatings

Moderator: S. Kodambaka, University of California Los Angeles, D. Frankel, Newcastle University

8:00am **H1-1-1 Preparation of Ni-P/Al$_2$O$_3$ Core-shell Structure Nanoparticles by Electroless Deposition with Pd-free Surface Activation**, ***H.T. Hsu****, W.S. Chang,* Feng Chia University, Taiwan*, C.H. Lin,* Industrial Technology Research Institute, Taiwan*, T.J. Yang (yangtj@fcu.edu.tw)*, Feng Chia University, Taiwan

The Al$_2$O$_3$ supported Ni-P core-shell structure nanoparticles has been prepared by electroless nickel plating with Pd-free surface activation method in this investigation. The Al$_2$O$_3$ nanoparticles as a support with diameter about 20-45nm were surface modified with alkaline solution and followed by adsorption of nickel ions at room temperature. Nickel clusters served as catalytic sites for electroless Ni-P plating were obtained by hydrogen gas reduction at 500°C for 2 hours. The Ni-P layers were successfully deposited on the surface of Al$_2$O$_3$ nanoparticles by electroless nickel plating. Characterization of the Ni-P(shell)/Al$_2$O$_3$(core) structure was studied by transmission electron microscopy (TEM), field-emission scanning electron microscopy (FE-SEM) and electron spectroscopy for chemical analysis (ESCA). Core-shell structure was clearly observed by TEM. Surface morphology of alumina nanoparticles with nickel adsorption was examined by FE-SEM. Distribution of nickel and phosphorus on alumina was identified by ESCA.

8:20am **H1-1-2 Gadolinium-Doped Ceria Particle Films for Intermediate-Temperature Gas Sensing Applications**, ***C.-Y. Chen*** *(chencyi@fcu.edu.tw), C.-L. Liu, P.-L. Sun, C.-J. Chang, C.-K. Lin*, Feng Chia University, Taiwan

In the present study, nanocrystalline ceria powders with and without various amounts of gadolinium (Gd) were synthesized by a spray pyrolysis (SP) process. The resulting powders were firstly mixed with organic binders, screen printed on alumina substrates and then sintered at 1200°C for 2 h in air. The SP powders were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM) and transmission electron microscopy (TEM). In addition, gas sensing properties of Gd-doped ceria (GDC) films printed from the corresponding powders were investigated as a function of operation temperature. Experimental results showed that the as-pyrolyzed GDC powders were nanocrystalline and spherical in shape with uneven surfaces. The grain size of ceria decreased with increasing Gd content. The coated particles showed a 3-D network structure with interconnected pores exhibiting a high surface area. The ionic conductivity of ceria films was increased with the increase of Gd content and the elevated operation temperature. The Arrhenius plots for the conductivity of GDC coatings indicated that the activation energy of ceria can be decreased from 1.11 eV for undoped ceria to 0.99 eV for 20GDC (20mol% Gd-doped ceria) at a temperature range from 650°C to 800°C .

8:40am **H1-1-3 Carbon Onions, Some Methods of Preparation and Possible Applications**, ***L. Siller*** *(Lidija.Siller@ncl.ac.uk)*, Newcastle University, United Kingdom **INVITED**

Carbon onions consist of closed fullerene-like shells enclosed within one another or multishell fullerenes. We will give short overview of various approaches for carbon onion synthesis, their properties and the most recent applications [1].

Our group has developed method of functionalsisation of carbon onions [2]. The functionalization of onion-like carbon (OLC) nanoparticles with anthracene by direct covalent bonding is confirmed by XPS and Mid-IR and UV spectroscopy [2]. The new chemical route is based in the bromine/lithium exchange, commonly used for aliphatic compounds, applied here to aromatic carbon. Our results provide a new procedure for the chemical functionalization of the OLC nanoparticles, which could be also a new route to functionalization of other families of carbon nanoparticles.

In addition we studied the potassium intercalation of onion-like carbon (OLC) samples consisting of aggregates of carbon onions by photoemission spectroscopy. OLC samples were initially prepared by annealing nanodiamonds (3-20 nm in diameter) at 1800 K in vacuum [3]. The resulting OLC consists of closed fullerene-like shells. The ‘closed’ OLC was subsequently treated with carbon dioxide at 1020 K in order to open the carbon shells by partial oxidation to create ‘opened’ OLC. Core-level and valence-band photoelectron spectroscopy have both been employed in characterizing the changes in electronic structure of the samples [3]. Upon intercalation of the closed OLC with K the C1*s* core-level and valence band features shift to higher binding energies and the density of states at the Fermi level increases, while this effect is significantly smaller for intercalated opened OLC. These results indicate that opening the shells of carbon onions allows potassium to penetrate inside the particles and thus opens up a possible route to fill carbon onions with desired substances and their application as nanocapsules [3].

[1] “Carbon Onions”**,** Y. V. Butenko, L. Šiller and M.R.C. Hunt in *Handbook of Nanophysics,* CRC Press LLC, *in press.*

[2] A.C. Brieva, C. Jeger, F. Huisken, L. Siller, Y.V. Butenko, *Carbon*, 47, 2912 (2009)

[3] Y.V. Butenko, A.K. Chakraborty, N. Peltekis, S. Krishnamurthy, V.R. Dhanak, M.R.C. Hunt and L. Siller, *Carbon*, 46, 1133 (2008)

9:20am **H1-1-6 Formation and Nonvolatile Memory Characteristics of W Nanocrystals by In-Situ Steam Generation Oxidation**, ***S.-C. Chen*** *(scchen0213@gmail.com),* National Tsing Hua University, Taiwan, *T.-C. Chang,* National Sun Yat-Sen University, Taiwan, *C.-M. Hsieh, S.M. Sze,* National Chiao Tung University, Taiwan, *W.-P. Nien, C.-W. Chan,* ProMOS Technologies, Taiwan, *F.-S. Huang*, National Tsing Hua University, Taiwan

The authors provide the formation and memory effects of W nanocrystals nonvolatile memory in this study. The charge trapping layer of stacked a-Si and WSi$_2$ was deposited by low pressure chemical vapor deposition (LPCVD) and was oxidize d by in-situ steam generation system to form uniform W nanocrystals embedded in SiO$_2$. Transmission electron microscopy analyses revealed the microstructure in the thin film and X-ray photon-emission spectra indicated the variation of chemical composition under different oxidizing conditions. Electrical measurement analyses showed the different charge storage effects because the different oxidizing conditions influence composition of trapping layer and surrounding oxide quality. Moreover, the data retention and endurance characteristics of the formed W nanocrystals memory devices were compared and studied. The results show the reliability of the structure with 2% hydrogen and 98% oxygen at 950℃ oxidizing condition has the best performance among the samples.

9:40am **H1-1-7 Fabrication and Memory Effect of Nickel Nanocrystals Formed by Co-Evaporating with Dielectric Pallets**, ***C.-W. Hu*** *(cwhu.ee94g@gmail.com),* National Chiao-Tung University, Taiwan, *T.-C. Chang,* National Sun Yat-Sen University, Taiwan, *C.-H. Tu,* National Chiao-Tung University, Taiwan, *Y.-H. Huang,* National Tsing Hua University, Taiwan, *C.-C. Lin,* National Chiao-Tung University, Taiwan, *M.-C. Chen,* National Sun Yat-Sen University, Taiwan, *F.-S. Huang,* National Tsing Hua University, Taiwan, *S.M. Sze, T.-Y. Tseng*, National Chiao-Tung University, Taiwan

In this work, we propose a novel method to fabricate nickel nanocrystals structure by co-evaporatin Ni and SiO$_2$ pallets, simultaneously. A high density nanocrystals distribution about 4.5×10^{12} cm^{-2} was found after a 800℃ rapidly thermal annealing process. Moreover, the co-evaporated method to form Ni nanocrystals reveals multi- and single-layer structure after 700 and 800℃ annealing process, respectively. The detailed formation mechanisms for the different nickel nanocrystals structure of each temperature have been discussed. It is believed that the distributed nucleation sites of the co-evaporated film play an important role in the nanocrystals formation. In addition, we also compared with the memory devices by using the formed nickel nanocrystals structures as the charge trapping layer. The nickel nanocrystals memory devices show an obvious memory and good reliability characteristics in the electrical measurements. The results also confirm that the co-evaporated method to form the nanocrystals structure is easy and potential to apply into the current memory device.

10:00am **H1-1-8 Observation of Single Colloidal Platinum Nanocrystal Growth Trajectories**, ***H. Zheng*** *(hmzheng@lbl.gov), R. Smith,* Lawrence Berkeley National Lab, *J.-W. Jun,* University of California at Berkeley, *C. Kisielowski, U. Dahmen,* Lawrence Berkeley National Lab, *P. Alivisatos*, University of California at Berkeley **INVITED**

Colloidal nanocrystals have shown great potential applications in advanced nanotechnological devices. In order to achieve the desired functionalities, it is essential to understand nanocrystal growth mechanisms and further control their syntheses. However, due to the lack of direct observations of their growth the proposed mechanisms of nanocrystal growth are still controversial. For example, the classical model for the growth of monodisperse nanocrystals assumes a discrete nucleation stage followed by growth via monomer attachment, but has overlooked particle-particle interactions. Recent studies have suggested that interactions between particles play an important role. In this work, we show that it is possible to directly observe the growth trajectories of individual colloidal platinum nanocrystals in solution using a liquid cell that operates inside a transmission electron microscope (TEM). It reveals a set of growth pathways more complex than those envisioned previously. Both monomer attachment from solution and particle coalescence have been observed. Through the combination of these two processes, an initially broad size distribution can spontaneously narrow into nearly monodisperse. We suggest that colloidal nanocrystals take different pathways of growth based on their size- and morphology-dependent internal energies. At the end of this talk, the significance of the ability of imaging through liquids with nanometer resolution in different nanocrystal systems as well as in different areas will be discussed.

10:40am **H1-1-10 Substrate-Induced Semiconducting Graphene on Palladium**, ***S.-Y. Kwon*** *(sykwon@unist.ac.kr),* Ulsan National Institute of Science and Technology (UNIST), Korea, *C.V. Ciobanu,* Colorado School of Mines, *V. Petrova,* University of Illinois at Urbana-Champaign, *V.B. Shenoy,* Brown University, *J.B. Bareno,* University of Illinois at Urbana-Champaign, *V.G. Gambin,* Northrop Grumman Space and Technology, *I. Petrov,* University of Illinois at Urbana-Champaign, *S. Kodambaka*, University of California Los Angeles

Using *in situ* variable-temperature scanning tunneling microscopy, we demonstrate the formation of epitaxial graphene during the deposition of ethylene on the Pd(111) surface. We observe the growth of monolayer graphene islands, 20 nm to 200 nm in size, upon exposure to ethylene (5×10^{-7} Torr-5×10^{-8} Torr) at temperatures between 723 K and 1023 K for prolonged times (> 1 h). The experiments show that graphene domains are bounded by Pd surface steps and have a Moiré superstructure with a typical spatial periodicity of 2.1±0.1 nm. Surprisingly, we find that the topographic image contrast reverses when the tunneling bias is reversed, which suggests a semiconducting nature of the epitaxial graphene layer. Scanning tunneling spectroscopy measurements indicate that the graphene islands are semiconducting, with a bandgap of 0.3±0.1 eV. Using density functional theory calculations, we attribute this phenomenon to a strong interaction between graphene and the nearly commensurate Pd substrate. Our findings suggest the possibility of preparing semiconducting graphene layers for future carbon-based nanoelectronic devices via direct deposition onto strongly interacting substrates.

11:00am **H1-1-11 Synthesis of Graphene Oxide (GO): Effects of Processing Steps and Parameters on the Resulting GO Thin Film**, ***T.T. Wu***, *J.-M. Ting (jting@mail.ncku.edu.tw)*, National Cheng Kung University, Taiwan

One of the popular synthesis methods for making graphene oxide (GO) is based on the Hummer process. However, little or no information is available regarding the details of the fabrication of GO. We have assessed in this study some critical steps and parameters during the synthesis of GO based on the Hummer process. They include the rates at which the relevant chemicals and solvents are added into the processing bath, the compositions and concentrations of the processing bath, and the bath temperature. The resulting GO were dispersed in either water or Tetrahydrofuran. The suspension fluids, having various GO concentrations, were then spun on to polyethylene terephthalate substrates. The obtained transparent, conducting samples are then subjected to flexibility tests and characterized for the optical and electrical properties. The characterizations were performed before and after the flexibility tests. Correlation between the GO processing steps and parameters to the characteristics of the transparent, conducting films are reported.

Bioactive Coatings and Surface Biofunctionalization
Room: Sunset - Session TS3-1

Moderator: S. Kumar, University of South Australia, E. Saiz, Lawrence Berkeley National Laboratory

8:00am **TS3-1-1 Functionalization of Implant Surfaces**, ***J. Jansen*** *(j.jansen@dent.umcn.nl)*, Radboud University Nijmegen Medical Center, The Netherlands **INVITED**

The increase in life expectancy is associated with an increase in diseases. As a consequence, there will be an increase in diseases that can be associated with ageing, like different types of cancer, diabetes, joint problems, tooth loss, etc. Those maladies do not have only a negative effect for the patient, but will also have a significant impact on our health care system. Therefore, it is extremely important that more active, less traumatic and less expensive methods and techniques are developed for the treatment and curing of these diseases.

Implants and tissue substitutes are made from (bio)materials that have one common property, i.e. biocompatibility. A promising application of nanotechnology is the development of better functioning biomaterials, as e.g. applied in craniofacial surgery for the replacement of lost teeth, bone and temperomandibular joints. The currently available biomaterials as used for the manufacturing of implants and tissue substitutes do not fulfill completely to its intended function. This is due to an un-natural response between the biomaterial and the surrounding tissue cells.

A recent approach to the design of next-generation tissue regeneration supporting biomaterials is focusing on the more dimensionally intricate characteristics of surfaces, i.e. structure at the nanometer scale. The underlying hypothesis is that nanometer structure matches with the natural extracellular matrix resulting in an improved interaction of the tissue-forming cells compared with conventional biomaterials. Recent developments in the field of nanotechnology offer powerful tools to modify the surface of biomaterials by introducing artificial topography and specific surface chemistry on the material. It is well-known that both topography and surface chemical composition affect the reactions of the biological environment to the device.

The current lecture will deliver the relevant knowledge of the biomaterial surface parameters that control the biological response and can be used for implant surface functionalization.

8:40am **TS3-1-3 Corrosion and Tribological Properties of PVD and CVD Coatings in a Simulated Biomedical Environment**, *L. Wang*, ***X. Nie*** *(xnie@uwindsor.ca)*, University of Windsor, Canada

PVD and CVD hard ceramic coatings are expected to be the new biomaterials for load-bearing devices including orthopedic implants, pacemakers, surgical instruments, orthodontic appliances and dental instruments. Currently, the investigations of PVD and CVD coatings for biomaterial applications are mainly focus on TiN and DLC coatings. The reports on other coating systems are very limited. In this study the corrosion property of coatings was investigated in a simulated body fluid (SBF) environment, and the tribological property against polyethylene biomaterial was characterized in order to exam the feasibility of various hard coatings for load-bearing medical devices and implants . The results indicated that TiN, CrN and DLC coatings could achieve higher corrosion polarization resistance and corrosion potential in the SBF environment than the uncoated SS316L. However, both TiAlN and CrAlN coatings had a much lower corrosion polarization resistance and corrosion potential, even worse than the uncoated stainless steel. The superior corrosion protection performance of CrN and TiN could be due to the Cr-O and Ti-O passive layer formation on the coating surfaces which protected the coating from further corrosion. The good corrosion property of DLC coating was likely due to its chemical inertness under the SBF condition. TiN and DLC coatings presented a good wear resistance and chemical stability during the sliding tests with SBF. The uncoated and CrN-coated stainless steel samples were not compatible with polyethylene materials in terms of their tribological properties in the tested SBF condition.

9:00am **TS3-1-4 Comparison of Tribological and Anti-Microbial Properties of CrN/Ag, ZrN/Ag, TiN/Ag, and CrN/Cu Nanocomposite Coatings**, ***P. Kelly*** *(peter.kelly@mmu.ac.uk), H. Li, K.A. Whitehead, J. Verran,* Manchester Metropolitan University, United Kingdom, *R.D. Arnell,* University of Central Lancashire, United Kingdom, *I. Iordanova*, University of Sofia, Bulgaria

Nanocomposite coatings including CrN/Ag, ZrN/Ag, TiN/Ag and CrN/Cu w ith varying silver or copper contents were produced by co-deposition in a dual pulsed magnetron sputtering system. The composition and structure of the coatings were characterised using energy dispersive X-ray spectroscopy (EDX), scanning electron microscopy (SEM) and X-ray diffraction (XRD), and the physical and tribological properties were assessed by means of nanoindentation, scratch adhesion testing and thrust washer wear testing. Although increasing silver content provided a reduction in the coefficient of friction, this was accompanied by reductions in hardness and wear resistance. Zones of inhibition were used to determine the extent of silver ion release from the coating surfaces, and a NBT (nitro-blue tetrazolium) redox dye was used to determine the anti - microbial effectiveness of the coatings following incubation. The microorganisms tested were *Pseudomonas aeruginosa, Escherichia coli (E. coli)* and *Staphylococcus aureus*. For the NBT assays, significant reductions in the number of viable cells were observed with increasing Ag or Cu content, compared to the 'pure' nitride surfaces. Whilst no zones of inhibition were observed for *S. aureus*, on any of the surfaces, the diameter of the 'kill' zones generally increased with increasing silver content for the other microorganisms.

9:20am **TS3-1-5 Development of Si_xO_y Surface Modifications for Improved Bonding in Biomedical Implants**, ***J Piascik*** *(jpiascik@rti.org),* RTI International, *S Wolter,* Duke University, *S Grego, B. Stoner*, RTI International

A contributing factor to orthopaedic implant and dental prosthesis failure is inadequate bonding between the device and underlying structure. Resin cements and adhesives have long been developed to increase bond strength through specific chemical bonding. More recently, there has been a significant push to use high strength ceramics (i.e. zirconia and alumina), but because of the non-reactive nature of such materials, a long-term, reliable chemical bond is difficult to achieve. An earlier study presented a promising surface-modification technology, whereby a silica-like thin film (<10nm) can be deposited on the surface thus enabling covalent bonding with conventional cements and silanation techniques [1]. A point of concern for such a thin coating is optimizing the coverage and correlating it with surface roughness. It was thus hypothesized that a surface with near 100 percent coverage would be optimal for bonding improvement. This study investigated the effect of silica coating thickness and post deposition treatments on the bonding structure and coverage of zirconia ceramics. X-ray photoelectron spectroscopy (XPS) was used to evaluate the chemical binding of the surface coating and atomic force microscopy (AFM) was used to analysis surface roughness. A novel surface modeling algorithm was also used to determine the percent surface coverage of the functional molecules in the context of a rough, non-planar surface. Initial data indicate that the chemical structure of the Si_xO_y surface modifications is thickness dependant and stochiometry may be modified via the aforementioned post-treatment. These data help to explain the earlier reported response to film thickness on zirconia-to-composite adhesion and enable the development of a more robust thickness and roughness independent pretreatment.

[1] J.R. Piascik, E.J. Swift, J.Y. Thompson, S. Grego, BR Stoner, "Surface modification for enhanced silanation of zirconia ceramics", Dent. Mat. **25** (2009) 1116-21.

9:40am **TS3-1-6 Study of Bactericidal Efficiency of Magnetron Sputtered TiO_2 Films Deposited at Varying Oxygen Partial Pressure**, ***I. Banerjee*** *(indranibanerjee@bitmesra.ac.in), A. Bihari Panda, P. Laha, K. Harish, B. Sarkar, P.K. Barhai,* Birla Institute of Technology, India*, A. Das,* Bhabha Atomic Research Center, India*, Mahapatra*, Birla Institute of Technology, India

TiO_2 thin films have been deposited at different O_2 / (Ar + O_2) gas ratios (0.2, 0.3, 0.5 and 0.6) by R.F reactive magnetron sputtering at a constant power of 200 watt. The formation of TiO_2 was confirmed by X-Ray Photoelectron Spectroscopy (XPS). The oxygen percentage in the films was found to increase with increase in oxygen partial pressure during deposition. Band gap of the films were calculated from the UV-Visible transmittance spectra. Increase in oxygen content in the films showed substantial increase in optical band gap from 2.2 eV to 3.6 eV. Optical contact angle and surface free energy of the films was found to vary with oxygen partial pressure. The films turned hydrophobic to hydrophilic (from 100.8^0 to 48^0) due to decrease in oxygen partial pressure during deposition. The surface free energy increased from 22.15 mN/metre to 56.36 mN/metre with the decreasing O_2 partial pressure. The bactericidal efficiency of the deposited films was investigated using Escherichia coli cells under 1hr UV irradiation. The growth of E coli cells was estimated through the Optical Density measurement by UV-Visible absorbance spectra. The qualitative analysis of the bactericidal efficiency of the deposited films after UV irradiation was observed through SEM. A correlation between the surface free energy, optical band gap and bactericidal efficiency of the TiO_2 films at different oxygen partial pressure have been studied.

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

Coatings to Resist High Temperature Oxidation
Moderator: Y. Zhang, Tennessee Technological University, D. Naumenko, Forschungszentrum Jülich GmbH

1:30pm **A1-2-2 NiAl(CrZrHfSi) High Temperature Overlay Coating for Gas Turbine Engines**, ***B.T. Hazel*** *(brian.hazel@ge.com), R. Darolia, M.H. Rucker*, General Electric

As jet engine high-pressure turbine (HPT) inlet temperature increase, new designs and materials are used to achieve the desired durability and reliability. Protective coatings on HPT blades have evolved from the use of simple aluminides to noble-metal aluminides as performance demands have increased. In the most demanding applications, insulating ceramic thermal barrier coatings (TBC's) are applied over the diffusion aluminides to further reduce the bulk and surface temperatures of the component. The use of advanced environmental coatings and TBC systems in turbine engines has become necessary for protection of turbine airfoils and other gas turbine components. The bond coat plays a significant role in the material system environmental resistance, adhesion of the ceramic TBC and the overall life and capability of the TBC system. Recent GE Aviation bond coat development has focused on reactive element modified beta phase NiAl overlay coatings to further reduce oxide growth rates. The result is longer TBC adherence lives and greater environmental resistance for turbine airfoil operation.

1:50pm **A1-2-3 Effects of Substrate Surface Roughness and Microstructure on the Properties of dc Magnetron Sputter Deposited NiAl-Hf and NiAl-Cr-Hf Coatings**, ***M.L. Weaver*** *(mweaver@eng.ua.edu), M.A. Bestor, M.S. Kirsch, J.P. Alfano*, The University of Alabama

This paper describes the influences of substrate roughness and processing variables on the properties of NiAl-Hf and NiAl-Cr-Hf overlay bond coatings deposited via dc magnetron sputtering. Coatings were deposited onto single crystal René N5 and CMSX-4 Ni-based superalloys followed by post deposition annealing at 1000°C for in flowing Ar+5%H_2. The as-deposited coatings were found to consist of a single phase, b -NiAl, with columnar zone 2 microstructures. All of the coatings were found to contain leader defects, the number of which could be significantly decreased by reducing substrate surface roughness. However, surface roughness was observed to have no significant influence on coating adhesion. Post-deposition annealing was conducted at 1000°C to induce interdiffusion and to bring solutes out of solid solution. This resulted in the formation of a series of nanometer-scale precipitates within the coating and in the formation of a thin interdiffusion zone. The influences of these post-deposition heat treatments and of post-deposition peening prior to heat treatment on the isothermal and cyclic oxidation performance at 1050°C will be discussed.

2:10pm **A1-2-4 Formation of High Temperature Multifunction Coatings on the Basis of Spherical Al Particles**, ***V. Kolarik*** *(vladislav.kolarik@ict.fraunhofer.de), M. Juez Lorenzo, P. Kodjamanova, H. Fietzek*, Fraunhofer ICT, Germany

Spherical Al particles in the size range of 2 to 10 µm oxidise at high temperatures forming hollow spheres from alpha-Al_2O_3. Depositing such Al particles on a substrate alloy by brushing or spraying and subjecting them to a heat treatment, coating structures are obtained that consist of an aluminised diffusion zone and an adherent quasi-foam top coat from sintered hollow alumina spheres, which has the potential to effectuate as a thermal barrier by gas phase insulation. The present work aims at understanding the mechanisms and investigating the appropriate parameters for the design of multifunction coatings.

Spherical Al particles sized in the range of 2 to 10 µm were deposited with different binder/plastisizer systems by brushing on Alloy 347H and IN738 obtaining a coating with an average thickness of 60 µm. For understanding the influence of temperature on the oxidation of the particles, the samples were subjected to a step-wise heating from room temperature up to 1400°C with steps of 50°C. At each step an XRD pattern was recorded in situ. The results show a temperature range, in which transient alumina phases with an amorphous structure are formed, followed by the formation of alpha-alumina on further heating.

For investigating the heat treatment for the coating formation, the samples were subjected to 1 to 4 h at 400°C and 500°C for curing and then to 5 h at 700°C to 900°C for forming the coating structure. Coating structures are encountered that consist of a quasi-foam top coat from hollow alumina spheres and a diffusion layer below that forms a protective alumina scale. Depending on the parameters of the thermal treatment, the sintering of the hollow alumina spheres to each other and the adherence of the top coat to the substrate is more or less pronounced. The formation of the diffusion zone and the adherence is influenced by the binder.

The structure stability and oxidation behaviour of the system was studied up to 2000 h. The adherence of the top coat depends strongly on a good and homogeneous contact during the thermal treatment. This can be controlled by the selection of an appropriate binder system. Only small amounts of brittle aluminide phases were found in the diffusion zone and no cracking was observed. A protective alumina scale is formed on the diffusion zone surface.

It can be concluded that the approach by particle size processing opens a potential for obtaining a complete thermal barrier coating system in one manufacturing step.

2:30pm **A1-2-5 Platinum Group Metal-Containing Bond Coats**, ***T. Pollock*** *(tresap@umich.edu), D. Widrevitz, R. Adharapurapu, J. Zhu*, University of Michigan, *D.M. Lipkin*, GE Global Research Center**INVITED**

Platinum group metal (PGM) additions and their influence on bond coat properties have been investigated in B2 and γ – γ’ bond coats. Overlay B2 coatings with Cr and varying amounts Hf and Pt or Pd on a superalloy substrate have been studied using a combinatorial technique. While Pd is diffusionally depleted to a greater degree than Pt during oxidation, the cyclic oxidation kinetics of Pd and Pt-containing coatings were similar in the temperature range 1100˚C – 1150˚C. During cyclic oxidation, the B2 coatings evolve to a γ’ structure. A synergistic, beneficial effect of Pt+Hf and Pd+Hf was observed. In two-phase γ + γ‘ materials, platinum additions as low as 2.5at% improve oxidation. Large changes in elemental partitioning between the γ and γ‘ phases occurs with additions of Pt, Ir and Ru. Changes in partitioning strongly influence precipitate-matrix misfit and the resultant creep resistance. Tradeoffs between creep resistance and oxidation in PGM-containing systems will be discussed.

3:10pm **A1-2-7 High-Temperature Behavior of Magnetron Sputtered Si-B-C-N Materials Far Above 1000°C**, ***P. Zeman*** *(zemanp@kfy.zcu.cz), S. Proksova, R. Cerstvy, J. Vlcek*, University of West Bohemia, Czech Republic

Operating a large number of construction materials in very aggressive environments of diverse industrial processes demands to develop new functional coatings protecting effectively the surface of these materials against oxidation and corrosion at temperatures exceeding 1000°C. Such coatings have to be thermally stable without any degradation of their structure and properties. Recently, novel amorphous Si-B-C-N coatings, which may accomplish all of these criteria, have been successfully prepared by magnetron sputtering in our laboratories. Their excellent oxidation resistance, due to the formation of an amorphous surface SiO_2-based layer containing boron [1-2], even above 1500°C during dynamical heating in flowing air, has stimulated the present study extending our knowledge about thermal stability and oxidation kinetics of these coatings. The Si-B-C-N coatings magnetron sputtered from a single B_4C-Si target in a nitrogen-argon gas mixture at optimum process parameters were investigated by means of differential scanning calorimetry (Labsys DSC 1600) and symmetrical thermogravimetry (TAG 2400). The structure of the coatings was characterized primarily by X-ray diffraction. Freestanding coating fragments without a substrate were used as specimens for the experiments in order to eliminate an influence of a substrate. It was found that the magnitude of the N/(Si+B+C) concentration ratio is of a key importance to achieve ultra-high thermal stability of the coatings. When this ratio is sufficiently high, the Si-B-C-N material retains its amorphous structure in inert gases up to 1600°C . Analysis of oxidation kinetics revealed concurrently that the oxidation rate constants at temperatures ranging from 1100 to 1300°C are very low, which is caused especially by a low number of diffusion channels in the protective oxide layer being formed on the surface of the Si-B-C-N coatings.

[1] J. Vlcek, S. Hreben, J. Kalas, J. Capek, P. Zeman, R. Cerstvy, V. Perina, Y. Setsuhara, J. Vac. Sci. Technol. A 26, 1101 (2008).

[2] J. Capek, S. Hreben, P. Zeman, J. Vlcek, R. Cerstvy, J. Houska, Surf. Coat. Technol. 203, 466 (2008).

3:30pm **A1-2-8 Oxidation Behavior of Si-Doped Nanocomposite CrAlSiN Coatings**, ***H.-W. Chen***, *J.-G. Duh (jgd@mx.nthu.edu.tw)*, National Tsing Hua University, Taiwan

Recently more and more hard coatings greatly emphasize the importance of oxidation characteristics, and this study thus attempts to dope Si into conventional CrAlN to form CrAlSi$_x$N coatings by RF magnetron sputtering on a silicon wafer to investigate how Si content affects oxidation behavior. The oxidation resistance of the CrAlSi$_x$N coatings was evaluated after annealing with temperature ranging from 800 to 1000 ℃ . The X-ray diffraction pattern revealed that CrAlSi$_x$N (x = 0.3~11.5) coatings exhibited better oxidation resistance than that of traditional CrAlN coatings. Observed from SEM, the CrAlSi$_x$N coatings presented denser structure than CrAlN coatings. The columnar structure, typically existing in CrAlN coatings and harmful to oxidation behavior, was also eliminated. Doping certain Si content could indeed help CrAlN coatings prolong diffusion paths due to their reduced gain sizes, thereby effectively inhibiting outside oxygen from penetrating into the coatings. Additionally, two fine Al_2O_3 and SiO_2 layers given by the CrAlSi$_x$N coatings when oxidized could also serve as protective layers to enhance oxidation resistance by slowing oxygen diffusion. To sum up, the overall antioxidative capability of the CrAlSi$_x$N coatings after doping Si was significantly improved at elevated temperature due to the barriers resulted from dense structure and the said two fine protective layers prevented outside oxygen from diffusing into the coatings.

3:50pm **A1-2-9 TaN$_x$ Diffusion Barrier on Cobalt Cemented Tungsten Carbide***, Y.-I. Chen (yichen@mail.ntou.edu.tw), B.-L. Lin,* ***Y.-C. Kuo***, National Taiwan Ocean University, Taiwan

To prevent the diffusion out of cobalt from cemented carbides at high working temperature, TaN$_x$ coatings were prepared as a diffusion barrier by direct current magnetron sputtering using a Ta target in an argon-nitrogen atmosphere. The nitrogen flow ratio, $N_2/(Ar+N_2)$, in the sputtering process varied from 0.1 to 0.4. The deposition rate reduced as the nitrogen flow ratio increased. Silicon wafers and 6 wt.% cobalt cemented tungsten carbide were used as the substrates. Effects of nitrogen flow ratio on crystalline characteristics and mechanical properties of the TaN$_x$ coatings were examined by X-ray diffraction and nano-indenter, respectively. The TaN$_x$ coatings were annealed at 500, 600, 700, and 800°C for 4 hours in air, respectively. The diffusion barrier performance was evaluated by Auger electron spectroscopy depth profiles and X-ray diffraction. Oxidation resistance of the TaN coatings was also investigated. Orthorhombic Ta_2O_5 was observed after annealing above 700°C. The hardness declined with increasing annealing temperature due to the formation of the oxide compound with a lower hardness.

4:10pm **A1-2-10 Advanced High Temperature Coatings for Turbine Blade Applications:** *A REVIEW, F. Ghadami (farzin.ghadami@gmail.com)*, University of Tehran, Iran

Within all coating systems, for protection tasks, advanced high temperature coatings are the most successful and utilizable because of the very wide range of coating materials and substrates that can be processed specially in turbine component application. Surface science and engineering is now a key materials technology in the design of future advanced turbine Engine parts especially for blades and vans. In this literature, the scope of turbine blade coating is described in terms of the various processes, requirements, coating properties and new applications. Besides, the variety of coating materials including diffusion and overlay coatings are presented. In addition, turbine blade deposition, coating deposition methods such as vapor deposition and plasma spray and also miscellaneous applications are investigated.

Hard Coatings and Vapor Deposition Technology
Room: Town & Country - Session B6-3

Hard and Multifunctional Nano-Structured Coatings

Moderator: C.P. Mulligan, U.S. Army ARDEC, Benét Laboratories, R. Sanjines, EPFL, P. Zeman, University of West Bohemia

1:30pm **B6-3-2 Hard and Decorative Coatings Based on Nanocomposites Consisting of Dielectric Matrixes Embedded with Metal Nanoparticles***,* ***A. Cavaleiro*** *(albano.cavaleiro@dem.uc.pt)*, University of Coimbra, Portugal **INVITED**

Colour derived from Au nanoparticles embedded in a dielectric matrix is a phenomenon well known from the Middle Age, used for producing coloured glass windows for cathedrals. Depending on either the size, content and distribution of the Au nanoparticles or the dielectric constants of the used matrix a large variety of colours can be obtained due to the so called Surface Plasmon Resonance (SPR) effect. SPR is related to the cooperative oscillation of the free electrons of Au which promote strong absorption of particular bands of visible light giving rise to intense colour.

The aim of this research was to use this "old" idea for producing hard and coloured coatings for decorative applications. It is intended to produce a matrix of a dielectric material with high hardness, in order to guarantee a high abrasion and wear resistance, and therein insert in a controlled way Au nanoparticles. Different matrixes based on oxides are being studied (Al-O, Ti-O, W-O and Sn-O) which allow to interfere directly and indirectly (by determining the ability for the precipitation of Au nanoparticles) on the final colour of the films. The Au parameters are being controlled by the Au amount added to the matrix, the deposition conditions and the post-deposition thermal treatment.

The coatings were deposited by sputtering from a metal (Al, W, Ti, Sn) target embedded with thin gold plates, in a reactive environment containing oxygen. The O_2 flow was high enough for working in compound mode producing transparent dielectric films. The Au content was varied from 0 up to 20 at.%. In the as-deposited conditions structures varying from amorphous, through nanocrystalline up to crystalline could be achieved. Subsequently, the films were heat treated to promote further segregation of the Au metallic nanocrystals. The precipitation is easily enhanced for the (nano)crystalline films but revealed quite difficult in case of amorphous matrixes. The size and distribution of the Au nanoparticles is being studied by X-ray diffraction and transmission electron microscopy. Hardness as high as 20 GPa is measured in some cases, being the hardest matrix the Al-O. The best optical behaviour from the point of view of varied colours is being obtained with coatings from the Ti-O and W-O systems.

2:10pm **B6-3-4 Ag Solid Lubricant Transport in CrN-Ag Nanocomposite Coatings***,* ***C.P. Mulligan*** *(c.mulligan@us.army.mil),* U.S. Army ARDEC, Benét Laboratories*, T.A. Blanchet, D.G. Gall*, Rensselaer Polytechnic Institute

Inclusions of noble metals such as Ag show promise as solid lubricating phases in hard matrices, providing reduced friction and increased wear resistance over a wide temperature range. CrN-22 at.% Ag composites were deposited by reactive magnetron co-sputtering at growth temperatures T_s = 300-700°C. 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 key parameter that determines lubricant transport is $\Delta T = T_a - T_s$. For $\Delta T < 0$, Ag is immobile and remains entirely within the CrN matrix, while $\Delta T > 0$ results in mass transport to the surface with a rate that increases with increasing ΔT. For example, the fraction of Ag that diffuses to the surface during annealing for 20 minutes increases from 0.7% to 8%to 26% for ΔT = 25, 125, and 225°C, respectively. In order to inhibit lubricant transport, a 200 nm thick dense CrN cap-layer is applied, providing additional control over mass transport to the surface. Ball-on-disk testing against alumina counterfaces shows sustained friction coefficients ≤ 0.2 over the testing temperature range of 450-650°C.

2:30pm **B6-3-5 Adaptive VN/Ag Nanocomposite Coatings in the 25 to 1000°C Temperature Rante***,* ***S.M. Aouadi*** *(saouadi@physics.siu.edu), D. Stone, D.P. Singh, A. Abu-Nada,* Southern Illinois University Carbondale*, K. Polychronopoulou, F. Nahif, C.G. Rebholz,* University of Cyprus*, C. Muratore, A.A. Voevodin*, Air Force Research Laboratory

A two-phase nanocomposite system that consists of inclusions of silver in a vanadium nitride matrix (VN/Ag) was investigated as a potential adaptive coating with reduced friction coefficient from 25 to 1000°C. This nanocomposite structure was selected based on the premise that silver will migrate to the surface of these coatings to act as a lubricant in the 25 to 500 °C temperature range. At higher temperatures, silver and vanadium were expected to react with oxygen to form a lubricious silver vanadate film on the surface. The VN/Ag coatings were deposited using unbalanced magnetron sputtering as a function of silver content and their elemental composition was evaluated using X-Ray photoelectron spectroscopy. The friction coefficients were measured to be 0.35, 0.30, 0.10 and 0.2 using a pin-on-disc tester at 25°, 350°C, 700°C, and 1000°C, respectively. Raman spectroscopy and x-ray diffraction (XRD) revealed the formation of silver orthovanadate (Ag_3VO_4) as well as vanadium oxide on the surface of these coatings. Finally, real time Raman spectroscopy and XRD were utilized to understand the structural and chemical changes that these materials go through as a function of temperature. These techniques revealed very useful information regarding processes that occur with an increase in temperature that include phase segregation, phase changes, and melting. These observations were correlated to the tribological properties of these materials under the selected testing conditions.

2:50pm **B6-3-6 Ag -T i(C, N)-Based Coatings for Biomedical Applications: Influence of Composition and Structure on the Mechanical/Tribological and Biological Behaviour**, *S. Ribeiro,* Universidade do Minho, Portugal, *J.C. Sánchez-Lopéz, M.D. Abad,* Instituto de Ciencia de Materiales de Sevilla (CSIC-US), Spain, *R. Escobar Galindo,* Instituto de Ciencia de Materiales de Madrid (ICMM -CSIC), Spain, *M. Henriques, **S. Carvalho** (sandra.carvalho@fisica.uminho.pt)*, Universidade do Minho, Portugal

Application of thin films in the biomedical engineering field represents an attractive challenge due to the multiple situations where they may improve or even functionalize a certain part of human body. Implants are one of such cases, representing one of the most active fields within the so-called biomaterials R&D. Implant failure is a huge problem for both the patient and governmental agencies, once it involves repeated surgeries and consequently considerable economical resources as well as patients' death. This failure can be attributed to excessive wear and wear debris and also to microbial infection. Additionally, the use of several kinds of carbon/nitride-based thin films has been carried out in the group, with some promising results. Thus, the main aim of the present work is to study such carbon/nitride-based thin films, namely in what concerns the Ag addition to well-known TiCN thin films by DC unbalanced reactive magnetron sputtering.

The obtained Ag-Ti(C,N) based coatings were characterized in terms of composition and structure as well as in terms of biological properties. Mechanical/tribological resistance of the films was achieved by hardness testing in combination with friction and wear measurements. The tribological response was studied under biological fluid using reciprocating pin-on disk configuration. Biological properties were assessed both in terms of cytotoxicity, by the evaluation of animal cell death induced by the material, and of microbial colonization, through the analysis of biofilm formation on the samples.

3:10pm **B6-3-7 Plasma Spray Deposition of Optical NanoComposites Coatings and Preforms**, ***M. Gell*** *(mgell@mail.ims.uconn.edu), E.H. Jordan, C. Muoto, J Roth*, University of Connecticut

NanoComposites represent a new approach for achieving transparent ceramics with enhanced optical and mechanical properties. Much of the current effort uses traditional nanopowder manufacturing and bulk consolidation methods. The consolidation methods involve multi-step processes to ensure the absence of light-scattering defects, full density, and the retention of a nanoscale structure following elevated temperature sintering and hot isostatic pressing. It may be possible to use a lower-cost, one-step plasma spray process to generate near-net-shape preforms with potentially finer nanostructures. This presentation will describe the state-of-the-art for plasma spray deposition of magnesia-yttria nanocomposites, using solution precursor and air plasma spray processes. The fabrication process, microstructure, mechanical and optical properties will be described.

3:30pm **B6-3-8 The Synthesis of Metal Oxides by Reactive Cathodic Arc Evaporation**, ***J. Ramm*** *(juergen.ramm@oerlikon.com), H. Rudigier, B. Widrig,* OC Oerlikon Balzers AG, Liechtenstein, *M. Döbeli,* Paul Scherrer Institute and ETH Zurich, Switzerland, *L. de Abreu Vieira, A. Dommann, A. Neels,* CSEM SA Neuchâtel, Switzerland, *J. Thomas*, Leibniz-Institut für Festkörper- und Werkstoffforschung Dresden, Germany

INVITED

There have been efforts for many years to establish cathodic arc evaporation for oxide deposition. Issues associated with process stability and droplet formation prevented the utilization of this technology on a large scale in production. Although cathodic arc technology is well understood and the dominant technology in the PVD tool coating business for conductive layer materials, the deposition of oxides utilizing this technology has been only recently enabled by the development of a dedicated production technology (P3e^{TM}) [1]. The robustness of this technology is based on its inherent broad process window which permits the arc operation in pure reactive gas, a variation in process pressure over several decades, the freedom in the selection of reactive gases and target materials, and the easiness of adjusting deposition rates. All these aspects make this technology unique amongst PVD technologies.

The straightforwardness in process control allows the deposition of oxides under very different conditions resulting in a variation of the coating microstructure. This is illustrated in a cross-sectional scanning electron microscopy analysis for the Al-Cr-O and Zr-Y-O coatings which demonstrate that the layer morphology can be adjusted from "glassy" to "columnar" in a simple way. XRD investigations show the influence of target composition and reactive gas flow on crystal structure and crystallite size of the synthesized oxides.

In additional investigations, an attempt has been made to correlate the deposition parameters with processes at the surface of the composite Al-Cr targets and the nucleation and phase formation of Al-Cr-O layers at the substrate surface. The oxygen partial pressure and pulsing of the arc current influence the formation of intermetallic phases and/or solid solutions at the target surface. The nucleation of the ternary oxides at the substrate site appears to be, to some extent, controlled by the composition of the intermetallics or solid solutions formed at the target surface. This in turn suggests that the formation of phases in the synthesized layer can be influenced by the processes at the target surface. This hypothesis is supported by the X-ray diffraction analysis of the layers as well as of the target surface. It is also confirmed by the results of cross-sectional transmission electron microscopy investigations of the synthesized oxide layers, especially by the results obtained from selected area electron diffraction.

[1] J. Ramm, M. Ante, T. Bachmann, B. Widrig, H. Brändle, M. Döbeli, Surf. Coat. Technol. 202 (2007) 876

4:10pm **B6-3-10 Mechanical and Tribological Behavior of TiCN Coatings Deposited by Large Area Filtered Cathodic Vacuum Arc**, ***Y.H. Cheng*** *(yh_cheng@yahoo.com), T. Browne, B. Heckerman*, American Eagle Instruments, Inc.

TiCN coatings were synthesized using a large area filtered arc deposition (LAFAD) technique from a Ti targets at an atmosphere of mixed N_2 and CH_4 gases. The hardness, elastic modulus, and tribological behavior of the TiCN coatings were characterized using nanoindentation and pin-on-disk tribometer. To investigate the influence of the C content in the coatings on the mechanical and tribological properties, CH_4 gas volume fractions in the gas were varied from 0 to 50%. It was found that with increasing C content in the coatings, the hardness and elastic modulus increase to a maximum at a C content of 2.8 at.%, then decreases rapidly with the further increase in the C content in the coatings. Adding a small amount of C into the TiN coatings leads to a significant decrease in the plasticity. Tribological test results show that there is no significant change in the friction coefficient (0.78-0.88) of the TiCN coatings against Al_2O_3 balls when C content in the coatings is below 4.6 at.%, but the friction coefficient decreases rapidly to 0.21 with the further increase in the C content in the coatings to 9.3 at%. With increasing C content in the coatings from 0 to 2.8 at.%, the wear rate decreases from 2.5×10^{-6} mm^3/Nm to 9.5×10^{-7} mm^3/Nm. The further increase in the C content in the coatings to 9.3 at.% leads to a gradual decrease in the wear rate to 5.3×10^{-7} mm^3/Nm, which is 21% of the wear rate of the pure TiN coatings.

Tribology and Mechanical Behavior of Coatings and Thin Films
Room: Pacific Salon 1 - Session E2-2

Mechanical Properties and Adhesion
Moderator: R. Chromik, McGill University, L. Davies, Caterpillar, J. Michler, Empa

1:30pm **E2-2-1 Double-Brittle Transitions in Micropillar Compression**, *P.R. Howie, S. Korte,* University of Cambridge, United Kingdom, *R. Ghisleni, J. Michler,* Empa, Switzerland, ***W.J. Clegg*** *(wjc1000@hermes.cam.ac.uk)*, University of Cambridge, United Kingdom

INVITED

There is widespread interest in using micropillar compression as a means of studying plasticity in hard brittle materials, particularly in complex structures where the flow stresses on different slip systems may be very different. Existing work has shown that below a certain pillar diameter, typically a few microns, cracking is completely suppressed. Ductile-brittle transitions in materials are normally associated with changes in temperature or strain-rate. However based on observations in the literature, it has been suggested that the transition observed in micropillars is associated with a size dependence in the fracture resistance. To investigate these ideas, the fracture behaviour of micropillars over a range of diameters and made of different materials have been studied. The changes in fracture behaviour are compared with predictions using analyses based on the different ideas.

2:10pm **E2-2-3 Yield Strength, Deformation, and Fracture of Coherently Strained InGaAs Superlattice by In-Situ Micropillar Compression**, ***R. Ghisleni*** *(rudy.ghisleni@empa.ch),* Empa, Switzerland, *B. Ehrler,* Queen Mary University of London, United Kingdom, *R. Raghavan,* Empa, Switzerland, *K. P'ng, A.J. Bushby,* Queen Mary University of London, United Kingdom, *J. Michler*, Empa, Switzerland

The mechanical response and deformation/fracture behaviour of a 2.5 µm thick InGaAs homogeneous film and coherently strained InGaAs superlattice are investigated by in-situ scanning electron microscope (SEM) micropillar compression experiments. The superlattice structure studied is composed of 50 layers having a constant thickness of 50 nm each. Focused ion beam (FIB) is used to fabricate 2 µm diameter micropillars in both homogeneous and superlatice systems. The yield strength is observed to decrease with increasing coherency strain at room temperature. This was an unexpected result, since coherency strain in metallic precipitation hardening alloys is normally associated with an increase in strength rather than a reduction. Moreover, the homogeneous and superlattice films reveal interesting differences in their deformation and fracture behaviour. While the homogeneous micropillars present sever plastic deformation in the form of large slip bands, the coherently strained superlattice micropillars present narrower slip bands initiating a crack in intersection. For the superlattice film, the splitting fracture toughness can be estimated in 0.84 $\text{MPa}\cdot\text{m}^{1/2}$.

2:30pm **E2-2-4 Analysis of the Mechanical and Tribological Properties of the Multilayer Ultrathin Films for MEMS Applications**, *K.A. Rzepiejewska-Malyska (karolina.rzepiejewska@empa.ch), R. Koodakal,* ***J. Michler***, Empa, Switzerland

Multilayered coatings of TiN/CrN, TiN/NbN and NbN/CrN of different thicknesses of alternating layers have been deposited by direct current (dc) magnetron sputtering onto Si<100>. For comparison, single layer reference coatings of TiN, CrN and NbN of ~700 nm thickness have been synthesized. The mechanical characterization was conducted using a combination of micro – and nano - indentation. In-situ SEM micro-/nano-indentation was used to observe the deformation process including any pile-up, sink-in, and fracture mechanisms specific to each coating. These information have been supplemented with the microstructural deformation mechanisms characterized by TEM studies on the cross-sections containing indentation imprints. Subsequently, the tribological properties have been characterized at both nanoscale (ex-situ nanoscratch and nanowear) and microscale (in-situ SEM microscratch). This gave an insight into the tribological resistance of the thin films independent of the substrate as well as in the film-substrate system collaboration.

In a result it was found out that the mechanical response strongly depends on the scale of analysis and the type of multilayer. The deformation mechanisms of the constituent layers in the multilayer stack combine in each multilayer film differently giving new characteristic deformation mechanism. From the nanotribological studies, it was revealed that the scratch deformation cannot be used for wear estimation. But, the microscratch results are in agreement with the micromechancial studies.

Finally, the finite element model of the multilayer deformation has been developed to elaborate the deformation and fracture response of the multilayers. The visualization of stress and strain distribution under the load and in the residual state supplements the information obtained in the experimental process. It also suggests that the interfaces play a critical role for the shear stress distribution.

The main conclusions from the point of view of particular applications will be presented.

2:50pm **E2-2-5 3D Finite Element Study of Scratch Tests Conducted on Coated Systems with Orthotropic Elastic-Plastic Material Properties**, ***N. Fukumasu*** *(fukumasu@gmail.com), R.M. Souza, A.P. Tschiptschin*, University of São Paulo, Brazil

In this work, three-dimensional finite element analyses were conducted to understand the stress distribution during scratch tests on coated systems with orthotropic material properties. Different from analyses commonly found in the literature, the mechanical behavior of both film and substrate was considered elastic-perfectly plastic. Besides, it is known from previous works that orthotropic materials may alter the contact stresses in the film surface, modifying the location and probability of nucleation and propagation of cohesive cracks. To study this material aspect, the orthotropic properties were analyzed for the substrate. Those material properties were the Young's modulus and the yield stress. Results were analyzed based on stress distribution in the film and substrate, which are mainly linked to the failure of this system. Results have indicated that systems with orthotropic properties are less prone to film failure commonly seen in experimental scratch tests.

3:10pm **E2-2-6 Scratch Resistance of Platinum Coatings**, *M. Topić (mtopic@tlabs.ac.za),* iThemba LABS, South Africa, ***G. Favaro***, CSM Instruments, Switzerland, *R. Bucher,* iThemba LABS, South Africa, *C.I. Lang*, University of Cape Town, South Africa

Metallic platinum is important for industrial applications and the demand has increased considerably in the past decade, particularly in applications such as jewellery and catalytic converters which together account for over 80% of platinum consumption. The platinum coated systems are used in many applications where the surface properties such as hardness, scratch resistance or electrochemical activity play an important role. Our research study was focused onto platinum-vanadium single and multilayered systems and we have been particularly interested to compare the scratch resistance of as deposited and annealed coatings. A single platinum layer and multilayer systems of platinum and vanadium (double and triple layers) deposited on vanadium substrates were used in this research. They have been annealed at 700^0C, 800^0C and 900^0C under vacuum conditions for 45 minutes and afterwards characterised using several complementary techniques.

The phase formation and coating morphology have been determined by x-ray diffraction and scanning electron microscopy respectively while the scratch resistance was tested using a nano-scratch tester. The phase analysis showed that several phases, PtV, Pt_2V_3 and Pt_2V were formed as a consequence of annealing. The coating morphology and roughness were also affected by elevated temperatures. More importantly, it was found that the scratch resistance of annealed coatings is significantly better in comparison to scratch resistance of as deposited coatings. It indicates that the platinum-vanadium phases formed during annealing process has significant role in increasing the scratch resistance and improving the adhesion properties of platinum-vanadium coated systems.

3:30pm **E2-2-7 Fundamentals of Adhesion of Thermal Spray Coatings: Adhesion of Single Splats**, ***E. Balić*** *(edin.balic@empa.ch), M. Hadad,* Empa, Switzerland, *P. Bandyopadhyay,* IIT Kharagpur, India, *J. Michler*, Empa, Switzerland

Indentation experiments were conducted inside a scanning electron microscope to measure adhesive strength of individual alumina splats plasma-sprayed atop a steel substrate. In-situ type of experimental evaluations made characterization of interfacial crack propagation possible by direct observation. Strain energy increase of brittle alumina splats originated from indentation deformation was correlated to the strain energy release rate through the characterization of the interfacial crack propagation. An analytical model previously reported and evaluated in the studies of adhesive strength of thin-films was employed. The average calculated strain energy release rate of 80 J/m^2 was determined for single splats. This high value suggests that splat adhesion can possess a significant contribution to the adhesion of thermal sprayed coatings.

3:50pm **E2-2-8 Evaluation of Ti Cold Spray Splats by Indentation and Ball Shear Testing**, ***R. Chromik*** *(richard.chromik@mcgill.ca), D. Goldbaum, J. Ajaja, S. Yue, J. Shockley,* McGill University, Canada, *E. Irissou, J.-G. Legoux,* National Research Council Canada (NRC), Canada, *N. Randall*, CSM Instruments

Cold spray is an emerging coating and material repair technology that makes use of a converging/diverging nozzle and a high pressure, heated gas source (usually nitrogen) to create a high velocity gas flow. Metallic particles in the size range of 10 – 100 microns are injected into this gas flow, propelled at supersonic velocities and impact and adhere to a substrate material with high forces, but relatively low temperatures compared to other spray technologies. When processing conditions are optimized, the technique can produce near fully dense metallic coatings with minimal contamination and near negligible modification of base material properties. Despite the promise this technique has shown, questions remain about the quality of the material deposited in terms of homogeneity of properties, adhesion strength of coating to substrate, and cohesion strength between cold sprayed particles that make up the coating. To address these concerns two experimental techniques have been developed through initial testing on cold sprayed cp Ti. First, to examine particle adhesion to substrate, a modified ball shear test was used to determine adhesion strength of single cold spray splats to a bulk Ti plate as a function of deposition conditions. Second, a combined method using nanoindentation and microindentation was implemented to determine the degree of indentation size effect in coatings. Examination of residual indents by optical microscopy, revealed a range of particle cohesion that agreed with trends identified in indentation size effect results. Both techniques will be discussed in terms of their possible applicability for laboratory scale demonstration of the quality of cold sprayed material when compared to traditional bulk manufactured parts.

4:10pm **E2-2-10 Adhesion of Composite Structured TiTaBN Coatings Deposited by Magnetron Sputtering**, ***I. Efeoglu*** *(iefeoglu@atauni.edu.tr),* Atatürk University, Turkey, *O. Baran,* Erzincan University, Turkey, *B. Prakash*, Luleå University of Technology, Turkey

The most important functional requirements for continuity and performance of hard wear-resistant coating is adhesion. Scratch test used to control and to measure adhesion of thin hard coatings. In this work, thin films of Ti-Ta-B-N with different nitrogen contents were deposited on Toolox and D2 substrates by closed-field unbanced magnetron sputtering (CFUBMS). Microstructure and phase composition of thin films were studied by X-Ray Diffractometer (XRD) and Scanning Electron Microscopy (SEM). To measure adhesion of Ti-Ta-B-N thin films have been scratch tested at the a standart mode using progressive load operation. The effect of different nitrogen contents and substrates (on adhesion) were investigated.

4:30pm **E2-2-11 High Temperature Testing of Transition Metal Nitride Materials**, ***F. Giuliani*** *(f.giuliani@imperial.ac.uk)*, Imperial College London, United Kingdom, *P.H. Mayrhofer*, Montanuniversität Leoben, Austria

Transition metal nitrides have been used routinely as coatings for cutting tools and their mechanical properties have often been measured by nanoindentation at room temperature. However, these materials are used at temperatures up to 1000˚C. In this work we have measured the high temperature properties of a range of transition metal nitrides, including TiN in bulk and thin film form and TiAlN with the aim of understanding how the materials behave at these elevated temperatures. It will be shown how simple nitrides soften considerably at temperatures far below their operating temperature and also how microstructural changes that might have little effect on the room temperature properties can become quite dominant at elevated temperatures. In this work the mechanical properties have been measured by high temperature nanoindentation and micropillar experiments while observation of the deformation has been carried out by TEM.

4:50pm **E2-2-12 High-Precision Determination of Residual Stress of Polycrystalline Coatings Using the Optimised XRD-sin$^2\psi$ Technique**, ***Q. Luo*** *(q.luo@shu.ac.uk)*, Sheffield Hallam University, United Kingdom

Residual stresses existing in most polycrystalline hard coatings have significant influence on the adhesion, mechanical properties and tribological performance. The aim of the research is to optimize the XRD-sin$^2\psi$ technique so that surface residual stresses can be determined with high precision and good reliability. In the X-ray diffraction (XRD) sin$^2\psi$ stress measurement, the value of residual stress is determined through a linear regression between two parameters derived from experimentally measured diffraction angle (2θ), whereas the linear regression precision factor R^2 reflects the accuracy of the stress determination. Thus, the accuracy of the obtained residual stress value depends strongly on how precise the 2θ values are measured out of a series of very broad and sometimes irregularly-shaped diffraction peaks. In practice, uncertainty arises when different diffraction peak positioning methods are applied, mainly including the maximum intensity (I_{max}) method, the middle point of half maximum (MPHM) intensity method, the area/gravity centre method, and the parabolic approaching method. However, up to date little comparative experimental research has been done on the precision of residual stresses determined by using the different 2θ measurements.

In this paper, glancing angle XRD experiments have been conducted to determine the surface residual stress of a large number of samples, including an electron beam evaporated ZrO_2 based thermal barrier coating and several magnetron sputtered transition metal nitride coatings, as well as a few shot-peened superalloy gas turbine components. On the XRD scans of each tested sample, the 2θ values were determined using the above mentioned peak-positioning methods, and then the obtained residual stress and the R^2 values were compared with each other.

The experiments reveal that, the residual stresses obtained range from -0.08 Gpa to -6.67 Gpa depending on the tested materials. The relative precision R^2 values vary between 0.25 and 0.99 depending on both the quality of the obtained diffraction curves and the methods of the 2θ value determination. The parabolic approaching method resulted in the highest precision of linear regression, with $R^2 = 0.93 \pm 0.07$ out of the obtained results, which showed low deviation of the determined residual stress value in all cases; both the MPHM ($R^2 = 0.86 \pm 0.16$) and gravity centre ($R^2 = 0.91 \pm 0.11$) methods could also give good results in most cases; and the I_{max} method ($R^2 = 0.71 \pm 0.27$) exhibited substantial uncertainty depending on the nature of individual XRD scans. Based on the experiments, an optimized surface residual stress measurement method is recommended.

5:10pm **E2-2-13 Boron Containing Coating Systems for Hot Forming Tools**, ***H. Paschke*** *(hanno.paschke@ist.fraunhofer.de)*, Fraunhofer IST, Germany

For hot forming tools classical wear protection coatings mostly are not sufficient for an industrial use. Due to high process temperatures the tribological properties are much different compared to room temperature conditions and the use of lubricants is limited. Additionally thermal shock conditions and the increase of sticking workpiece material are leading to severe wear.

Recent developed Ti-B-N coatings are thermally stable, antiadhesive against workpiece material and wear resistant. Examples for these ternary boron based coatings obtained through plasma-enhanced chemical vapor deposition will be presented.

Coatings of the ternary Ti-B-N system could be adapted to the requirements of hot forming applications by variation of the boron and nitrogen content. The deposition of gradient coatings was also developed to adapt the different material properties to the coating. The coatings exhibit a nanostructured crystal morphology in means of a nanocomposite assembly where amorphous regions are containing nanocrystalline components. This can be used in different layer designs for further enhancements of the mechanical load capabilities of tool surfaces. In the presentation the properties of different multilayer systems with altering material contents from pure TiB2 to nitrogen containing regions will be shown. Boron containing systems are also known as thermally stable against degradation and chemically stable against molten aluminium.

An additional pretreatment by plasma nitriding in so called 'single-duplex processes' additionally enhances the mechanical load ability. Generally there is some need to optimize the nitriding parameters which have a significant influence on the nitriding depth, the maximum hardness near the surface and the gradient of the hardness decrease. Different nitriding processes were developed and studied concerning the influence on the crack formation behaviour of tool surfaces.

Current developments showed in different fields of forming applications a very high potential of these coatings. In aluminium die casting applications the sticking of casted material could be significantly reduced resulting in better product surfaces and an increased lifetime of dies. In precision forging processes an overall stabilization of the planned tool life could be achieved and enabled a continuous production without needs of reworking the tools. Finally an increase in process reliability paired with a longer tool life has been possible.

Characterization: Linking Synthesis Properties and Microstructure
Room: Royal Palm 1-3 - Session F1-2

Advances in Characterization of Coatings and Thin Films
Moderator: P. Schaaf, Ilmenau University of Technology

1:30pm **F1-2-1 Femtosecond Laser Spectroscopy of Spins: Magnetization Dynamics in Thin Magnetic Films with Spatio-Temporal Resolution**, ***E. Carpene*** *(ettore.carpene@fisi.polimi.it)*, ULTRAS, CNR-INFM, Dipartimento di Fisica, Politecnico di Milano, Italy, *E. Mancini, D. Dazzi, C. Dallera,* ULTRAS, CNR-INFM, Italy, *E. Puppin,* CNISM, Italy, *S. De Silvestri*, ULTRAS, CNR-INFM, Italy **INVITED**

In order to fully characterize the magnetization dynamics in thin magnetic films we have developed an experimental set-up, based on Magneto-Optical Kerr Effect (MOKE), that allows to measure, with the same configuration of the apparatus the longitudinal, transverse and polar components of the magnetization vector M. Besides, through the use of the pump-probe technique it is possible to extract the time dependence of each individual components with sub-picosecond resolution. This method has been exploited to observe the variation of the magnetization vector M (modulus and orientation) induced by an ultrashort laser pulse in thin epitaxial iron films.

The initial, sub-picosecond demagnetization is established at the electronic level through electron-magnon excitations. The subsequent dynamics is characterized by a precessional motion on the 100 picosecond time-scale, around an effective, time-dependent field. Following the full dynamics of M, we have been able to unambiguously determine the temporal evolution of the magneto-crystalline anisotropy, providing the experimental evidence that the precession is triggered by the rapid, optically-induced misalignment between the magnetization vector and the effective field.

2:10pm **F1-2-3 In-Situ XRD Observations of Rapid Reactions in Nanoscale Ni-Al Multilayer Foils Using Synchrotron Radiation**, *C.G. Rebholz,* ***I.E. Gunduz*** *(emreth@yahoo.com), K. Fadenberger, C. Tsotsos,* University of Cyprus, *B. Schmitt,* Paul Scherrer Institut, Cyprus, *C. Doumanidis*, University of Cyprus

The observation of rapid reactions in magnetron sputtered nanoscale multilayers present challenges that require sophisticated analysis methods. Recent advances in fast x-ray diffraction (XRD) detector technology in synchrotron light sources allows direct observation of rapid reactions that occur within milliseconds. We present high-resolution *in-situ* XRD analysis of rapid reactions in nanoscale foils of $Ni_{0.9}V_{0.1}$-Al using the Mythen II solid-state microstrip detector system at the Material Science beamline of the Swiss Light Source Synchrotron at Paul Scherrer Institut in Villigen, Switzerland along with high speed optical imaging at 40000 fps.

The results reveal a two-step temperature evolution corresponding to the rapid sequential formation of intermetallic phases Ni_2Al_3 and NiAl, vanadium segregation during cooling and formation of internal stresses, determined with high temporal (0.125 ms) and angular (0.004^0) resolution over a full angular range of 120^0.

2:30pm **F1-2-4 XRD In-Situ Study of Time and Thickness Dependence of Crystallization of Amorphous TiO$_2$ Thin Films and Powders**, ***R. Kuzel*** *(kuzel@karlov.mff.cuni.cz), L. Nichtova, Z. Matej,* Charles University in Prague, Czech Republic*, J. Musil*, University of West Bohemia, Czech Republic

It is known that photocatalytic activity and hydrophilicity of titanium dioxide depends also on phase composition, microstructure and crystallinity. Time and thickness dependences of crystallization of amorphous magnetron-sputtered thin films (of thickness 50−2000 nm) were studied by XRD on post-annealed samples and by in-situ measurement in high-temperature chamber. At room temperature, the films were measured in parallel beam geometry with low angles of incidence and/or exit and by XRD total pattern fitting with our own software the phase composition, lattice parameters, crystallite size and microstrain were obtained. The density, thickness and roughness of the film were estimated from X-ray reflectivity. The roughness increased with the film thickness. Detailed stress/texture analysis revealed the presence of tensile stresses after crystallization. They increased rapidly with the decreasing film thickness. Temperatures of "fast" crystallization (15 min annealing) were found and later refined by in-situ XRD measurements to 220°C for thicker films and 280°C (below 100 nm). For time investigations, lower temperatures (180°C) were selected in order to slow down the process and perform detailed studies in laboratory. Strong dependence of crystallization on the film thickness was confirmed, in particular below about 300 nm. The crystallization was characterized by integrated intensities I_{hkl} of a few diffraction peaks of anatase. Their evolution could be described by the modified Avrami equation, $I = 1\text{-}\exp[-b(t–t_0)^n)]$, where the onset of crystallization t_0 is related to the first appearance of diffracted intensity above the background level. It increases abruptly with decreasing thickness while the rate of crystallization b decreases. Low values of n (~ 2) indicate two- dimensional character of the crystallite growth. Profile widths were relatively small from the very beginning of crystallization and did not change with time. This was due to the rapid growth of a few crystallites and it means that it is impossible to prepare nanocrystalline TiO$_2$ films by annealing of amorphous ones unlike the powders for which this is a technique of preparation of nanocrystals of predefined mean crystallite size. Evolution of preferred orientation and stress generation during the crystallization were observed. Initial (00l) preferred orientation was smoothed out with the time for thicker films (above 100 nm). It was also confirmed from the shifts of diffraction peaks with the time that tensile residual stresses are formed during the crystallization. They were studied in detail at room temperature by direct stress measurement and by total pattern fitting.

2:50pm **F1-2-5 Resistive Switching Characteristics of IGZO Thin Films for Nonvolatile Memory Applications***, **M.-C. Chen** (d962030002@student.nsysu.edu.tw), T.-C. Chang, S.-Y. Huang, S.-C. Chen,* National Sun Yat-Sen University, Taiwan*, C.-W. Hu, S.M. Sze*, National Chiao Tung University, Taiwan

In this study, the bipolar resistive switching characteristics of the transparent resistive random access memory (RRAM) device based on sputter–deposited IGZO thin film was investigated. The ITO/IGZO/ITO structure exhibits a high transmittance above 80% within the visible light region. The forming process was not required for this RRAM due to the nature of the numerous oxygen vacancies preexisting in IGZO film. Moreover, the bipolar resistance switching behavior is dominated by the conducting filaments consisted of oxygen vacancies in the IGZO thin films. In addition, the conduction mechanisms of the low resistance state (LRS) and the high resistance state (HRS) are dominated by Ohmic behavior and Poole-Frenkel emission, respectively. The resistance window defined by HRS to LRS is about 10 times at a reading voltage of -0.5V within 100 cycles test.

Applications, Manufacturing, and Equipment Room: Pacific Salon 3 - Session G6

Coatings, Pre-Treatment, Post-Treatment and Duplex Technology

Moderator: N. Bagcivan, RWTH Aachen University, E. Kusano, Kanazawa Institute of Technology

1:30pm **G6-1 Characterization of Duplex Layer Structures Produced by Plasma-Assisted Low Temperature Nitrocarburizing Treatment of Austenic Stainless Steel 316L**, *Y. Guo,* ***G. Marcos*** *(gregory.marcos@mines.inpl-nancy.fr), T. Czerwiec, T. Belmonte*, Ecole des Mines de Nancy, France

Austenitic stainless steels are attractive materials for various industrial applications where corrosion resistance especially in wet environment is a primary requirement. In order to improve their tribological properties, low thermochemical diffusion treatments as plasma assisted nitriding (PAN), plasma assisted carburizing (PAC) or their combination i.e. plasma assisted nitrocarburizing (PANC), are developed and improved since the 1980s.

PAN and PAC are treatments in which nitrogen and carbon atoms diffuse respectively in a metallic material from moderate to elevated temperatures. Below 420°C, a plasma assisted nitriding treatment of austenitic stainless steel produces a specific phase usually called expanded austenite, S phase, m phase or or ?N phase. Expanded austenite is a metastable nitrogen supersaturated solid solution with a disordered fcc structure and a distorted lattice. This phase is hard, wear resistant and a paramagnetic to ferromagnetic transition takes place for nitrogen contents higher than 14 at%. Other features of the expanded austenite are its high nitrogen content (from 10 to 35 at%) and compressive residual stress in the nitrided layer. Replacing nitrogen by hydrocarbon for conducting a low temperature PAC leads to a carburized layer containing the carbon expanded austenite phase ((?C). These two phases can be obtained simultaneously by combining hydrocarbon and nitrogen in the gas phase through a low temperature PANC.

We perform PAN and PAC treatments by using a multi-dipolar plasma, based on the Distributed Electron Cyclotron Resonance concept. The microwave power is supplied through eight microwave antennas arranged in a two-dimensional network. The resonant magnetic field is produced by permanent magnets located in front of the antennas. The resulting plasma mixture (N$_2$/H$_2$/Ar or C$_3$H$_8$/H$_2$/Ar) diffuses towards the substrate-holder that can be independently heated and/or biased.

In this work, we show results obtained with sequential treatments: carburizing followed by nitriding and nitriding followed by carburizing. It was found that nitrogen and carbon atoms can simultaneously be dissolved into the austenite lattice during the nitrocarburising process, forming a dual layer structure with an extremely hard nitrogen-enriched layer near the substrate surface and above a hard carbon-enriched layer. Our investigations indicate that the carbon content is higher when carburizing is followed by nitriding. X-Ray Diffraction is used to identify the presence and structure of the expanded austenite. The layer thickness is observed by optical microscopy and the composition of the layers is determined by SNMS.

1:50pm **G6-2 Adaption of Chromium Interlayer Thickness to Cemented Carbide Substrates' Roughness for Improving the Adhesion of HPPMS PVD Films and the Cutting Performance**, ***K.-D. Bouzakis*** *(bouzakis@eng.auth.gr), S. Makrimallakis, G. Katirtzoglou, G. Skordaris, S. Gerardis,* Aristoteles University of Thessaloniki, Greece / Fraunhofer PCCM, Germany, Greece*, E. Bouzakis,* Fraunhofer PCCM, Germany, Greece*, T. Leyendecker, S. Bolz, W. Koelker*, CemeCon AG, Germany **INVITED**

High Power Pulsed Magnetron Sputtering (HPPMS) has been identified as a powerful tool for manufacturing hard and well-adherent coatings. Recent investigations have revealed the immense importance of the substrate pretreatments and of the adhesive nanointerlayers materials on the films' adhesion and on the wear behavior of coated hardmetals. In this context, HPPMS techniques jointly with the deposition of a Cr-nanointerlayer can increase the film adhesion and consequently the coated tool life. These improvements depend on the roughness of the employed cemented carbide substrates. Considering these results, the investigations described in the present paper intent to explain the effect of Cr-interlayer thickness and substrate roughness on the coating adhesion and cutting performance. To attain various roughnesses, the applied cemented carbide inserts were superficially treated. These treatments were grinding at a medium roughness level, or grinding with subsequent polishing for enhancing the surface integrity and finally, in all cases, micro-blasting by fine Al$_2$O$_3$ grains. After Ar-ion etching, Cr adhesive layers with different thicknesses were deposited by HPPMS technology on the variously pretreated substrates. Subsequently, an approximately 3µm thick (Ti,Al)N film was deposited by HPPMS PVD on all used inserts. Rockwell C indentations and inclined impact tests were performed to assess qualitative and quantitative the films' adhesion. The cutting performance of the coated tools was investigated in milling. FEM supported calculations of the developed stresses during the material removal process contributed in explaining the obtained tool wear results. In these calculations, the adhesion, dependent on the substrate roughness characteristics and on the adhesive interlayer thickness, was taken into account. The results revealed that the effectiveness of HPPMS adhesive Cr-nanointerlayer strongly depends on the substrate surface integrity and on the interlayer thickness. Thus, the film adhesion and consequently the cutting performance can be significantly improved if the interlayer thickness is adapted to the substrate roughness.

2:30pm **G6-6 Effect of Process Duration on Structure, Chemistry, and Mechanical Properties of Borided Low Carbon Steels**, ***G. Kartal****, S. Timur,* Istanbul Technical University, Turkey*, O.L. Eryilmaz, A. Erdemir (erdemir@anl.gov), G. Krumdick*, Argonne National Laboratory

In this study, we employed an ultra-fast boriding technique to grow hard, wear, and corrosion resistant boride layers on low carbon steel substrates using an induction furnace at 900°C. The technique utilizes an electrochemical cell in which it is possible to achieve 100 micrometer thick boride layers in about 30 minutes. The effect of the electrolysis time on boride layer thickness, composition, and structural morphology was investigated and an empirical equation was derived for the growth rate of boride layers. In depth analyses of the boride layers were carried out by microscopy and X-ray diffraction (XRD) which revealed that different boride phases (FeB, Fe_2B, Fe_3B) could be formed depending on the process duration. The growth rate of boride layers is nearly linear up to 30 minutes of treatment. However during much longer treatments, the growth rate has a parabolic character which can be represented with the equation (**d = 1.4904 (t)$^{0.5}$ + 11.712**); where d (in µm) is the growth rate, t (in sec) is duration. The mechanical characterization of the borided surfaces in plane and in cross-sections has confirmed hardness values as high 19 GPa at or near the borided surface (where FeB phase is the most dominant) but gradual decrease in hardness to 14 to 16 GPa beneath the surface where Fe_2B phase is present.

2:50pm **G6-9 Effect of Plasma Nitrocarburizing on Properties of AISI 4340 Steel Submitted to Different Heat Treatments**, ***V.H. Baggio-Scheid*** *(scheid@ieav.cta.br), J.A. Abdalla*, Institute of Advanced Studies, Brazil

The AISI 4XXX steel series are structural steels, widely used in the automobile and aerospace components. Plasma thermochemical treatments are commonly used when a hard case is also necessary in order to improve tribological and corrosion properties. In this work the AISI 4340 steel, treated by different heat treatments and by plasma nitrocarburizing process, has been characterized. Three different heat treatments were used. The steel samples were austenitized; austenitized, quenched in oil and tempered; and austenitized, quenched in salt bath and cooled in water (isothermic). After the heat treatments the samples were plasma nitrocarburized at 500°C for 3h. The samples were characterized by microhardness test, SEM, and XRD. Multphase structures predominantly bainitic and martensitic with hardness between 500 and 580 HV have been formed by the heat treatments. The nitrocarburizing process has resulted in a compound layer with 10 µm and hardness higher than 900 HV, containing predominantly the ε - {$Fe_{2\text{-}3}N$} phase. A diffusion layer with a thickness of 130 mm has also been formed. The results concerning the influence of the plasma treatment on the microstructures of the samples are presented and analyzed.

3:10pm **G6-10 Duplex Plasma Technology for Aluminum**, ***S. Meier*** *(sven.meier@iwm.fraunhofer.de)*, Fraunhofer IWM, Germany

An innovative approach to improving behavior of aluminum surfaces and meeting long-term durability requirements of aluminum devices is to design and develop novel systems incorporating duplex diffusion/plasma coating treatments. The composite layers consist of a N-diffusion zone obtained by rf-plasma nitriding, followed by a rf-plasma deposited DLC film. A PACVD processing technology is described that helps to overcome some of the most important limitations of existing technology to generate duplex coatings on technical aluminum substrates. Application of this technique to plasma assisted nitriding of pure aluminum and different aluminum alloys is demonstrated. The influence of the process parameters on the discharge characteristics was examined. Material properties and tribological testing results are shown.

3:30pm **G6-11 Improvement of the Cavitation Erosion Resistance of UNS 31803 Stainless Steel by Duplex Treatment**, *D.H. Mesa,* Technological University of Pereira, Colombia*, C.E. Pinedo,* Heat Tech Ltd., Brazil, ***A.P. Tschiptschin*** *(antschip@usp.br)*, University of São Paulo, Brazil

A duplex surface treatment consisting of a High Temperature Gas Nitriding (HTGN) followed by a Low Temperature Plasma Nitriding (LTPN) was carried out in an UNS 31803 stainless steel. HTGN was performed at 1,200ºC for 8 hours, in a 1 atm N_2 atmosphere while LTPN was carried out in a 75% N_2:25% H_2 atmosphere, at 400ºC for 12 hours. A duplex structure consisting of a ~12 µm thick expanded austenite g_N layer with 1,400 HV0.025 hardness was formed on top of a 1.0 mm thick fully austenitic layer, with 350 HV. The HTGN layer was intended to give mechanical support to the more hard and brittle expanded austenite layer. A less steep hardness gradient was obtained between the expanded austenite layer and the UNS 31803 stainless steel matrix. The duplex treated specimens were tested in vibratory cavitation erosion testing equipment. The incubation time for the onset of cavitation for the duplex treated steel was 1.5 times higher than the HTGN UNS 31803 steel and 20 times higher than the UNS 31803 untreated steel. The mass loss rates decreased from 1.5 mg/h for the untreated stainless steel to 0.25 mg/h for the HTGN steel and 0.15 mg/h for the duplex treated steel.

3:50pm **G6-12 Low Temperature Plasma Carburizing of AISI F51 Duplex Stainless Steel**, ***C.E. Pinedo,*** Heat Tech Ltd., Brazil*, J.D. Bressan,* State University of Santa Catarina, Brazil*, A.P. Tschiptschin (antschip@usp.br)*, University of São Paulo, Brazil

Duplex stainless steels are nowadays being used in a variety of applications within the refining and petrochemical industry, where high corrosion resistance and mechanical properties are required. The surface properties of these steels may be optimized in order to attain better performance in highly stressed tribological systems. AISI F51 (EN 1.4462) duplex stainless steel was DC-Plasma carburized at 480 ^{o}C, using CH_4 as carbon carrier gas. Although the carburized layer showed an apparently duplex structure inherited from the matrix, XRD results, using the Rietveld method, showed only peaks of expanded austenite. The carburized layer attained a surface hardness of 1600 HV0.05 and XRD results showed that this strong hardening effect is related to the formation of a highly stressed carbon expanded austenite on the surface of the specimens. When tested in a ball on disk tribometer in dry conditions wear coefficients as low as 4 x 10^{-15} m^3/(N m) were obtained. The corrosion resistance of the expanded austenite layer in 10% HCl solution was two-fold better than the uncoated F51 steel.

4:10pm **G6-13 Mechanical and Corrosion Properties of Duplex Treated AISI301 Stainless Steel**, ***M. Azzi****, M.B. Benkahoul, J.-E. Klemberg-Sapieha (jsapieha@polymtl.ca), L. Martinu*, Ecole Polytechnique de Montreal, Canada

Plasma nitriding is a very common technique used to increase the surface hardness of stainless steels, and consequently to improve their tribological properties. It is also used to create an interface between soft stainless steel and hard coatings to improve adhesion. This paper reports on the mechanical and corrosion properties of AISI301 stainless steel (SS) after a duplex treatment consisting of plasma nitriding followed by the deposition of hard CrSiN films prepared by magnetron sputtering. More specifically, we investigated the effect of deposition parameters, such as nitriding temperature and substrate bias, on the mechanical and corrosion characteristics of the duplex-treated SS. Mechanical properties of the deposited films such as hardness (H) and reduced Young's modulus (E_r) were measured using depth-sensing indentation. Potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) were applied to evaluate the resistance to localized and general corrosion, respectively. The corrosion behavior is correlated with the microstructure and the composition of the surface layers determined by complementary characterization techniques including XRD, EDS, and SEM. The CrSiN layers exhibited an H value of 23 GPa, whereas the nitrided layer was shown to present a gradual increase of the H value from 5 GPa (for the non-nitrided SS) to almost 14 GPa at the surface. Electrochemical results revealed that the nitriding temperature is a critical parameter defining the corrosion properties of the duplex-treated SS. At relatively high temperatures (673 K), the nitrided layer exhibited poor corrosion resistance due to the precipitation of chromium nitride compounds and the depletion of Cr in the stainless steel matrix. This, in turn, leads to a poor corrosion performance of the duplex-treated SS since the pores and defects in the CrSiN film were the potential sites for pitting. On the contrary, at relatively low temperatures (573 K), the nitrided interface exhibited excellent corrosion resistance due to the formation of compound-free diffusion layer. The latter effect is shown to favor passivation of the material at the electrode/electrolyte interface of the duplex-treated SS.

4:30pm **G6-5 Improvement of Press Dies Used for the Production of Diamond Composites by Means of DUPLEX-PVD-Coatings**, *W. Tillmann (wolfgang.tillmann@udo.edu), E. Vogli,* ***S. Momeni***, TU Dortmund, Germany

In the machining of hard materials such as glass or stone, cemented carbides have been recently replaced by diamond tools, consisting of a metallic carrier, on to which diamond segments are brazed. One of the most economic ways for the production of diamond segments is the cold compaction of the mixture of a metallic powder and diamond particles. Due to a highly abrasive sliding contact between diamond particles and the die walls, the wear rate of the press dies is very high. As a result of a low lifetime of the press dies, they must be replaced in short time periods. To avoid the costly and time-consuming substitution of the press dies, in this work PVD-coatings were deposited on the inner surface of the pre-plasma nitrided press dies (DUPLEX treatment). Thereby, various high and low alloy tool steels were treated by means of plasma nitriding process. Subsequently, a nanocomposite PVD coating, titanium aluminum supernitride, was deposited by means of a high ionization magnetron sputtering device on nitrided and non-nitrided steel substrates. The mechanical and tribological properties of these coating systems were studied by means of several standard tests such as nanoindentation, ball-on-disc and scratch test. The most wear resistant coating system was chosen to employ on the inner surface of the press dies. The wear resistance of the press dies developed in this study was tested under real loading condition during compaction of the mixture of diamond particles and cobalt powder. It was revealed that employing plasma nitrided tool steels coated with titanium aluminum supernitride enhances the lifetime of the press dies up to 500%. Furthermore it was shown that the press dies with different surface treatments possess different failure modes during the compaction process.

4:50pm **G6-4 Effects of Post Deposition Annealing on Resistive Switching Characteristics of $SrZrO_3$ Thin Films**, ***M.-H. Lin*** *(kenny701010.ee95@nctu.edu.tw), M.-C. Wu, S.W. Jan, Y.H. Huang,* National Chiao Tung University, Taiwan, *C.-H. Lin,* Windbond Electroncs Corporation, Taiwan, *T.-Y. Tseng*, National Chiao Tung University, Taiwan

In this paper, the effects of post deposition annealing (PDA) in O_2, N_2, and Ar at 600°C for 1 min on the resistive switching characteristics of $SrZrO_3$ (SZO) thin films were investigated. The SZO resistive memory devices exhibited the large dispersion of resistive switching parameters such as turn-on voltage and high resistance state (HRS) current, further restricting their development in the future nonvolatile memory (NVM) applications. The severe dispersion is more greatly reduced by O_2 600°C- PDA than N_2 and Ar 600°C- PDA owing to that the suppression of the oxygen vacancies in thin films could be significantly enhanced by O_2 600°C- PDA . Furthermore, device yield is dramatically increased to 90% by O_2 600°C-PDA in comparison to the other devices. T he oxygen-annealed SZO memory devices can be successively switched between HRS and low resistance state (LRS) by applying voltage signal over 150 times, and the resistive ratio of LRS and HRS is still kept more than 1000 . The retention characteristics of both HRS and LRS are stable up to 10^6 s at room temperature (RT) and 85°C. Besides, the resistive ratio of HRS and LRS still remains nearly 1000 more than 14000 s under successive reading voltage stress at RT and 85°C. The oxygen-annealed SZO memory device with its superior memory characteristics is a promising candidate for the next-generation NVM applications.

5:10pm **G6-7 Plasma Modification of Al_2O_3 for Improved Adhesive Strength in Composite Materials**, ***A. Bujanda*** *(aubjanda@arl.army.mil), D. Pappas, C. Ho, B.E. Stein, R.E. Jensen*, U.S. Army Research Laboratory

Adhesive bond strength of ceramic components in composite systems is an area of growing interest due to the wide range of applications. The adhesive bond between the ceramic and the adhesive is, in many cases, the point where failure originates. In order to combat this debonding mode of failure, the surfaces of the ceramic materials are modified to promote strong, uniform bonding. The surface pretreatment regiment currently being used includes aggressive surface cleaning with alumina particles (grit blasting) in addition to chemical treatments such as priming and the application of silane coupling agents like glycidoxypropyltrimethoxy silane (GPS). Grit blasting, while effective at removing surface contaminants detrimental to adhesive bonding such as carbon, also acts to reduce flexural strength by exacerbating existing surface flaw populations. As an alternative to grit blasting, atmospheric plasma treatments were used to remove surface contamination and chemically functionalize the surface in one step. Atmospheric plasma processing of polymer systems removes the weak boundary layer residing on the surface, and chemically alters the surface of the material, improving surface wettability and chemical reactivity. It is postulated that ceramic surfaces subjected to a glow discharge would undergo similar improvements in wettability and surface reactivity.

In this study, surface modification of aluminum oxide (Al_2O_3)) specimens due to helium (He), helium-oxygen (He-O_2), and helium-nitrogen (He-N_2) dielectric barrier discharges was compared to that of as-received and grit blasted specimens. Contact angle goniometry, x-ray photoelectron spectroscopy (XPS) were used to track chemical changes on the surface, while atomic force microscopy (AFM), and flexural strength testing were used to track surface roughness and surface damage, respectively. Wettablility tests showed an improvement in the hydrophilic character of the ceramic surface as the water contact angle decreased by 24% with the He-O_2 plasma. XPS results show a reduction in surface carbon similar for both grit blasted and He-O_2 plasma treated surfaces. Flexural strength data show no measurable reduction in strength due to plasma exposure, while grit blasting reduces the characteristic strength by ~10%.

New Horizons in Coatings and Thin Films
Room: Royal Palm 4-6 - Session H1-2

Nanoparticle, Nanowire, Nanotube, and Graphene Thin-Films and Coatings
Moderator: S. Kodambaka, University of California Los Angeles, D. Frankel, Newcastle University

1:30pm **H1-2-1 Surface Energy of Carbon Fullerenes and Nanotubes**, ***D. Holec*** *(david.holec@unileoben.ac.at), M.A. Hartmann,* Montanuniversität Leoben, Austria, *F.G. Rammerstorfer,* Vienna University of Technology, Austria, *O. Paris, F.D. Fischer, P.H. Mayrhofer*, Montanuniversität Leoben, Austria

Carbon based nanostructures, such as nanotubes or single-wall and onion-like fullerenes, have outstanding mechanical, thermal and electrical properties for which they attract a lot of theoretical as well as experimental attention. One of the key issues for determining the mechanical stability of complex systems such as onion-like carbons and fullerenes is detailed knowledge of the stresses originating from the curved surfaces inherent to these structures.

In this study we present *ab initio* calculations of the curvature energy of a variety of carbon-based nanostructures: graphene, zig-zag and armchair single-wall nanotubes and C_{60}, C_{70}, C_{180}, and C_{240} fullerenes. It turns out that the curvature energy as a function of radius follows a power law in all cases. Moreover, when only single-wall nanotubes are considered, this law is independent on other properties such as the nanotube type (armchair or zig-zag) or electronic properties (conductor or semiconductor).

In order to strengthen the conclusions for fullerenes, we present two approximations of larger buckyballs (i.e. with more than 240 atoms) which are difficult to handle fully *ab initio*. The first approach uses parts of curved surfaces composed of hexagons having the outer bonds being passivated with H atoms. The second approach uses *ab initio* data to construct inter-atomic potentials which are subsequently used in Monte Carlo simulations. Both approaches give comparable predictions for the curvature energy power law exponent. Drawbacks and advantages (e.g. decomposing the total energy into stretching, bending and torsion contributions as done in Monte Carlo simulations gives the possibility to compare various contributions to the total surface energy) of both approaches will be discussed in detail.

The calculated properties of curved carbon surfaces may be readily used in large-scale continuum based models of complex structures.

1:50pm **H1-2-2 Growth Mechanisms of Carbon Nanotubes (CNTs) by RF or DC PECVD at Low Temperature**, ***H.Y. Wang*** *(huwang@mines.edu), J.J. Moore, M. Brajendra*, Colorado School of Mines

Vertically aligned carbon nanotubes were synthesized using FeNi or Fe sputtered catalyst layers on glass substrates using radio frequency plasma enhanced chemical vapor deposition (RF-PECVD) or direct current PECVD (DC-PECVD). This paper will compare the growth mechanisms of CNTs synthesized by RF-PECVD and DC-PECVD, based on gas flow rate, plasma power, and catalysts. Tip growth CNTs were produced at 180°C, 10 sccm CH_4, and 30 W by RF-PECVD using 8 or 4 nm FeNi or 4nm Fe island films sputtered onto glass substrates. CNTs could not be grown using DC-PECVD under the same deposition conditions (180°C, 10 sccm CH_4 and 30 W). Tip growth of CNTs occurred at 180°C, 15 sccm CH_4, and 50 W using DC-PECVD with sputtered FeNi island catalysts on increasing the plasma power and CH_4 flow rate.

RF-PECVD provided more efficient decomposition of gas molecules than DC-PECVD. The major difference between RF-PECVD and DC-PECVD is the higher concentration of reactive radicals in the former. However, in DC-PECVD, the CNT growth was well aligned vertically. FeNi thin film catalysts exhibited higher activity and better wetting ability than the Fe island thin film catalysts.

2:10pm **H1-2-3 Silver Vanadate Nanorods: Synthesis, Characterization and Performance**, ***K. Polychronopoulou*** *(kyriakip@ucy.ac.cy),* University of Cyprus, *D.P. Singh,* Southern Illinois University Carbondale, *A. Hadjiafxenti, C.G. Rebholz,* University of Cyprus, *S.M. Aouadi*, Southern Illinois University Carbondale

Nanostructured materials such as thin films, nanotubes, nanowires and nanorods are playing a crucial role in electronics, optoelectronics, magnetic and thermal devices. One-dimensional materials, due to their low dimensions of nm-sized magnitude, exhibit exceptional physical and chemical properties in comparison with their bulk counterparts. Transition metal oxides (TMOS) have received considerable attention both from the fundamental science and technological applications (solid lubricants, catalysis, magnetic media, etc.), point of view. In the current study, β-$AgVO_3$ (silver vanadate) nanorods were synthesized using a room temperature wet chemical approach (hydrothermal method). Structural and morphological characterization using X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) and Raman spectroscopy was performed. In situ Differential Scanning Calorimetry (DSC)/Thermogravimetric Analysis (TGA) and High Temperature X-ray Diffraction (HT-XRD) studies were carried out between 25-1200ºC and 200-650ºC, respectively, to study the thermal properties and monitor the phase evolution as a function of temperature. The length of the β-$AgVO_3$ nanorods, based on the SEM studies was found to be 20-40 µm, whereas the width and the thickness were found to be between 300-600 nm and 50-100 nm, respectively. TEM studies revealed the existence of Ag nanoparticles at the surface of the nanorods. A strong correlation was found between data obtained from HT-XRD and tribological performance. The tribological performance of these materials deposited on H13 steel substrates was evaluated at room temperature and 600ºC in humid air against Si_3N_4 balls of a diameter of 6 mm. The room temperature coefficient of friction (CoF) was found to be 0.85, whereas this value drops to 0.2 at 600ºC tests due to crystallization of silver nanoparticles at high temperatures, acting as a solid lubricant.

2:30pm **H1-2-4 Fabrication of Nanodevices from Horizontally Grown Silicon Nanowires Using a Thin Aluminum Film as a Catalyst**, ***H. Mohammed*** *(kxm005@uark.edu),* University of Arkansas, *H. Abu-Safe,* Lebanese American University, Lebanon, *B. Newton, S. El-Ghazaly, H. Naseem*, University of Arkansas

We present a new method for the fabrication of nano electronic devices with horizontal silicon nanowires. A web of horizontally connected silicon nanowires is grown on a silicon substrate using thin aluminum film as a catalyst. A thin layer of oxide is thermally grown on a silicon substrate. The oxide layer is then etched at selective places using photolithography. A thin layer of aluminum is thermally evaporated on the substrate with the patterned oxide layer. When the sample is annealed above the eutectic temperature, we show that the silicon gets deposited along the grain boundaries of aluminum in the form of thin nano wires. We show that this phenomenon is due to the high solubility of silicon in aluminum at high temperatures.

The surface morphology was analyzed using Scanning Electron Microscopy (SEM). The compositional analysis was done using Energy Dispersive X-ray spectroscopy (EDX).

2:50pm **H1-2-5 Characterization and Optical Properties of Cu_2O Nanowire Arrays Growth by PAM Template**, ***Y.M. Shen***, *Y.-T. Shin,* 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

Cu_2O is a non-stoichiometric p-type semiconductor which exhibits wide band gap (2.1 eV) and high bonding energy (~150 meV). It has been proposed to be very attractive as a potential photocatalystic and photoelectric material under visible light irradiation. In this work, Cu nanowire arrays have been synthesized via porous alumina membrane (PAM) template with high aspect ratio, uniform pore size (120~140 nm) and ordered pore arrangement . The Cu_2O nanowire arrays are prepared from oxidization of Cu metal nanowire arrays. The electrochemical deposition potential of Cu metal nanowire (0.282V vs. SCE) is determined by cyclic voltammetry. The microstructure and chemical composition of Cu nanowire arrays have been characterized by field emission scanning electron microscopy (FE-SEM), high resolution transmission electron microscopy (HR-TEM), X-ray diffraction (XRD), and dispersive x-ray spectrometer (EDS). The photoluminescence spectra (PL) is employed to analyze the Cu_2O/PAM nanowire arrays luminescent properties. The results indicate that the Cu nanowire arrays are assembled into the nanochannel of porous alumina template with diameter of 120~140 nm. The valence of copper is controlled by porous alumina template during annealing process. Copper nanowires have been transformed to Cu_2O phase without the space limitation of PAM template, however Cu_2O phase nanowire arrays are obtained under the template embedded.

3:10pm **H1-2-6 Size Reduction of One-Dimensional ZnO Through the Addition of NaOH into $Zn(NO_3)_2/(NH_4)_2CO_3$ Mixture**, ***W.-Y. Wu*** *(wanyu@mail.mse.ncku.edu.tw),* National University of Tainan, Taiwan, *J.-M. Ting, W.-Y. Kung*, National Cheng Kung University, Taiwan

Hydrothermal synthesis of ZnO nanorods/nanowires in an autoclave is reported. Mixtures of $Zn(NO_3)_2$ and $(NH_4)_2CO_3$ water solutions was used as the reactant. It was found that t he nature of the autoclave process leads to wide diameter distributions. The reduction of the distribution width was made possible through the addition of NaOH. The addition of NaOH also resulted in diameter reduction and therefore high aspect ratios. Moreover, the growth time can be as short as 30 min, which is much less than previously reported. The activation energy of the slower lateral growth [11-20] was determined to be 4,836 cal/mole.

3:30pm **H1-2-8 Selective Growth of ZnO Nanorods for Gas Sensors using Ink-Jet Printing and Hydrothermal Processes**, *C.-J. Chang (changcj@fcu.edu.tw),* ***S.-T. Hung***, *C.-K. Lin, C.-Y. Chen, E.-H. Kuo*, Feng Chia University, Taiwan

Vertically aligned ZnO nanorod films with well-defined areas were deposited onto the glass substrate by the ink-jet printing and hydrothermal processes, which allowed the control of the dimensions and positions of the nanorods. At first, the seed solution (zinc acetate in ethanol) was ink-jet printed on the interdigitated electrodes. Then, vertically aligned ZnO nanorods were grown on the patterned seed layer by the hydrothermal approach. The influences of seed-solution properties and the ink-jet printing parameters on the printing performance and the morphology of the nanorods were studied. Unlike screen printing or lithography, inkjet printing does not require stencils or masks, therefore allowing rapid design and prototyping. The effects of nanorods structure, nanorods size and dye sensitization on the gas-sensing capability of ZnO-nanorod gas sensors were demonstrated. Due to the high surface-to-volume ratios and high crystallinity of the nanorod-array structure, devices with promising sensor characteristics were obtained.

Bioactive Coatings and Surface Biofunctionalization Room: Sunset - Session TS3-2

Moderator: S. Kumar, University of South Australia, E. Saiz, Lawrence Berkeley National Laboratory

1:30pm **TS3-2-1 Engineering Nanostructured Devices for Bioadhesive Drug Delivery**, ***T. Desai*** *(Tejal.Desai@ucsf.edu)*, University of California **INVITED**

Bioadhesive drug delivery platforms are desirable because they can adhere semi-permanently to tissues of interest and release drugs in a localized manner. Bioadhesive polymers have been investigated as particle carriers or as coating agents aiming to overcome the rapid elimination. By prolonging particle residence time, some types of bioadhesive polymers may establish specific interactions with the gastrointestinal mucosa allowing opportunity for target drug delivery. Numerous of drug molecules (particularly macromolecular drugs) presenting low oral bioavailability as well as low stability in the tract could be incorporated in such systems. Previous work has almost entirely concentrated on polymers or chemical strategies to improve bioadhesion. Polymer adhesives typically target mucin, instead of cells, allowing the devices to be rapidly cleared in mucous flows. Lectins have been successful as chemical modifications, binding specifically to cells. However, it may be possible to improve upon the chemical modifications by integrating topographical features which have previously been shown to direct and improve adhesion. Following research on gecko setae adhesion, nanowires and nanotubes have been shown to be highly adhesive due to Van der Waals forces arising from their increased surface area. Although it is known that nanostructures can enhance dry adhesion of films, no work has been carried out to investigate the adhesive properties of nanowire interfaces in physiological settings, particularly for drug delivery. Here we demonstrate that silicon-based nanowire interfaces can help anchor the particle to the cell surface and allow for greater residence time and localized drug release.

In particular, the adhesivity of devices with silicon nanowires was investigated under biological conditions, and showed superior bioadhesive properties in vitro. Adhesion studies under static and dynamic conditions, in conjunction with AFM studies, quantitatively show that nanowires adhere to cells better than conventionally used chemical bioadhesives. In vivo studies show enhanced retention with nanowire devices compared to uncoated devices. In combination with advancements in biosensing and microfabrication, the use of nanowires at a biointerface is a significant step in the direction of creating responsive drug release systems.

2:10pm **TS3-2-3 Freeform Plasma Generated Maskless Cell Patterning for Tissue Engineering Applications**, *E. Yildirim-Ayan (EDY22@DREXEL.EDU),* Drexel University*, H. Ayan,* Murray State University*,* ***D. Pappas***, U.S. Army Research Laboratory*, A. Fridman, W. Sun*, Drexel University

Up to date, wide variety of techniques including conventional photolithography, soft lithography, self-assembled monolayers (SAMs), direct writing, and laser ablation have been developed to functionalize the surface of interest with patterns to align cells and to control their functions. These techniques require masks, master stamps which may further need necessitates clean room instrumentation, long processing time, complex chemistry that may denature or degrade the deposited bio-organic layer. In addition, the requirement of mask and master stamps restrict the flexibility in patterning process while increasing the operating costs. In current study, we are introducing a versatile cell patterning approach; called freeform plasma generated maskless cell patterning.The freeform maskless patterning on biopolymer surface is done by the plasma nozzle system being able to create pattern on a substrate without using any chemical, solvent and mask. The plasma nozzle system is based on the principle of dielectric barrier discharges (DBD) operating with microsecond pulsed power supply and electrode system. To move the plasma nozzle system in freeform the nozzle system is integrated into data processing system, and the 3D motion system.

In current study, through freeform plasma generated maskless cell patterning approach the authors patterned mouse osteoblast cells on polyethylene. As working gas O2/He mixture was used. In order to create a line pattern on polymer surface, the plasma nozzle was navigated on a straight line with a 2mm/s speed. Following the patterning, the cells were deposited on the substrate to observe the effectiveness of effect of freeform plasma generated maskless cell patterning approach. The surface characterization was done by SEM and XPS. The SEM data showed that the surface functionalized with plasma nozzle system increased the surface roughness along the patterned line while rest of the substrate surface presented smooth surfaces. The XPS data showed that the atomic concentration of oxygen increased from 5% for virgin polymer to 18% for the center of the plasma treated line. This increment showed higher value on the line center and started to decrease by the lateral distance. The biological characterization has been done by Hoechst Stain 33258 through staining the nucleus of the patterned cells. The data showed that the cells only attached and survived on plasma functionalized patterned line while untreated surface showed no viability. Based on these data, we can say that it is possible to pattern the cells and dictate their shapes through freeform plasma generated maskless cell patterning approach.

2:30pm **TS3-2-4 Surface Modification of Polyurethane and Silicone for Therapeutic Medical Technics by Means of Electron Beam**, ***C. Wetzel*** *(christiane.wetzel@fep.fraunhofer.de), J. Schönfelder, W. Schwarz,* Fraunhofer Institute for Electron Beam and Plasma Technology, Germany*, R.H.W. Funk*, University of Technology Dresden - Institute of Anatomy, Germnay

To enhance biocompatibility of implant materials surface modification technologies are becoming in use steady more.

But concerning electron beam applications only little is reported for such purposes, despite of a few of advantages like adjustable degree of modification and efficacy in depth as well as simultaneous sterilising effects; in summary a careful treatment of sensible substrates by this method.

Therefore in the frame of our examinations the surfaces of polyetherurethane and silicones, two typical flexible implant materials, have been modified by non-thermal electron beam processing. After doing this the new surfaces were characterized with regard to wetting behavior, surface energy, chemistry and morphology. The cell adhesion was examined too.

The results reveal that the electron beam is a proper tool for surface modification of polymers.

2:50pm **TS3-2-5 Modification of the Surface of Polymer Implants by Deposition of Multifunctional Bioactive Nanostructured Films (MuBiNaFs) With and Without Stem Cells**, ***D.V. Shtansky*** *(shtansky@shs.misis.ru), I.A. Bashkova, A.N. Sheveiko,* National University of Science and Technology "MISIS", Russia*, M.C. Jimenez de Haro,* Instituto de Ciencia de Materiales de Sevilla, Spain*, A.S. Grigoryan*, Central Research Dental Institute, Russia

Recently, a new approach to design perspective films for metallic implants has been developed by our group. Multifunctional bioactive nanostructured films (MuBiNaFs) were deposited by magnetron sputtering of composite targets based on $TiC_{0.5}$ and (Ti,Ta)C with various inorganic additives CaO, TiO_2, ZrO_2, $Ca_3(PO_4)_2$, Si_3N_4, and $Ca_{10}(PO_4)_6(OH)_2$. While Teflon (polytetrafluoroethylene, PTFE) is widely used for the construction of surgical implants in restorative surgery, the surface of Teflon 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 multifunctional bioactive film. The present work is focused on the investigation of the structure and properties of MuBiNaFs deposited on the surface of PTFE. 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. The biocompatibility and bioactivity of the films were evaluated by both in vitro and in vivo experiments. In vitro studies involved the investigation of adhesion, spreading and proliferation of human fibroblast cells. Two groups of the in vivo investigations were fulfilled. Polymer fibres, 15% porosity, with MuBiNaFs were implanted in the rat hip defect and hybrid implants [stem cells from rabbit adipose tissue/MuBiNaFs/PTFE porous membrane] were implanted in the rabbit calvarian defect. The MuBiNaFs/PTFE samples demonstrated hardness H=0.6 GPa, Young's modulus E=5 GPa, and percentage of elastic recovery We=57-62% that is higher then that of PTFE sample without film (H=0.04 GPa, E=0.9 GPa, and We=31%). Static water contact angle measurements showed hydrophilic nature of the film surfaces. Critical load measurements using scratch tester with Al_2O_3 ball as counterpart material indicated high adhesion strength. Human fibroblasts were well adhered and spread on the surface of polymer coated with MuBiNaFs. The MuBiNaFs/PTFE implants revealed a high level of biocompatibility and osteointegration in the experiments in vivo.

3:10pm **TS3-2-6 Nanotechnology for Improving Regenerative Medicine**, ***T. Webster*** *(thomas_webster@brown.edu)*, Brown University **INVITED**

Much work is needed to design more effective tissue engineering materials. This could not be more evident by the fact that the average lifetime of current orthopedic implants is less than 15 years. Frequently, current implants fail due to insufficient integration into juxtaposed tissues (for example, bone, vascular, etc.). Nanotechnology offers exciting alternatives to traditional implants since our tissues are composed of constituent nanostructured components. For example, bone is composed of nanofibered hydroxyapatite well-dispersed in a mostly collagen matrix. Thus, it stands to reason that cells are accustomed to interacting with nanostructured (not conventionally-structured) surfaces. For these reasons, we have synthesized novel nanophase (that is, materials with dimensions less than 100 nm in at least one direction) ceramics, metals, polymers, and composites thereof. To date, increased synthesis of bone, cartilage, vascular, and bladder tissue have been observed on nanophase compared to conventional materials. Recently, increased functions of neurons have also been observed on nanophase materials. In this manner, results of studies demonstrating increased tissue regeneration on nanophase compared to conventional materials pertinent for the regeneration of a wide range of tissues will be presented in this talk.

3:50pm **TS3-2-8 Osteoblast Growth Affected by Micro-arc Oxidized β-titanium Alloy**, ***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, Taiwan*, T.-C. Yang,* Feng Chia University, Taiwan, R.O.C.*, I.P. Chiang, C.-H. Tang,* China Medical University, Taiwan*, K.-C. Chen, J.-L. He*, Feng Chia University, Taiwan

β-titanium (β-Ti) alloys are known for their excellent physical properties and biocompatibility, and are therefore considered as next-generation metals for orthopedics and dental implants. To improve the osseous integration between β-Ti alloys and bone, this study develops a titanium dioxide (TiO_2) coating on the surface of β-Ti alloys by using micro-arc oxidation (MAO) technique. The anatase (A) rich and rutile (R) rich TiO_2 layer, were formed on β-Ti, respectively. In vitro tests were carried out using pre-osteoblast cell (MC3T3-E1) to determine biocompatibility and osteogenesis performance. Biocompatibility includes cell adhesion, cell proliferation, and ALP activity, while the later includes osteopontin (OPN), osteocalcin (OCN) and calcium content. Cell morphology was also observed. In addition, raw β-Ti, A rich TiO_2 and R rich TiO_2 were implanted into the distal femora of Japanese white rabbits for 4, 8, and 12 weeks to evaluate its in vivo performance.

Experimental results show that TiO_2 coating can be grown on and well-adhered to β-Ti. The anatase phase formed under a low applied voltage, while the rutile phase formed under a high applied voltage, indicating that crystal structure is strongly influenced by applied voltage. A porous morphology was obtained in the TiO_2 coating regardless of the crystal structure and exhibited superior bone formation performance than β-Ti. In vivo analysis and in vitro test show similar trends. It is also noticeable that the R rich TiO_2 coating achieved better biocompatibility, osteogenesis performance. Therefore, a MAO-treated R rich TiO_2 coating can serve as a novel surface modification technique for β-Ti alloy implants.

4:10pm **TS3-2-9 Development of Surface Modification Techniques for the Covalent Attachment of Insulin-Like Growth Factor-1 (IGF-1) on PECVD Silica-Coated Titanium**, ***S. Kumar*** *(sunil.kumar@unisa.edu.au), E. Szili,* University of South Australia, *M. DeNichilo,* TGR BioSciences, Australia, *R. Smart,* University of South Australia, *N. Voelcker*, Flinders University of South Australia

Osseointegration is a complex process governed by the interaction of many cell types including blood cells (erythrocytes, platelets and leukocytes), phagocytic cells (macrophages) and bone cells (osteoblasts and ostecoclasts) on or near the implant surface. The implant surface can be modified through a variety of methods in order to achieve control of some of these cellular interactions and consequently increase the degree of implant fixation with the surrounding bone tissue. In the work presented in this paper, titanium, a common bone implant material, was modified with hydroxylated silica deposited using plasma enhanced chemical vapour deposition (PECVD) to increase the surface hydrophilicity and generate reactive surface silanol groups. Subsequently, the silica-coated titanium surface was further modified through silanisation to generate surfaces bearing different reactive chemical functionalities consisting of aldehydes, epoxides and isocyanates, which can react with the amino groups of proteins and growth factors. 2,2,2-trifluoroethylamine (FEAM) was reacted on these surfaces to determine the coupling efficiency of the different surface chemical functionalities. The amino group of FEAM can react with an amino-reactive surface functional group to form a surface terminated with 3 fluorine atoms per FEAM molecule that can be detected by X-ray photoelectron spectroscopy. By analysing the techniques used for protein attachment with the FEAM model molecule, a successful method was found and later adapted for tethering IGF-1 molecules to the functionalised PECVD silica-coated titanium surface. Therefore, this simple method of preliminary testing protein reactivity may prove to be a cost effective strategy in the development of new biomaterial surfaces modified with tethered protein bioconjugation methods.

Coatings for Use at High Temperature
Room: Sunrise - Session A1-3

Coatings to Resist High Temperature Oxidation

Moderator: Y. Zhang, Tennessee Technological University, D. Naumenko, Forschungszentrum Jülich GmbH

8:00am **A1-3-1 Determination of the DBTT of Aluminide Coatings and its Influence on the Mechanical Behavior of Coated Specimens**, ***S. Dryepondt*** *(dryepondtsn@ornl.gov),* Oak Ridge National Laboraotry*, B.A. Pint*, Oak Ridge National Laboratory

A high temperature indenter has been developed to determine the Ductile to Brittle Transition Temperature of diffusion aluminide coatings deposited by Chemical Vapor Deposition or pack cementation on martensitic-ferritic steels, austenitic steels and Ni-based alloys. An estimate of the transition temperature was based on hardness measurements as well as characterization of coating deformation and cracking after indentation at increasing temperatures. Creep tests were performed at temperatures below and above the DBTT to assess the impact of that parameter on the lifetime of coated specimens. The influence of the substrate and the coating process will be discussed.

8:20am **A1-3-2 Oxidation Performance of Low-Temperature Pack Aluminide Coatings on Ferritic-Martensitic Steels**, ***B.L. Bates****, Y. Zhang (yzhang@tntech.edu),* Tennessee Technological University*, B.A. Pint*, Oak Ridge National Laboratory

Aluminide coatings were synthesized at temperatures ≤ 700°C via pack cementation on commercial ferritic-martensitic alloys. Binary Cr-Al masteralloys were utilized to reduce the Al activity in the pack aluminizing process to prevent the formation of brittle intermetallic phases such as Fe_2Al_5. With the Cr-25Al masteralloy, the coating consisted of a thin Fe_2Al_5 outer layer (~4 µm) and an FeAl inner layer (~12 µm). When the Cr-15Al masteralloy was used, the lower Al activity led to the formation of FeAl coatings of ~12 µm thick. The oxidation performance of these low-temperature pack coatings was evaluated for up to 10,000 h in air + 10 vol.% H_2O at 650-700 °C, and compared to the coatings made by chemical vapor deposition at higher temperatures. The thin pack coatings on T91 substrates showed good oxidation resistance in the water vapor environment. Cross-sectional examinations of the coating samples after 10,000 h exposure were conducted to evaluate their microstructural and compositional changes.

8:40am **A1-3-3 The Dependence of High Temperature Resistance of Aluminized Steel Exposed to Water Vapour Oxidation**, *C.-J. Wang,* ***M. Badaruddin*** *(D9603801@mail.ntust.edu.tw)*, National Taiwan University of Science and Technology, Taiwan

The oxidation behaviour of hot-dipping aluminized steel was investigated at temperatures ranging from 700 to 800°C in air containing 100% water vapour (steam) at atmospheric pressure. The oxidation tests in 100% water vapour + $N_{(g)}$ were also performed to justify effect of water vapour in the atmosphere without air. After oxidation test, the morphology, composition and structure of the scale were examined by means scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), X-ray diffraction (XRD) and electron probe micro analysis (EPMA). The experimental results show that significant failure of protective coating occurred, resulting in substantial weight increase. The kinetics curve obeys linear law after long exposure times in the steam oxidation. The growth of Al_2O_3 scale and sporadic iron oxide nodules on the coating surface as well as at the interface are accelerated by the presence of water vapour in the atmosphere. In addition, when the temperature increases up to particularly 800ºC, the presence of water vapour greatly gives rise to internal oxidation of Al at the grain boundary in the substrate due to high atomic diffusion rate at this temperature.

9:00am **A1-3-4 Thin Pure-Metal Films Allowing to Rapid Development of α-Al_2O_3 Scale on High-Temperature Alloys and Coatings**, ***S. Hayashi*** *(hayashi@eng.hokudai.ac.jp), Y. KItajima, T. Narita, S. Ukai*, Hokkaido University, Japan **INVITED**

Rapid formation of slow growing oxide scale on heat resistant alloys and coatings is one of the most important issues in order to improve reliability and lifetime, particularly of materials which have a low total aluminium content, such as coatings and thin foils. Al_2O_3 forming alloys and coatings usually form so-called "meta-stable" (γ, θ)-Al_2O_3 at an initial stage of oxidation, and later transforms to stable (α)-Al_2O_3. This meta-stable to stable phase transformation is known to require longer time when the alloys and coatings are exposed to temperatures below about 900ºC. Moreover, reactive element additions to alloys and coatings, in order to improve scale spallation performance, are known to be significantly detrimental by delaying this phase transformation. The growth rate of meta-stable Al_2O_3 is more than two orders of magnitude higher than stable Al_2O_3, therefore rapid formation of α-Al_2O_3 and suppression of metastable-Al_2O_3 scale formation are directly linked to improvement of the performance of heat resistant alloys and coatings.

The aim of this study was to investigate methods to accelerate the meta-stable to α-Al_2O_3 transformation. In this presentation we will introduce the direct formation of α-Al_2O_3 scale without the formation of meta-stable Al_2O_3 on Fe-50Al and Ni-50Al alloys with and without deposition of thin films, ~50nm, of various elements such as Fe, Cr, Ni, Ti, and Al at 900ºC in air. Additionally, the effect of coating elements on initial development of α-Al_2O_3 as well as the meta-stable to α-Al_2O_3 phase transformation will be discussed.

Acknowledgements

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9:40am **A1-3-6 Development of Thermally Grown Oxide on β-NiAl During Initial Stages of Oxidation at 1100ºC**, ***H. Choi,*** University of Central Florida*, J. Jedlinski,* AGH University of Science and Technology, Poland*, Y. Sohn (ysohn@mail.ucf.edu)*, University of Central Florida

Phase transformations and microstructural evolution of thermally grown oxide (TGO) scale on polycrystalline β-NiAl, with and without Yttrium implantation, were examined by X-ray diffraction, photo-stimulated luminescence (PL), scanning and transmission electron microscopy (SEM & TEM). Implantation of yttrium ion was carried out with a beam energy of 70 keV up to 2 x 10^{16} ions/cm^2. The polycrystalline β-NiAl specimens were oxidized at 1100ºC in air for 15 minutes up to 24 hours. TEM specimens were prepared by using focused ion beam (FIB) in-situ lift-out (INLO) technique. After 15 minutes oxidation, the TGO consisted of islands of flat scale, 300 nm in thickness, in 550 nm-thick scale that exhibited needle-like morphology. This initially-developed scale consisted of θ- and δ-Al_2O_3 (θ >δ) with traces of equilibrium α-Al_2O_3. Pores were observed at the TGO/NiAl interface. The islands of flat TGO grew to 500 nm and the needle-like, rough TGO grew to 800 nm after 6 hours. The scale consisted mostly of α-Al_2O_3 with traces of θ-Al_2O_3. After 24 hours, two distinct layers in the TGO scale were observed: 1300 nm thick upper layer and 1600 nm thick lower layer in contact with NiAl. Both layers consisted of α-Al_2O_3. In addition, pores were observed at the interface between these two TGO layers, and Al-depleted γ'-Ni_3Al phase, 150 nm in thickness, was observed at the TGO/ Ni_3Al interface. With addition of Yttrium, the thickness of the TGO scale was in general thicker, and the transformation to the equilibrium α-Al_2O_3 was slower. However, the development of the microstructurally distinct two-layer was faster. While the upper TGO layer consisted mostly of the α-Al_2O_3, the bottom layer in contact with Y-implanted NiAl consisted of α, δ-, and θ-Al_2O_3 phases after 6 hours of oxidation at 1100ºC (α > δ > θ). Average compressive residual stress within the α-Al_2O_3, estimated by PL, was determined to be lower for Y-implanted NiAl.

10:00am **A1-3-7 Influence of Thermal Exposure on the Stability of Non-Equilibrium Microstructures of Sputter Deposited Nanocrystalline 304 and 310 SS Coatings**, ***N.S. Cheruvu*** *(sastry.cheruvu@swri.org), R. Wei,* Southwest Research Institute*, D.W. Gandy*, Electric Power Research Institute

It is well known that the sputter coating deposition technique produces coating with metastable structures. Though the standard 304 and 310 stainless steels (SS) have a face-centered cubic (fcc), the microstructure of the as sputter deposited 304 and 310 SS coatings exhibits metastable bcc (αFe) and fcc (γFe) + bcc structures, respectively [1],[2]. However, the effect of thermal exposure on the stability of the metastable structure as a function of temperature is unknown and hence, a systematic study has been undertaken to identify the metastables phases present in the as sputter deposited 304 and 310 SS coatings and assess the stability of the phases as a function of aging time and temperature. The 304 and 310 SS coatings were deposited on 304 SS samples using a magnetron sputtering technique. The coated samples, along with a 310 SS target sample, were exposed to 500ºC, 650ºC, and 750ºC for up to 5000 hrs. For phase identification, x-ray diffraction (XRD) radiation was conducted on the as-deposited and exposed samples. The XRD results revealed that the microstructures of the as-deposited 304 and 310 SS coatings consisted of σ + αFe and γFe + αFe phases, and as expected, the target material exhibited fcc. Thermal exposure at the three temperatures investigated resulted in the reduction of σ phase and precipitation of γFe phase in the 304 SS coating. On the other hand, thermal exposure of the 310 SS coating led to precipitation of the σ phase and the amount of σ phase in the coating increased with the exposure time. The results will be discussed in terms of variation of composition and alloy segregation between the as-deposited 304 and 310 SS coatings.

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[1] Childress, J., Liou, S.H., and Chien, C.L. “Ferromagnetism in Metastable 304 Stainless Steel with bcc Structure.” *Journal of Applied Physics*, 64(10), 15 Nov 1988, pp.6059-6061.

[2] Malavasi, S., Oueldennaoua, Foos, M., and Frantz, C. “Metastable Amorphous and Crystalline (α,σ) Phase

in Physical Vapor Deposited Fe-(Cr)-Ni-(C(Deposits.” *Journal of Vacuum Science Technology A*, 5(4), July/August 1987, pp. 1888-1891.

10:20am **A1-3-8 Microstructure and High Temperature Oxidation Behavior of Hot Dip Aluminized Coating on High Silicon Ductile Iron**, ***M.B. Lin*** *(d9603506@mail.ntust.edu.tw)*, National Taiwan University of Science and Technology, Taiwan

In this study, high silicon ductile iron was coated by hot-dipping in pure Al and Al-10Si melt .their high temperature oxidation behaviour was tested at 750°C to 950°C for virous exposure time. After high temperature oxidation tests, the microstructure analysis of all samples were investigated by means of metallographical examination, scanning electron microscopy (SEM) equipped with energy-dispersive X-ray spectrometer (EDS) and X-ray diffractometry (XRD).The results showed that hot dipping in Al-10Si could reduce the thinkness of intermetallic layer. Hot dipping Al/Al-Si on high silicon ductile iron improved high temperature oxidation resistence by over 10 times compared with the uncoated high silicon ductile iron.

10:40am **A1-3-10 A review of Sulphidation and Oxidation Processes in Gasturbines, their Simulation and Modelling via Laboratory Tests**, ***D.S. Rickerby*** *(david.rickerby@rolls-royce.com)*, Rolls-Royce plc, United Kingdom **INVITED**

Turbine hardware is subjected to a wide range of environmental degradation processes and these will be reviewed and their impact on component life discussed. Progress on the development of laboratory tests aimed at simulating these various environmental factors will be outlined along with their impact on the mechanical performance of coating systems. The extension of these simulation techniques into lifing methodologies for coated turbine hardware will be reviewed and areas for further work discussed.

Hard Coatings and Vapor Deposition Technology
Room: Town & Country - Session B2

Arc and E-Beam Coatings and Technologies
Moderator: I. Gorokhovsky, Southwest Research Institute, J. Vetter, Sulzer Metaplas GmbH

8:00am **B2-1 Arc Plasma Acceleration: A Method for Improving Coating Quality by Decreasing Macro Particle Inclusions**, ***V. Khominich*** *(viktor.khominich@phygen.com)*, Phygen Coatings, Inc.

Macro particle inclusions are a major contributor to coating system failure in conventional PVD cathodic arc evaporation processes. Surface roughness produced by these inclusions can also require the use of expensive post coat finishing processes. Phygen Coatings has developed and patented an improvement to cathodic arc PVD coating technology that results in the reduction of the macro particles produced in comparison to conventional arc evaporation processes while maintaining comparable deposition rates. The Arc Plasma Acceleration process results in smoother finishes and a denser non-columnar coating microstructure which leads to outstanding coating performance. Phygen's process allows for depositing a wide range of materials at deposition rates similar to conventional cathodic arc processes while improving properties and can eliminate the need for post coat finishing.

8:20am **B2-2 The Electron Beam High Rate Deposition in Combination with Guided Arc Discharges - Present State and Actual Developments**, ***J.-P. Heinß*** *(Jens-Peter.Heinss@fep.fraunhofer.de)*, FEP, Germany **INVITED**

The different PVD methods have found a wide-spread distribution in many industrial applications in the past. The electron beam (EB) evaporation with axial type guns is especially useable for depositions with a very high material throughput. Under such conditions EB-evaporation becomes economical and very attractive in comparison with other coating technologies.

We demonstrate the technical base for the large area and high productive electron beam evaporation. In special configurations it was realized to deposit a wide variety of alloys and compounds.

The plasma activation of the metal vapor and of the working gas gives further possibilities to control the layer growth and so the layer properties. We combined the EB evaporation with arc discharges so that the high arc discharge current density corresponds with the high rates of the EB-evaporation. We demonstrate the needed technical equipment for it and characterize a few plasma parameters. Whereas the first industrial applications were focused on the corrosion protection nowadays a couple of applications in modern technologies are under development. We present results of oxidic and carbon containing hard coatings and of electrical conducting layers for solar cells, which were deposited by using the plasma activated electron beam high-rate deposition.

9:00am **B2-4 Structure and Mechanical Properties of Single- and Multilayer Hard TiAlN/TiAlYN-based Coatings, Produced by Reactive Cathodic-Arc Evaporation**, ***V. Goltvyanytsya*** *(vladtnt@gmail.com), S. Goltvyanytsya,* Real Ltd., Ukraine*, A. Demchyshyn, L. Kulak*, Institute of Problems in Material Science, NANU, Ukraine

The main reason of emergency and development of protective coatings was a purpose to increase details and components life. Production of optimal coatings provides for selection of necessary composition of coating, its structure, porosity and adhesion taking into account technological parameters of deposition process.

Hard coatings like TiAlN considerably enhance performance of tools or product, which are coated. It allows to increase working temperature and hardness of coatings. Moreover, using PVD-technology it is possible to develop multilayer composition coatings with nano thickness of each layer on the basis of refractory metal compounds. By varying of technological parameters of coating condensation it is possible to influence on their properties.

Multilayer combined deposits with alternate layers ensure optimal combination of wearability, strength and fracture strength.

Single- and multilayer systems were produced via vacuum-arc atomization of Ti-Al, Ti-Al-Y, Al-Ti cathodes in nitrogen atmosphere with further coatings condensation on steel substrates. Singlelayer coatings TiAlN with thickness 5-8 μm had microhardness Hμ=35-40 GPa. For creation of system with different layer thickness the time of one layer deposition varied from 10 to 30 sec. Total deposition time of coatings was the same and equal to 30-60 min. Thickness of sublayers was less than 100 nm. Microstructure, elemental and phase composition were studied by means of scanning microscopy, Auger-electron spectroscopy, X-ray microanalysis and X-ray structure analysis. Microhardness of vacuum-arc condensates was measured by means of systems PMT-3M and “Micron-Gamma”.

In this study influence of sublayers on structure properties of multilayer deposits TiAlN/TiAlYN (150-300 layers) with fixed total thickness 10-15 μm was examined.

Formed multilayer TiAlN/TiAlYN deposits had enhanced hardness and oxidation resistance in comparison with monolayer TiAlN owing to creation of protection amorphous Al_2O_3-Y_2O_3 layer, which prevented their further oxidation was established.

Improved mechanical properties of multilayer coatings in comparison with homogeneous deposits, which were formed on the basis of mononotrides of transition metals, can be widely adopted as protective heat resistant and anti-wear coatings.

9:20am **B2-5 Microstructure Evolution of Ti_3SiC_2 MAX Phase Cathodes During Reactive Cathodic Arc Evaporation**, ***J.Q. Zhu*** *(zhu@ifm.liu.se), A. Eriksson, N. Ghafoor,* Linköping University, Sweden*, M. Johansson,* SECO Tools AB, Sweden*, J. Rosen, L. Hultman, M. Odén*, Linköping University, Sweden

The Ti-Si-C-N quaternary system is a promising candidate for wear resistant coatings due to its good mechanical and thermal properties. MAX phase Ti_3SiC_2, due to its unique combination of mechanical, electrical and thermal properties, could potentially yield an attractive cathode material for reactive cathodic arc evaporation synthesis of Ti-Si-C-N coatings. The evolution of the surface microstructure and composition of sintered Ti_3SiC_2 cathodes during reactive cathodic arc evaporation in a pure N_2 atmosphere and non-reactive cathodic arc evaporation in an Ar atmosphere with the arc current of 50 A is presented here. The results show that the cathodic arcing induces a converted layer on the cathode surface, in a form of overlapping craters with a diameter of 3-100 μm. The craters are shallow bowl-shaped pits with a raised outer rim, regardless of an Ar or N_2 atmosphere. The microstructure and composition of the converted layer differs from the virgin Ti_3SiC_2 and it contains different features depending on the evaporation conditions. The virgin cathode consists of approximately 12 μm Ti_3SiC_2 grains mixed with a small amount of TiC grains of similar size. Under reactive N_2 atmosphere conditions, the converted layer is 3-10 μm thick and consists of 100-500 nm TiC and TiN grains surrounded by a matrix that is rich in Si. Minor amounts of nanosize Ti_3SiC_2 grains also exist in this layer. In the non-reactive case, the converted layer is 10-40 μm thick and contains comparable amounts of 200-700 nm large TiC and Ti_3SiC_2 grains in a Si rich matrix. The surface roughness Ra-value of the worn cathodes increases from 2.4 μm to 6.2 μm when N_2 is introduced in the deposition chamber.

9:40am **B2-6 Influence of Process Parameters on Structure of TiAlN Coating Prepared by a System With Rotary Arc Cathodes**, *P. Vogl,* PIVOT a.s., Czech Republic, ***M. Jilek Jr.*** *(jilek.jr@shm-cz.cz)*, SHM, s.r.o., Czech Republic

It is advantageous to have a tool for a coating stoichiometry calculation to control coating deposition made from two different cathodes. Stoichiometry depends not only on arc currents ratio, but also on intensity and shape of magnetic field. This relation has been experimentally verified and is presented for TiAlN coating prepared by a new coating device Pi111. With the aid of this tool, it is possible to estimate coating parameters and to reach the desired Al/Ti ratio in a coating.

With increasing content of Al in a coating, cubic structure shifts to hexagonal structure. This change proves itself not only by hardness decrease, but also by a change of coating growth rate. For detailed description of this effect, method of calculation of coating stoichiometry described above was used.

10:00am **B2-7 Optimization of Micro Arc Oxidation Processes for Corrosion Resistance of Ti6Al4Valloys by Using Taguchi Method**, ***E. Demirci*** *(e_ebrudemirci@hotmail.com), E. Aslan, Y. Totik, I. Efeoglu*, Atatürk University, Turkey

Micro Arc Oxidation (MAO) is a novel technique used to improve surface properties of Ti6Al4V alloys. A number of studies have been carried out for producing a corrosion resistant coating on Ti6Al4V alloys by micro arc oxidation processes. However, there are very few studies on the optimization of the MAO process parameters for corrosion resistance of Ti6Al4V alloys. In this study, Taguchi experimental analysis method was used to systematically investigate the effects of four parameters (deposition time, frequency, current density, and concentration of electrolyte) with three levels on the corrosion resistance of coatings. Potentiodynamic polarization measurements were conducted to determine the corrosion resistance of the samples. The percentage contribution of each factor was determined by the ANOVA. The optimum coating parameters that affected the corrosion resistance were determined by using Taguchi method. The results showed that which parametre was the most significant factor affecting on the coatings's corossion resistance.

10:20am **B2-8 Phase Formation of Alumina Thin Films Deposited by Ionized PVD**, *K. Sarakinos, D. Music,* RWTH Aachen University, Germany, *F. Nahif,* University of Cyprus, *K. Jiang, A. Braun, C. Zilkens,* ***J.M. Schneider*** *(schneider@mch.rwth-aachen.de)*, RWTH Aachen University, Germany

Al_2O_3 films are deposited employing a monoenergetic Al^+ beam generated by a flitered cathodic arc [1]. A critical Al^+ ion energy of 40 eV for the formation of the α-Al_2O_3 phase at a substrate temperature of 720°C is determined. This energy is used as input for classical molecular dynamics and Monte-Carlo based simulations of the growth process, as well as *ab initio* calculations. The combination of theory and experiment indicates that in addition to surface diffusion the previously not considered diffusion in sub-surface regions appears to be an important atomistic mechanism for the phase formation of α-Al_2O_3.

[1] A. Atiser, S. Mraz, and J. M. Schneider, J. Phys. D: Appl. Phys. **42**, 015202 (2009).

10:40am **B2-9 Processing With Pulsed Plasmas: A Comparison of Cathodic Arcs and High Power Impulse Magnetron Sputtering**, ***A. Anders*** *(aanders@lbl.gov)*, Lawrence Berkeley National Laboratory **INVITED**

Deposition by high power impulse magnetron sputtering (HIPIMS) is emerging as the new paradigm for metal ion etching and self-ion-assisted deposition. While HIPIMS has indeed many advantages, some features are re-invented in light of the already forgotten accomplishments with arcs, and especially filtered arcs and pulsed arcs. Therefore, it seems appropriate to present a comparative study highlighting the common features and as well as the distinct differences, both in terms of plasma parameters and film properties.

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

11:20am **B2-11 Evaluation of Residual Stress and Coating Composition on Rounded Surfaces and Edges by Measurements and Cutting Tests**, ***J. Bohlmark*** *(johan.bohlmark@sandvik.com), H.I. Blomqvist, M.L. Ahlgren*, Sandvik Tooling Sverige AB, Sweden

Throughout the last decades various PVD technologies have grown to become large volume production methods for tool coaters. Today, the two most common PVD techniques are arc evaporation and magnetron sputtering. Both techniques are plasma based, and with that follow some typical features that in the end affect the coating performance. One typical feature of a plasma is the formation of a sheath region around the object to be coated. The formation of the sheath has some implications on the coating of three dimensional objects, since rounded surfaces and edges are subjected to different ion flux density. For example, it is well known that the coating often grows thicker on an edge than on a flat surface. Other differences may be observed in the coating composition and residual stress. Many publications reports data recorded on flat surfaces, but in real cutting applications the critical point is often close to an edge or curved surface. This paper presents measurements of the coating composition by EDS and residual stress with X-ray diffraction in coatings produced by arc evaporation on rounded surfaces and edges. It is observed that the coating composition changes with curvature. The concentration of materials that are more likely to be ionized in the plasma, such as Ti, is higher on objects with a high curvature. For example, the Ti content is about 10 % higher on a 1 mm diameter drill compared to an 18 mm drill. The residual stress in the coating is measured, and shows higher residual stress on and near the cutting edge as compared to a flat surface. The measurements also show that the residual stress in the coating is more dependent on the measurement location than the bias voltage. In addition, the observations are also correlated to metal cutting tests.

11:40am **B2-12 Highly Transparent and Conductive ZnO:Al Thin Films Prepared by Laser Induced High Current Pulsed Arc at Low Deposition Temperature**, *J.-B. Wu (wujinbao@itri.org.tw), C.-Y. Chen, J.-J. Chang, C.-T. Shih,* ***M.-S. Leu***, Industrial Technology Research Institute, Taiwan

Highly transparent conductive Al-doped ZnO (AZO) thin film were deposited at 100℃ by laser induced high current pulsed arc (LIHCPA) from a Al-Zn alloy target. A pulsed current more than 1 kA was generated on the Al-Zn target in order to make highly ion energy and fully ionization plasma. The films properties were correlated with the growth conditions, including O_2 flow rate, pulsed arc current apply to the target and Al doping content. The microstructure properties of the films such as surface morphology, crystallinity and chemical composition were studies using scanning electron microscopy (SEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). The electrical and transmittance of the AZO films were investigated by the Hall measurement and UV/VIS spectrometer. The experimental XRD results show that the AZO films has preferred c-axis orientation along the (002) plane. The minimum resistivity is as low as 4.2×10^{-4} Ω-cm with the carrier concentration of 7.3×10^{20} cm^{-3} and Hall mobility of 20 $cm^2V^{-1}s^{-1}$ and the average transmittance of films in the visible range (400-700 nm) is above 84 %. It was found that the O_2 flow rate affected not only the electrical properties of the films but also the band gap. The results clearly showed that when the O_2 flow rate increased from 30 sccm to 150 sccm, the resistivity increased from 4.2×10^{-4} to 3.7×10^{-3} Ω-cm, and also the band gap of the AZO films calculated by UV/VIS spectrometer measurement would decrease from 3.76 eV to 3.58 eV.

Fundamentals and Technology of Multifunctional Thin Films: Towards Optoelectronic Device Applications
Room: Royal Palm 1-3 - Session C3

Optical Characterization of Thin Films
Moderator: U. Beck, BAM, E. Schubert, University of Nebraska-Lincoln

8:00am **C3-1 Photoluminescence, Photoacoustic and Raman Spectra of Zinc Oxide Films Grown by LP-MOCVD Using Diethylzinc and Water as Precursors**, ***T. Terasako*** *(terasako@eng.ehime-u.ac.jp), T. Yamanaka, S. Yura,* Ehime University, Japan, *M. Yagi,* Kagawa National College of Technology, Japan, *S. Shirakata*, Ehime University, Japan

One of the most conceivable candidates for replacing widely used transparent conducting oxide In_2O_3:Sn (ITO) is zinc oxide (ZnO). Among various growth methods, low pressure metalorganic chemical vapor deposition (LP-MOCVD) is known to be an effective method for obtaining high-quality films under good controllability of growth rate and composition. In this paper, we will discuss photoluminescence (PL), photoacoustic (PA) and Raman spectra of polycrystalline ZnO films grown on alkali-free glass substrates by LP-MOCVD in terms of substrate temperature (T_S).

In our LP-MOCVD apparatus, diethylzinc (DEZn) and water (H_2O) were used as precursors and transported to the vertical reactor by the N_2 carrier gas. To obtain films with good surface homogeneity, the LP-MOCVD reactor has a rotatable substrate stage and a shower head for feeding DEZn.

PL spectra of all the films were composed of a near-band-edge (NBE) emission at ～3.3 eV and an orange band (OB) emission at ～2.0 eV. For the films grown at lower temperatures than 200℃, the NBE emission extended to higher energies than the bandgap energy of ZnO (3.37 eV), implying the existence of the secondary phase. In fact, Raman spectrum of the film grown at T_S=125℃ showed a broad Raman peak ranging from 750 to 850 cm^{-1} peculiar to $Zn(OH)_2$ with a larger bandgap than that of ZnO. The relative intensity of the OB emission to the NBE emission (I_{OB}/I_{NBE}) decreased with increasing T_S. Since interstitial oxygen atoms (O_is) are responsible for the OB emission, the decrease in I_{OB}/I_{NBE} can be interpreted as the decrease in O_I concentration with increasing T_S.

PA measurements were done for investigating optical absorption processes. For the films grown at T_S=125-200℃, the PA edge (which is characteristic "knee" on each PA spectrum) shifted towards lower energies with increasing T_S. This tendency is probably related to the decrease in $Zn(OH)_2$ secondary phase. On the contrary, for the films grown at T_S=200-300℃, the PA edge shifted towards higher energies with increasing T_S, resulting from the decrease in concentration of O_i and/or zinc vacancy (V_{Zn}) related defects accompanied with nonradiative transitions.

8:20am **C3-2 ZnO Preferred Orientation Control by Homo- and Hetro-Structure Buffer Layer Growth on Si (111) Using Atomic Layer Deposition with Flow-Rate Interruption Method**, ***C.-S. Ku***, National Synchrotron Radiation Research Center, Taiwan, *J.-M. Huang, C.-M. Lin,* National Hsinchu University of Education, Taiwan, *H.-Y. Lee (hylee@nsrrc.org.tw)*, National Synchrotron Radiation Research Center, Taiwan

ZnO thin film growth on Si (111) substrate using atomic layer deposition (ALD) at 25-260ºC without buffer layer result indicated polycrystalline structure verified by x-ray diffraction (XRD). Both homo- and hetro-structure buffer layer growth by ALD or RF sputtering showed orientation change to (002) or (101) direct preferred. The photoluminescence (PL) results showed near-band-edge narrowing and blue-shift as preferred Bragg peak intensity increased with raised ZnO growth temperature from room temperature. Both PL and XRD intensity were increased with grain size grow up as increased the buffer layer thickness. The buffer layer also reduced the surface roughness respect to no buffer layer ZnO thin films. The resistivity measure from hall measurement showed will change with different orientation and ZnO growth temperature. All results showed that buffer layer will control the preferred orientation not only enhanced the XRD and PL intensity due to large grain size reduced defect come from the grain boundary but also influence the hall mobility and resistivity.

8:40am **C3-3 Study of Magnetic Interfaces with Polarized Soft X-Rays**, ***C.S.-H. Sánchez-Hanke*** *(hanke@bnl.gov)*, Brookhaven National Laboratory **INVITED**

The definition of interface "a surface forming a common boundary of two bodies, spaces", is so generic that almost every system has an interface to study. The reality is that in most of the cases research focus more on the characteristics of the bulk, layers of the systems, meanwhile interfaces are almost not considered but as elements that perturb their characteristics. Fortunately there is a growing interest in understanding the contribution and influence that interfaces provide to the properties of the materials.

Synchrotron sources are an excellent tool for materials characterization. The wide energy range, from Infrared to hard x-rays, together with the high intensity of their photon beams, the tunability of the incident photon energy and the possibility to perform polarization sensitive experiments provides with a large range of possibilities for materials characterization. In the special case of interfaces the question remains what is an interface and how deep into the system goes. An important limiting factor to answer these questions is the spatial resolution as well as the wavelength to be used at the characterization experiment. In the presentation we will provide a brief introduction of common surface and interface sensitive experimental techniques that can be performed at synchrotron sources. Additionally we will show the efforts to characterize magnetic interfaces of magnetic interfaces characterized by means of elliptically polarized soft x-rays.

9:20am **C3-5 Vectorial Scattering Spectroscopic Ellipsometry Analysis of Dielectric Thin Films on Textured Solar Cells**, *M.F. Saenger,* University of Nebraska-Lincoln, *C.M. Herzinger,* J.A. Woollam Co., Inc., *M. Schadel,* Q-Cells A.G., Germany, *J. Hilfiker (jhilfiker@jawoollam.com), J. Sun,* J.A. Woollam Co., Inc., *T. Hofmann,* ***Schubert***, University of Nebraska-Lincoln, *J.A. Woollam*, University of Nebraska-Lincoln and J.A. Woollam Co., Inc.

State of the art silicon solar cells commonly use surface texturing and antireflective coatings to optimize the device efficiency. Optical characterization of thin films on textured substrates has been difficult due to scattering caused by substrate texture. Recently spectroscopic ellipsometry with non-traditional measurement geometry has been demonstrated capable of collecting specular reflections from orientated surfaces on textured silicon. Previous attempts for data analysis used an effective medium approximation to determine the thickness and refractive index of antireflection coatings. However, discrepancies exist depending on the measurement geometry [1]. Here we present a new method where scattering effects can be quantified in the data analysis. With our method it is possible to obtain consistent results, regardless the measurement geometry, for anti-reflection coatings on textured multi- and mono-crystalline silicon based solar cells.

[1] M.F. Saenger, J. Sun, M. Schädel, J. Hilfiker, M. Schubert, and J.A. Woollam, Thin Solid Films, (2009). (in press)

9:40am **C3-6** ***In-Situ*** **Studies on Thin Functional Polymer Films by Ellipsometry and Vibrational Spectroscopy**, ***K.-J. Eichhorn*** *(kjeich@ipfdd.de)*, Leibniz-Institut für Polymerforschung Dresden e.V., Germany **INVITED**

The control and understanding of biomolecule-surface interactions are very important for biosensor, biomedical and antibiofouling application. Specific desired properties can be incorporated into material surfaces by their modification using thin functional polymer films. So, "smart" surfaces can be developed for controlled adsorption and release of biomolecules.

Two surface engineering approaches will be presented:

- Coatings with thin layers of hyperbranched polyesters having tuned molecular architecture and functionalities.
- Fabrication of stimuli-responsive surfaces using immobilized thermo-responsive hydrogel films (PNIPAAM-PEG copolymers) or pH-responsive binary polyelectrolyte brushes (PAA and P2VP).

The properties of the surfaces and films in appropriate aqueous media (swelling/deswelling), their switching with temperature or pH as well as the resulting adsorption and release of biomolecules (model proteins such as Human Serum Albumin, Lysozym, Chymotrypsin, and cells) were studied in real time using optical *in-situ* methods: Spectroscopic Vis- and IR-Ellipsometry, Imaging Ellipsometry, FTIR-ATR Spectroscopy, and Microscopy.

10:20am **C3-8 Monitoring Protein Deposition of Self-Assembled Monolayers of Alkanethiols on Gold *In Situ* with Combined Quartz Crystal Microbalance and Spectroscopic Ellipsometry**, ***K.B. Rodenhausen*** *(kbrod@cox.net), B.A. Duensing, A.K. Pannier, Schubert*, University of Nebraska-Lincoln

We report a new combinatorial approach to study organic thin films. This novel technique consists of in-situ spectroscopic ellipsometry and quartz crystal microbalance methods. In contrast to the quartz crystal microbalance, which is sensitive to the total mass attached to the surface, including the trapped solvent, spectroscopic ellipsometry only measures the amount of adsorbant on the surface. By using these two techniques in tandem, we are able to determine the thickness and water fraction of visco-elastic thin films.

We investigate cetyltrimethylammonium bromide (CTAB) thin films deposited onto a gold-coated quartz crystal as a model system. CTAB grown from a 2.5 mM solution demonstrates several phases in porosity evolution, including a temporary hold in water fraction as the film is rinsed off the substrate with water; these effects may be related to the structure of a CTAB bi-layer.

In addition, a variety of self-assembled monolayers (SAMs) of alkanethiols on gold-coated quartz crystals were used as model biomaterials to determine the water fraction of an adsorbed fibronectin layer. The porosity information was used to distinguish the proteins' conformation, dictated by the defined surface chemistries of the SAMs. Two protein concentrations in PBS buffer were studied (0.1 mg/mL and 0.01 mg/mL) to isolate how protein concentration affects the above variables.

10:40am **C3-9 Evolution of Crystalline Phase Formation of Titanium Oxide Thin Films using Reactive Magnetron Sputtering and Annealing**, *C.-K. Chung (ckchung@mail.ncku.edu.tw), **M.-W. Liao***, National Cheng Kung University, Taiwan

Titanium oxide (TiO_x) thin films were deposited on the Si(100) substrates by direct-current reactive magnetron sputtering at 100~200 W Ti-target power and 3~10 % oxygen flow ratios ($FO_2\% = FO_2 / (FO_2+FAr) \times 100\%$), and then annealed by rapid thermal annealing (RTA) in atmosphere at 350, 550 and 750 °C for 2 min . The morphology, chemical composition, phase formation, and bonding behavior of the as-deposited and annealed TiO_x thin films were analyzed by scanning electron microscopy (SEM), energy dispersive spectrometry (EDS), grazing incidence X-ray diffraction (GIXRD), and Raman spectroscopy, respectively. The as-deposited and 350 °C annealed TiO_x films were amorphous from GIXRD and showed weak Raman intensity. In contrast, the distinct crystalline peaks of anatase or rutile phases were detected after RTA at 550~ 750 °C from both GIXRD and Raman spectra. The peak intensity of rutile phase increases with oxygen flow ratio and anatase phase increases with Ti-target power . Contrast with EDS results, a mixture of anatase and rutile phases was obtained by RTA at 750 °C when the stoichiometry x of as-deposited TiO_x films is between 1.57 and 1.97. The pure anatase and pure rutile phase were detected in x>1.97 and x<1.57 specimens after RTA, respectively.

11:00am **C3-10 Pulsed Laser Deposition of $(MoO_3)_{1-x}(V_2O_5)_x$ Thin Films: Preparation, Characterization and Gasochromic Studies**, ***C.-C. Chang** (ccchang1978@phys.sinica.edu.tw), T.K. Chen, J.-Y. Luo, T.-W. Huang, K.-W. Yeh, C.-T. Ke, P.-C. Hsu, M.-J. Wang, M.-K. Wu*, Academia Sinica, Taiwan

In this study $(MoO_3)_{1-x}(V_2O_5)_x$ mixed oxide films were fabricated by KrF (l = 248 nm) pulsed laser deposition (PLD), from mixed pressed powders of $(MoO_3)_{1-x}(V_2O_5)_x$, x = 0, 0.1, 0.2, and 0.3, at 300 mtorr oxygen partial pressure and 25 0℃ temperature on glass substrates. The hydrogen gas sensing performance of platinum (Pt) catalyst activated modified $(MoO_3)_{1-x}(V_2O_5)_x$ thin films were investigated. The behavior of $(MoO_3)_{1-x}(V_2O_5)_x$ thin films exhibited a gasochromic effect; i.e., a reversibly change in color from transparency when in air to blue when in H_2. The all processes proceeded rapidly at room temperature. A layer of platinum (Pt) was then evaporated onto the surface of $(MoO_3)_{1-x}(V_2O_5)_x$ film. The cycling of the coloration was obtained from UV-Vis spectra and the mechanism deduced from both visible and Fourier transform infrared (FTIR) spectra.. Therefore, we could detect the existence of H_2 by the coloration of $(MoO_3)_{1-x}(V_2O_5)_x$ thin film. Sensor properties of $(MoO_3)_{1-x}(V_2O_5)_x$ (Pt) films were investigated at room temperature in H_2–N_2 mixtures containing 0-50 mole% of H_2. The results show that the transmittance change(ΔT) of the $(MoO_3)_{1-x}(V_2O_5)_x$ hydrogen sensor.

11:20am **C3-11 Numerical Ellipsometry: Advanced Analysis of Thin Absorbing Films in the n-k Plane**, ***F. Urban** (fk_urban@yahoo.com), D. Barton*, Florida International University

A major challenge for those utilizing ellipsometry is numerical processing of the measured data. The transcendental, multivalued equations arising from the physics of simple reflection are problematic for the least-squares numerical methods in common use. Previously we have applied Complex Analysis in the n-k plane and this has led to a growing array of new numerical methods which achieve computational accuracy at the limit of the computer (~10-14 decimal digits) rather than functioning to a mean square value of a large number of measurements. The work presented here applies new numerical methods for use with absorbing films deposited on transparent and on absorbing substrates. The method finds intersections of projections of three “twisted curves” resulting from three (or more) light incidence angle measurements at three film thicknesses. The method is employed here to determine the thickness and optical properties of chromium films (between 10 and 25 nm nominal thickness) deposited onto two different substrates, silicon and silica oxide, employing measurements made at three different angles of incidence for light wavelengths between 280 and 2500 nm. Treatment of an oxide overlayer and alloy or compound underlayer is included.

Tribology and Mechanical Behavior of Coatings and Thin Films
Room: Pacific Salon 1 - Session E2-3

Mechanical Properties and Adhesion
Moderator: R. Chromik, McGill University, L. Davies, Caterpillar, J. Michler, Empa

8:00am **E2-3-1 Viscoelastic Properties of Thin Polymer Film on Rigid Substrate**, ***J.-L. Loubet** (jean-luc.loubet@ec-lyon.fr), S. Bec, S. Pavan*, Ecole Centrale de Lyon, France

The increasing use of polymeric materials as thin coatings requires appropriate mechanical characterization methods at micro and nano-scale taking into account time-dependent and temperature effects. A dynamic nanoindentation technique has been developed for viscoelastic analysis of polymer thin films.

This study is focused on the case of polymer layer thickness larger than 1 µm. For these polymer layers three scales has to be considered as a function of the ratio penetration depth (h) to the thickness layer (t).

For very small h, lower than 100 nm, and very small h/t ratio some changes from the bulk behaviour can be obtained. Experiments have demonstrated that the glass transition temperature of thin polymer films can be shifted as compared to the same polymer in the bulk. Using dynamic nanoindentation technique some changes from the bulk behaviour are here related.

For the middle range regime small h/t ratio and h bigger than 100 nm it can be possible to consider material as bulk material. Dynamic nanoindentation technique had shown agreement between bulk measurements and those on polymer thin films. In this talk it is shown how a quantitative thermorheological analysis can be done.

For larger h and h/t ratio, this study discusses the interaction between mechanical properties of thin layer and those of their substrate. The underlined questions are: how the substrate's mechanical properties affect those of the film; how the layer's thickness affects its mechanical properties. Model was used to estimate the elastic modulus of the film from the global measured value. For thin and "compliant" polymer layers deposited on "hard" substrates, an increase of the film elastic modulus was observed along indentation. This increase is attributed to the "anvil effect": the bulk elastic modulus increases with the hydrostatic pressure which results from the compression of the film.

8:20am **E2-3-2 Mechanical Properties Determined Via Probing of Freestanding Thin Films**, ***M.R. Begley** (begley@virginia.edu)*, University of California, Santa Barbara **INVITED**

This talk will discuss the design and interpretation of experiments on freestanding thin films to extract mechanical properties, such as modulus, residual stress, yield stress and adhesion. A central challenge in such tests is to identify combinations of dimensions, material properties, and loads for which closed-form load-deflection solutions will be accurate: a regime map will be presented which clearly identifies combinations that lead to classical plate, linear (pre-stretched) and nonlinear membrane behaviors. This map provides test designers with a clear pathway to identify dynamic load/ deflection ranges and dimensions that facilitate accurate property extraction. The feasibility and advantages of testing in each regime (and combinations of them) will be illustrated through various experiments on freestanding circular films of metals, polymers and elastomers. The talk will summarize robust and reliable methods to create freestanding circular films across a broad range of length- scales, which are amenable to testing with existing mechanical probes (e.g. nanoindenters and atomic force microscopes). The description of these experiments will briefly summarize recent mechanics descriptions that facilitate test design and interpretation, such indenter size effects during indentation with spheres, and comprehensive closed-form solutions for mode-mixity in blister tests.

9:00am **E2-3-4 Numerical Study of Tensile Tests Conducted on Systems with Elastic-Plastic Films Deposited onto Elastic-Plastic Substrates**, *N. Fukumasu (fukumasu@gmail.com), C.M. Angelo,* University of São Paulo, Brazil, *M. Ignat,* Universidad de Chile*, **R.M. Souza***, University of São Paulo, Brazil

In this work, a series of two-dimensional plane-strain finite element analyses was conducted to further understand the stress distribution during tensile tests on coated systems. Besides the film and the substrate, the finite element mesh also considered a number of cracks perpendicular to the film/substrate interface. Different from analyses commonly found in the literature, the mechanical behavior of both film and substrate was considered elastic-perfectly plastic. The variables in the analysis were the number of cracks in the film, the distance between two consecutive cracks and the film yield stress. Results were analyzed based on the normal stresses parallel to the loading axis (σ_x), which are responsible for cohesive failures that are observed in the film during this type of test. Results indicated that the presence of plasticity in the film has significantly reduced the value of σ_x at the film/substrate interface and close to the pre-defined crack tips. Thus, thin film plasticity favors new crack nucleation at film surface, similar to what is commonly seen in practice, and not at the interface.

9:20am **E2-3-5 Thermal Fatigue of Ion Nitrided and Duplex-Treated Hot-Work Tool Steel**, *M.A. Quiñones-Salinas (maqs73@hotmail.com),* ***R.D. Mercado-Solis,*** Universidad Autonoma de Nuevo Leon, Mexico, *J. Smolik, A. Mazurkiewicz*, Institute for Sustainable Technologies, Poland

Thermal fatigue is one of the most notorious failures in hot metal working tools. In addition to the high mechanical and tribological loads, tools are also subjected to repeated thermal loadings due to localised temperature gradients between their free surface and their core. Thermal load fluctuations result in the nucleation and subsequent propagation of thermal fatigue cracks. The application of surface treatments like ion nitriding, PAPVD coatings and their combination in duplex treatments has been effective to reduce tool oxidation, corrosion, erosion and wear. However, it is still uncertain whereas tool nitriding and duplex treatments have any real mitigation effects (and if so, to which extent) on the nucleation and growth of thermal fatigue cracks on the surface of the tools.

This paper presents an experimental investigation on thermal fatigue of ion nitrided and duplex-treated (ion nitriding followed by PAPVD coatings) AISI H13 hot-work tool steel. One ion nitrided system and five duplex-treated systems [TiN, TiAlN, (CrN/TiN)x3, CrN, (Cr/CrN)x8] were categorised based on the intensity of thermal fatigue cracks observed after testing. An apparatus based on high frequency induction heating and water spray cooling was used for thermal fatigue testing under the following conditions: maximum temperature at specimen surface 600°C, minimum temperature at specimen surface 80°C, heating time per cycle 15 seconds, cooling time per cycle 10 seconds and total number of thermal cycles for test termination: 500, 1000 and 2000. The behavior of the diffusion layer (ion nitriding), mono- and multi-layered coatings upon thermal fatigue intensity was discussed according to surface crack density and crack propagation depth at different test intervals. Finally, based on the results of the investigation, the applicability of surface treatments in hot metalworking tools subjected to thermal fatigue is discussed in this paper.

9:40am **E2-3-6 Contact Resonance Force Microscopy Technique to Determine Local Elastic Properties**, ***J.H. Hahn*** *(juny@kriss.re.kr)*, Korea Research Institute of Standards and Science, South Korea, *D.H. Kim, H.S. Ahn*, Seoul National University of Technology, South Korea

We have used contact resonance force microscopy(CRFM) technique to determine quantitative values for the elastic properties of multiple materials integrated on the sub micrometer scale. The CRFM approach measures the frequencies of an AFM cantilever's first two flexural resonances while in contact with a material. The plane strain modulus of an unknown or test material can be obtained by comparing the resonant spectrum of the test material to that of a reference material. We examined bumping materials for flip chip: under bump metallization (UBM), solder and under filled epoxy using copper electrode as a reference material. Data were analyzed by conventional beam dynamics and contact dynamics. 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.

10:00am **E2-3-7 Semiconductor Nanowires in Novel Device Concepts: the need for Structural and Mechanical Integrity and Ways to Reliably Characterize these Properties**, ***S. Christiansen*** *(sechrist@mpi-halle.mpg.de),* Max-Planck-Institute of Microstructure Physics, Germany, *Th. Stelzner, V. Sivakov,* Institute of Photonic Technology, Albert Einstein, Germany, *A. Berger,* Max-Planck Institute of Microstructure Physics & Institute of Photonic Technology, Albert Einsteinstr, Germany, *S. Hoffmann, J. Michler*, Empa, Switzerland **INVITED**

Semiconducting nanowires, e.g. from silicon (Si NWs) can be grown either epitaxially on crystalline substrates or e.g. on glass so that no epitaxy is involved. This so called /bottom up /growth/ /approach is explored now next to the well established /top down /technology which is based on materials removeal using masks. Both methods for nanowire realization are studied and 1D structures are realized between 10 nm and 1µm in diameter, i.e. in structure dimensions that permit new applications in sensors photonic and electronic devices. In order to be able to incorporate these SiNWs in new device designs, their physical properties have to be known. This presentation shows structural and mechanical characterization of SiNWs and already integrated SiNWs for example embedded in transparent conductive or insulating oxide layers.

The SiNW characterization is based on a combination of microscopy techniques. Transmission electron microscopy to reveal the structural properties down to the atomic scale and scanning electron microscopy

(SEM) to reveal SiNW morphology. In addition, a nanomanipulator built into an SEM is used to contact the nanowires and characterize them electrically (e.g. /p/-/n /doping profiles can be detected by electron beam induced current imaging). This nanomanipulator inside the SEM is used to manipulate the SiNWs so that bending as well as tensile testing are possible with real time visual feedback. In particular, tensile experiments can be performed in which the specimen is strained uniformly. This is important to reduce the influence of surface effects, for example when measuring Young's modulus of an unknown material or a composite material such as a SiNW with a conformally wrapped oxide layer. In order to precisely and automatically extract data from the experiments, an image analysis tool is used that can track objects with subpixel resolution. Finite element calculations support measurements.

The example of SiNWs as the absorber in a novel thin film solar cell concept will be discussed in terms of mechanical integrity and electrical capabilities.

10:40am **E2-3-9 Development of a Biaxial Tensile Module at Synchrotron Beamline for the Study of Mechanical Properties of Supported Thin Films**, ***P.O. Renault*** *(pierre.olivier.renault@univ-poitiers.fr), S. Djaziri, E. Le Bourhis, P. Goudeau,* University of Poitiers-France, *G. Geandier, D. Thiaudière, A. Bouaffad,* Synchrotron Soleil, France, *O. Castelnau, R. Chiron, R. Randriamazaoro, D. Faurie*, LPMTM-CNRS, France

In the frame of an ANR Pnano project (Cmonano), we develop a biaxial tensile module at the French synchrotron facility SOLEIL in order to study and model the elastic behavior of nanostructured thin films. The mechanical characterization of such structures and the relationship with the microstructure required for further development of technological applications, are still poorly explored. The project encompasses the elaboration of thin films of controlled microstructure, the experimental characterization of their mechanical response under biaxial loading and synchrotron X-ray diffraction, and the modeling of the observed mechanical behavior in view of the nanostructure. Metallic thin films are produced using PVD methods onto polymeric substrates, i.e. polyimide cruciform-shaped substrates. The film-substrate composites are then deformed in situ in an X-ray goniometer. The morphology and texture of the coatings are characterized using TEM and XRD respectively. The modeling using homogenization methods, is developed and takes into account both the crystallographic texture and morphology of the metallic films. The first results concerning W thin films in situ deformed with this new biaxial tensile modulus will be presented.

11:00am **E2-3-10 Determination of Residual Stresses and their Relaxation in Brush-Plated Gold and Silver Coatings Depending on Current Density**, *H. Lille (harri.lille@emu.ee), J. Kõo,* ***A. Ryabchikov***, Estonian University of Life Sciences, Estonia, *R. Veinthal, V. Mikli*, Tallinn University of Technology, Estonia

Brush-plating (selective plating) of gold and silver is mainly used for decorative or electric applications. This process is up to 60 times faster than bath plating and has made reductions in amount of deposited materials possible. The laying of the coating, however, is accompanied by generation of residual stresses in it. Residual stresses are in many cases high and may cause significant shape changes or contribute to damage development (cracking, delamination due to poor bonding between the coating and substrate). Thus, accurate measurement and prediction of residual stresses is important for an understanding and ultimate control of delamination and cracking of coatings.

In this study residual stresses were determined in gold and silver coatings deposited from a commercial SIFCO Dalic Solution (Gold (Hard Alloy), Code SPS 5370, and Silver Hard Heavy Build, Code SPS 3080) on brass unclosed thin-walled ring substrates.

The calculation formula is extended Brenner and Senderoff˝s formula which takes into consideration the real shape of the substrate, and the difference between the elasticity moduli of coating and substrate materials [H. Lille, et al., Materials Science, Lithuania, 3(2008), 226]. Residual stresses in the coating were investigated depending on current density. D eposition took place at the current densities 0.05 to 0.50 amp/cm^2 and the cathode velocity 23.4 m/min. The sensitivity of the method was studied and the expanded uncertainties of the computed mean values of the residual stresses are presented. Residual stresses represented tensile stresses and their values ranged from 191±29 to 402±61 N/mm^2 and 43.6±7.1 to 102.0±16.6 N/mm^2 for gold and silver, respectively. These values are higher than the respective values of stresses in coatings obtained from bath solution.

Relaxation of residual stresses was observed. The values of residual stresses in the gold (deposited at the current densities 0.15 to 0.35 A/cm^2) and silver coatings decreased markedly. After one week they were about two times lower and after nineteen months more than four times lower than the respective values obtained immediately after deposition. However, residual stresses in the gold coatings deposited at the current densities 0.05; 0.10; 0.40 and 0.50 A/cm^2 decreased somewhat less: for example, after nineteen months their values were more than twice lower than the respective initial values.

The microstructure of the studied coatings was investigated by means of scanning electron microscopy (SEM) and atomic force microscopy (AFM).

Keywords: Brush-plating; Unclosed ring substrate; Cold and silver coatings; Residual stress; Stress relaxation

11:20am **E2-3-11 Nano Mechanical Characterization of Ultra Thin DLC Coatings by Nanoindentation and Nano Scratch Testing**, *N. Randall (nra@csm-instruments.com),* CSM Instruments, USA, *G. Favaro,* CSM Instruments, Switzerland, ***R. Nair***, CSM Instruments, USA

Diamond Like Carbon (DLC) thin films are being developed for use in a wide range of applications (biomedical, semiconductor, etc). In order to simulate (and if possible extend) the service life of a particular coating system and to improve efficiency, it is important to characterize the true coating material properties. This can be particularly difficult for thin films whose thickness is often less than 50 nm (common in the magnetic hard disk industry, for example). This paper will focus on the particular challenges which are encountered when attempting to measure a wide range of properties, including hardness, elastic modulus, coating adhesion, strain-hardening exponent, fracture toughness, viscoelasticity and creep. A specific focus will be placed on the ability of a thermal-drift-free nanoindentation system to accurately and reproducibly measure the elastic/plastic transition in such thin films and why this can be of importance in obtaining stress-strain information about the coating. The advantages of measuring creep decay over significant time periods (> 5 minutes) and guaranteeing that such creep is entirely material-dependent (and not having a component originating from the measurement equipment) will also be covered.

Applications, Manufacturing, and Equipment
Room: Pacific Salon 3 - Session G2

Coatings for Automotive and Aerospace Applications
Moderator: H. Rudigier, OC Oerlikon Balzers AG, G.V. Dadheech, General Motors

8:00am **G2-1 Plasma Coatings for High Efficient Power Train in Automobile**, *K. Bobzin, N. Bagcivan,* RWTH Aachen University, Germany, *N. Goebbels,* ***K. Yilmaz*** *(yilmaz@iot.rwth-aachen.de)*, Surface Engineering Institute RWTH Aachen, Germany

There is a great motivation to increase the efficiency of automobiles. This motivation mainly arises from the fulfillment of Kyoto protocol, which states the participating countries to reduce their CO_2 emission until 2012. A reasonable amount of CO_2 is produced by transporting vehicles; hence, increasing their efficiency enables reducing CO_2 emission significantly. Enhancing of the efficiency can be achieved by decreasing the friction behavior or increasing the load carrying capacity of the power train elements. These requirements can be fulfilled by means of plasma coating technologies like PACVD (plasma activated chemical vapor deposition) and MSIP (magnetron sputter ion plating). Using PACVD technology, it is possible to deposit DLC (diamond like carbon), which shows excellent tribological performance, i.e. low friction and high wear resistance, under boundary and mixed lubrication regime. The low temperature ternary coating system Cr-Al-N promises to improve the load carrying capacity and wear resistance of the power train elements, with which same performance can be achieved for decreased weight that leads in return to reduction of CO_2 emission. Introduction of new tribological surfaces for the sake of efficiency increase leads to the question, how lubricants are compatible with these new surfaces, which are normally developed for steel surfaces. Therefore the wettability of the new surfaces with conventional lubricants is still a challenging question. DLC and CrAlN show chemical inactive behavior, therefore the physical interactions can be considered for their wettability with lubricants.

In this study, the physical interactions between the plasma coatings and lubricants are investigated by spreading coefficients and adhesion energy, which are determined by contact angle measurement technique. The plasma coatings are a-C:H (DLC-Star®, Oerlikon Balzers) and CrAlN. The lubricants investigated are mineral oil, polyalphaolefin, synthetic ester, polyether and polyglycol. The tribological behavior of the coatings a-C:H and CrAlN with lubricants are determined in a pin-on-disk tribometer. The tribological results are compared with the physical interactions of the lubricants with the plasma coatings. For an optimum wettability of the plasma coated surfaces with lubricants, it is found that it is important to adapt both the adhesion energy and spreading coefficient, such that increasing the adhesion energy of the lubricants on DLC and CrAlN, whilst decreasing their spreading coefficients leads to a significant decrease of the friction coefficient.

8:20am **G2-2 Wear and Corrosion Protection of AJ62 Mg Alloy by Plasma Electrolytic Oxidation (PEO) Process for Mg Engine Application**, ***P. Zhang***, *X. Nie (xnie@uwindsor.ca)*, University of Windsor, Canada

In order to reduce the fuel consumption and pollution, automotive companies are developing magnesium-intensive engines. However, due to the low wear and corrosion resistance of the Mg alloys, Mg cylinder bore and Mg engine coolant channels are vulnerable to the sliding wear and corrosion attack, individually. In this paper, Plasma Electrolytic Oxidation (PEO) process was used to produce oxide coatings on AJ62 Mg alloy, developed for Mg engine block, to battle against wear and corrosion attack. The PEO coatings exhibited a much better wear resistance, as well as a smaller friction coefficient, than the AJ62 substrate. According to the potentiodynamic polarization corrosion tests, the PEO coatings had a much higher corrosion resistance than the substrate. The galvanic corrosion property of AJ62 Mg coupled with stainless steel and aluminum (Al) was also investigated via immersion corrosion test in an engine coolant. With proper coating thickness, the PEO coatings can effectively protect the Mg alloy from the galvanic corrosion attack without significantly affecting the thermal conductivity of the Mg.

8:40am **G2-3 A Study on the Influence of Bond Material on Honing Engine Cylinder Bores with Diamond Coated Stones**, *L. Sabri (leila.sabri@renault.com),* ***S. Mezghani***, *M. El Mansori*, Arts et Métiers Paris Tech, France

A consistent increase in demand for special tools designed to an efficient honing of engine cylinder bores is observed. Metallic Bonded Diamond Stones (MBD) are more and more used for their wear resistance and their high tool life. However, the hardness of this metallic bond leads to the degradation of the honed surface aspect by the formation of smudgy grooves edges (*Blechmantel*). This torn and folded metal affects the required functional performances of the cylinder bore. In this study, two new diamond coated stones with Vitrified and Resinoid Bond (respectively VBD and RBD) are tested and compared to the MBD sticks. The influences of bond material on the honing reliability are studied in terms of honed surface aspect, material removal rate and wear properties. Results reveal that the stiffness and the openness structure of the Resinoid bond lead to a better trade off between surface aspect and tool life.

9:00am **G2-4 Opportunities and Challenges to Coatings Applications in the Automotive Industry - Select Case Studies**, ***M.L. Lukitsch*** *(Michael.lukitsch@gm.com)*, GM Research & Development Center **INVITED**

Several case studies that showcase successful applications of coatings and thin films in the automotive industry will be examined in detail. Emphasis is on the diverse performance requirements of thin films and coatings that are unique to vehicle design and performance. These requirements are presenting challenges to materials development by physical vapor deposition (for example) and quantitative materials characterization.

Finally, existing opportunities and some exciting new challenges for coating and thin film materials related to vehicle electrification are reviewed.

9:40am **G2-7 Influence of Simulated Stamping Force on Coating Failure Behavior**, ***J.F. Su***, *X. Nie (xnie@uwindsor.ca),* University of Windsor, Canada, *T. Mulholland*, General Motors Company

Due to the increasing use of advanced high strength steels, die wear prevention has become an important issue in the stamping of automotive parts. Since physical vapor deposition (PVD) coatings usually has a much higher hardness and resistance of wear than electroplated or electroless coatings and nitrided steels, PVD coatings have been considered as necessary top layers on dies surface to battle the wear problems.

Since most lab tests use operating conditions that do not correspond to actual conditions in production stamping dies, the lab tests may provide misleading results. In this work, a ball-on-plate impact fatigue test was proposed as a novel experimental technique to simulate the wear and fatigue behavior of a coating-substrate system. The simulated stamping force consists of an impact load and a pressing load, which can be adjusted by changing the distance between the impact ball and the sample (plate) surfac and by regulating air pressure in the air cylinder of the impact tester, respectively. Various hard coatings (CrN, TiAlN and TiC) were tested at various combinations of impact/pressing loads (i.e., 200N/400N, 400N/400N, 600N/400N and 800N/400N) for 10,000 cycles. The study provides experimental results concerning cohesive and adhesive failure modes. The failure mechanisms of the tested coatings are determined by means of optical microscope, scanning electron microscope and energy dispersive x-ray analysis. It was shown that among all the tested coatings the CrN coating is the best against fatigue.

10:00am **G2-8 From Coatings to Electrochemical Energy Storage for Automotive Applications**, ***Y.T. Cheng*** *(ycheng@engr.uky.edu)*, University of Kentucky **INVITED**

I will present an overview of our recent work on surface engineering for automotive applications, including coatings and nanostructured materials for electrochemical energy storage.

(1) Is the lotus leaf truly superhydrophobic?

This question was studied by observing water on lotus leaves and lotus-like surfaces at the micro- and macro-meter scales. Our work suggests that these surfaces can be either hydrophobic or hydrophilic. This finding may have significant ramifications on how to make and use "superhydrophobic" surfaces.

(2) Shape memory surfaces

Using micro- and nano-indentation techniques, we demonstrated the existence of shape memory and superelastic effects under complex loading conditions at the micro- and nano-meter scales. These effects form the basis for applying shape memory alloys as "self-healing" surfaces and "metallic-based adhesion" materials. The microscopic shape memory effect can also be exploited to create surfaces with reversible roughness and texture for applications such as friction control and information storage.

(3) Understanding diffusion-induced-stresses in nanostructured materials for durable lithium ion batteries

We examined the effects of surface tension and surface modulus on diffusion-induced stresses in spherical nano-particles. We showed that both the magnitude and distribution of stresses could be significantly affected by surface mechanics. In particular, a tensile state of stress may be significantly reduced in magnitude or even be reverted to a state of compressive stress with decreasing particle radius. This reduction in tensile stress may be responsible for the observed resilience to fracture and decrepitation of nanostructured materials used in electrochemical energy storage.

These examples suggest a wide range of applications of nanostructured materials for the automotive industry and beyond.

10:40am **G2-6 Wear-Resistant HVOF- Coatings of Aluminum Steel Hybrid Structures**, *W. Tillmann (wolfgang.tillmann@udo.edu), E. Vogli,* ***B. Ruether***, TU Dortmund, Germany

The constant increasing requirements on modern materials and tools regarding mechanical, thermal and tribological characteristics require the application of innovative and novel material systems. Composite materials are a promising solution due to the combination of different properties in one system. By using aluminum as matrix-material and steel as reinforcement, innovative aluminum steel hybrid structures are attained. These structures are characterized through a high strength by a low specific weight.

However aluminum steel hybrid structures possess disadvantages due to the different hardness and wear behavior of aluminum and steel. While aluminum alloys with strength up to 700 N/mm^2 exhibit linear wear rates of max. 2.2 mm, possesses steel with a maximum strength of 2200 N/mm^2 a linear wear rate of only 300 µm. Under high wear exposure the surface becomes non-uniformly due to the wearing out the soft aluminum matrix. If there is additionally a weak bonding between both partners, it comes to delamination associated with decreasing the composite material strength.

The aim of this research work was to develop and study novel sprayed hard coatings deposited on aluminum substrates, which fulfill the targeted requirement profile under extreme demands. Thereby NiCrBSi- and $Cr_3C_2$25NiCr-powders were sprayed by means of high-speed-oxy-fuel-flame spraying (HVOF). To study the adhesion between hard coatings and soft aluminum substrates different blasting conditions were applied. The effects of this surface pretreatment on the composite material properties were examined by means of light microscopy, Vickers hardness measurement, ball-on-disc tests and 3D-surface topography analysis.

New Horizons in Coatings and Thin Films
Room: Royal Palm 4-6 - Session H3

Surface Engineering of Coatings: Tribo, Bio and Nano-Corrosion Effects
Moderator: M. Stack, University of Strathclyde, M.T. Mathew, Rush University Medical Center

8:00am **H3-1 Nano-Scale Surface Engineering for Tribological and Biomedical Applications**, ***M. Zou*** *(mzou@uark.edu)*, University of Arkansas **INVITED**

Surfaces engineered with nano-scale topographies and/or chemistries are finding more and more applications in various fields. For example, they are used to improve tribological properties in micro-electro-mechanical systems (MEMS) and computer hard drives, to facilitate cell adhesion and growth in tissue engineering, and to enhance water-repellency of surfaces for anti-corrosion and self-cleaning applications. Herein we show the application of aluminum-induced crystallization (AIC) of amorphous silicon (a-Si) technique to nanoscale surface-topography-engineering for reducing adhesion and friction forces for tribological applications and for enhancing *E. coli* cell adhesion on glass substrates in an *E. coli*-based whole-cell chemical sensor . The AIC of a-Si process involves sequential deposition of a-Si and Al films on a substrate, thermal annealing of the substrate, and etching to remove the excess Al. Traditionally, AIC of a-Si has been studied extensively to produce poly-Si films for electronic and photovoltaic applications, such as thin-film transistors, sensors, solar cells, and display panels; while our efforts have been focusing on fabricating nano-topography-engineered surfaces (NTESs) using rapid AIC of a-Si. Our studies show that nano-engineered surfaces have significantly reduced adhesion and friction forces than smooth surfaces with the same chemistry. NTESs were also found to significantly enhance *E. coli* cell-to-surface adhesion compared to smooth surfaces. Cell adhesion efficiency was found to be controlled by the texture density of the NTESs.

8:40am **H3-3 Influence of Rare Earth Element Incorporation on the Behavior of Magnetron Sputtered Al Based Alloys**, ***J. Creus*** *(jcreus@univ-lr.fr), C. Rebere, C. Berziou, A. Perez, S. Touzain,* Université de la Rochelle, France*, A. Billard*, Lermps, Utbm, France

Aluminum coatings are widely used for the protection of steel structures, but nowadays, structural materials are subjected to more severe conditions combining multi-physical parameters. A reinforcement of the properties of PVD aluminum coatings is necessary to check the new operating conditions of the materials. One problem of aluminum in corrosive media is the susceptibility to localized corrosion, and particularly to pitting corrosion in saline solution that drastically reduces the lifetime of the coatings. So it could be interesting to modify the corrosion mechanism from a localized type to a uniform mode.

Aluminum based alloys were deposited on glass substrates by magnetron sputtering PVD technique. Rare earth (RE) alloying elements (Ce, Y or Gd) were added in order to improve the properties of the aluminum coatings. The influence of the addition of different RE elements is discussed. The incorporation of RE elements has a very limited effect on the mechanical properties. For the 3 RE elements, a shift of the corrosion potential towards more negative values was observed when the content of RE elements increased. Extended immersion tests revealed that the corrosion potential of these alloys slightly evolves towards more positive values due to the formation of a passive film. The composition of this passive film will affect the mechanism of pitting corrosion, that could be less harmful for the lifetime of the Al based coatings.

9:00am **H3-4 Corrosion Resistance of Amorphous Niobium Oxide Thin Films**, ***S.E. Rodil***, *G. Ramirez (enggiova@hotmail.com), D. Turcio-Ortega, S. Muhl,* Universidad Nacional Autónoma de México, Mexico*, L. Escobar-Alarcon, E. Camps*, Instituto Nacional de Investigaciones Nucleares, Mexico

The evaluation of the corrosion resistance provided by insulating coatings to stainless steel is challenging due to the insulating properties of the coatings. Potentiodynamic studies are possible when the coatings have defects (micro pores) that allows the flow of the carriers (electrons or ions) between the substrate and the electrolyte. However, the interpretation using standard Tafel analysis is not accurate for quantitative evaluation of the corrosion properties. The ac techniques, such as, electrochemical impedance spectroscopy (EIS) provides an appropriated interpretation with detailed information of the processes occurring at both the coating-electrolyte interface and the localized corrosion through the small pores.

Niobium oxide ceramic coatings deposited on medical grade stainless steel, could be used as protective coatings in biomedical applications, such as, orthopaedical or dental implants. As a ceramic, it is a very stable material with good mechanical properties and previous studies have shown that it is not-toxic to human cells and tissues. Niobium oxide might occur in different crystalline phases; Nb2O5, NbO2 and NbO and the production of these phases by physical vapor deposition (PVD) methods require deposition at substrates temperature above 300°C. This will lead to a crystalline but columnar microstructure, as common for PVD coatings, where the inter-columnar space always constitute an open porosity where the electrolyte can reach the substrate with the subsequent failure of the coating. Therefore, in this work, we decide to evaluate the corrosion resistance of amorphous niobium oxide (a-NbOx) films using NaCl 0.89% solution, which are known as simulated biological solutions. The films were deposited by magnetron sputtering on stainless steel (AISI 316L) and the corrosion resistance was evaluated using potentiodynamic, polarization resistance and EIS. The deposition conditions and thicknesses were varied to find the ideal coating that could significantly improve the corrosion resistance of stainless steel to a chloride solution. The results showed that 500 nm constitutes a good thickness where there is no interconnected porosity and therefore the a-NbOx film forms a barrier between the electrolyte and the substrate.

9:20am **H3-5 Electrochemical Behavior of the TiN Coating for the Orthopedic Applications: Influence of Immersion Time and Protein Content**, *M.T. Mathew (mathew_t_mathew@rush.edu),* Rush University Medical Center, *R. Pourzal,* University of Duisburg-Essen, Germany, ***M. McFarland,*** Acree Technologies Incorporated, *N.J. Hallab,* Rush University, *A. Fischer,* University of Duisburg-Essen, Germany, *M.A. Wimmer*, Rush University

Recently, metal-on-metal hip joint implants are regaining attractiveness due to their low wear rate, design flexibility and post-operative stability. Due to this fact, improving the surface properties and cell/metal matrix interactions of the implant metals, through the existing/new coating methods or imposing optimum surface texture are the topical issues in orthopedic implant research. Titanium nitride (TiN) coating is one of the methods to improve the surface hardness and performance of the implant surface. However, biocompatibility and corrosion resistance of such modified surfaces *in-vivo* provoke concerns.

In this study, the electrochemical behavior of a TiN film deposited by cathodic arc method (substrate: Ti6Al4V) was investigated in bovine calf serum (BCS, protein: 30 g/L) and ringer solution at 37°C. The corrosion behavior was studied by measuring open current potential (OCP) and Potentiodynamic test. Further, the electrochemical behavior was investigated as a function of immersion time (1hr, 15 hrs, 40 hrs, 115 hrs) in both solutions. Electrochemical impedance spectroscopy (EIS) technique was used to characterize the electrochemical double layer and corrosion kinetics. Optical and SEM images were used to characterize the corroded surface. Results indicate that the presence of the protein in the solution increases the possibility of pit formation on the surfaces and may adversely affect the overall corrosion resistance of the TiN coated surface.

9:40am **H3-6 Surface Nanocrystallization in a NiTi Alloy Subjected to Surface Mechanical Attrition Treatment**, ***T. Hu,*** City University of Hong Kong, China, *C. Chu,* Southeast University, China, *R.K.Y. Fu, P.K. Chu (paul.chu@cityu.edu.hk),* City University of Hong Kong, China, *J. Lu,* The Hong Kong Polytechnic University, China, *K.W.K. Yeung*, The University of Hong Kong, China

Among various shape memory alloys, intermetallic NiTi alloy is an important material which has been widely used. Recently, the fabrication of nanocrystalline NiTi alloy has attracted a lot of attention due to both scientific and technological benefits. Several techniques such as high pressure torsion (HPT), equal channel angular pressure (ECAP), and mechanical alloying (MA) have been employed to synthesize nanocrystalline NiTi. However, these techniques can only produce nanocrystalline NiTi specimens with a small size thereby limiting further applications. S urface mechanical attrition treatment (SMAT), which has been successfully applied in synthesis of nanocrystalline metals in many materials systems, has some unique advantages compared to HPT, ECAP and MA. For example, the size of the specimen fabricated by SMAT meets many engineering application requirements. In this work, we utilize SMAT to create a nanocrystallines layer in NiTi alloy. The cross-sectional microstructure of the NiTi alloy processed by SMAT is characterized by X-ray diffraction (XRD), optical microscopy (OM) and transmission electron microscopy (TEM). The results show that SMAT produces nanocrystallines in the surface layer of the NiTi alloy. Besides, a graded microstructure along the cross-sectional depth is created in the NiTi alloy after SMAT due to the gradient evolution of strain and strain rate from the treated surface into the substrate. The results provide useful information pertaining to nanocrystallization of NiTi alloy with the evolution of strain and strain rate.

10:00am **H3-7 Bio-Corrosion and Cell Culture: Implications in Dentistry and Orthopedics**, ***C. Sukotjo*** *(csukotjo@uic.edu),* University of Illinois, *M.A. Wimmer*, Rush University **INVITED**

Usage of implants in human body has a long history of more than thousand years, and it is accepted as an effective clinical method, particularly in dentistry and orthopedics. Recently the implant usage is dramatically increased, for example, 500,000 stainless steel cardiac stents are now implanted in the US, every year. In dentistry, implant supported overdenture has been accepted as a standard of care in many countries.

However, in addition to the functional requirement, the nature of implant metals in the body environment always invites some concerns, particularly the issues such as the interactions with adjoining tissues and release of metal ions and its transport to the remote organs. Due to the clear clinical evidences (tumors, hyper sensitivity etc.) of such influence, during last 10 years, many studies were reported on the corrosion behaviour of the implant metals, based on the specific applications and environments, (For example, Cp Ti, in artificial saliva as a function pH). The main challenges in the area of Bio-corrosion is the need of researchers from materials science, physicians, biochemists, electrochemist, mechanical engineers, tribologist and microbiologist and evaluating their new finding in the light of clinical experience and effective practical implementations.

Hence this presentation addresses the progress made in the area of bio-corrosion, specifically, in the dentistry and orthopedics and some insights in methodologies in studying together electrochemistry, surface chemistry and cell culture. The influence of protein content in a biofluids on corrosion kinetics is highlighted. Further, importance of research area called tribocorrosion which simulates natural conditions, such as mastication or artificial joint, where the implants are exposed to movements in the chemical environment is outlined. Keeping this view, Dental school at UIC and Tribology Section, Dept of Orthopedic surgery (RUSH University, Chicago) established a strong research collaboration to address such issues and some recent outcomes and a road map and scope of this research area are included.

10:40am **H3-9 Identification of Tribo-Corrosion Regimes for Dental Materials and Coatings**, ***M. Stack*** *(m.m.stack@mecheng.strath.ac.uk), C. Hodge*, University of Strathclyde, United Kingdom

In studies of tribo-corrosion, the performance of dental materials is becoming of increasing interest. This is because in oral environments, corrosion, together with wear arising from oral processing, provide a tribo-corrosion environment which can vary significantly in pH, load, and size of wear debris. In such conditions, the performance of materials may be difficult to predict.

In tribo-corrosion, there has been significant research into descriptions of regimes of degradation. More recently the distinctions of wear affected corrosion ("additive behaviour) and "corrosion affected wear ("synergistic behaviour") have also been made. Such categories enable a mechanistic description to be assigned for the various tribo-corrosion processes.

In this work, the performance of a candidate dental material and a hydroxyapite coating were compared with a reference material-steel- in various micro-abrasion-corrosion environments. The environments included acidic conditions i.e. in orange juice and neutral solutions i.e. milk. Regimes of tribo-corrosion were identified based on the results enabling a new mechanistic description to be defined for dental materials and coatings

11:00am **H3-10 Comparison of the Properties of Al-Ti and Al-Mg EBPVD Coatings**, ***A. Perez*** *(andrea.perez@univ-lr.fr),* Université de La Rochelle, France, *F. Sanchette,* CEA, France, *A. Billard,* Lermps, Utbm, France, *C.R. Rébéré, C. Berziou, S. Touzain, J. Creus*, Université de La Rochelle, France

Aluminum based alloys were deposited on glass substrates by electron-beam evaporative PVD technique. Alloying elements (Ti or Mg) were added in order to improve both mechanical and corrosion behaviors of aluminum films. This approach aims to develop sacrificial protection of flat steel products. Since their vapour pressures are different, aluminum and alloying elements were co-evaporated from two separate sources. Different contents of transition metals were examined

The electrochemical characterizations were carried out in saline solution. It is shown that aluminum can be mechanically reinforced with preserving sacrificial behaviors. The evolution of the properties is strongly linked to the nature of the incorporated element. A comparison with a previous study on the electrochemical and mechanical behaviors of Al-Cr and Al-Gd EBPVD coatings will permit to complete the analysis of the influence of the incorporation of transition metal in aluminum.

11:20am **H3-11 Influence of pH on the Tribocorrosion Nature of the CpTi in an Oral Environment: Mechanisms and Synergism**, ***S. Abey***, University of Illinois, *M.T. Mathew (mathew_t_mathew@rush.edu), D.J. Hall,* Rush University Medical Center, *N.J. Hallab, M.A. Wimmer,* Rush University, *C. Sukotjo*, University of Illinois

Dental implants have been used in restorative dentistry as a predictable therapy approach to replace missing teeth. Due to its acceptable mechanical properties and minimum inflammatory reaction, titanium is commonly selected for dental implants. However, early failure of some implants invites concerns for long-term survival and the subsequent effects on the patients. A new research area called tribocorrosion, combining the study on wear behavior, i.e. tribology, and its response to the chemical environment, i.e. corrosion, has developed. Applying tribocorrosion principles to dental materials, specifically dental implants, will help manufacturers and practitioners understand product capabilities and limitations prior to use.

In this study, the tribocorrosive nature of titanium (CpTi) was investigated in artificial saliva as a function of pH (3,6,9) and load (20N). The sliding duration (2000 cycles), frequency (1.24 Hz) and load parameters were selected to closely mimic the oral environment and mastication process. The evolution of the current (at potentiostatic condition of Ecorr (E vs SCE)) and friction coefficients were measured during the test. Electrochemical impedance spectroscopy (EIS) measurements were made before and after the sliding (wear test) to comprehend the changes in the corrosion kinetics and surface chemistry. The results indicate that there is a major influence of pH on the tribocorrosion mechanisms and the synergistic interactions of wear and corrosion. Particularly, the high weight loss at pH 6.5 invites some concerns on the implant behavior in a normal oral environment.

11:40am **H3-12 In-Situ Impedance Spectroscopy Characterisation of Plasma Electrolytic Oxidation Process for Deposition of Ca- and P-Containing Coatings on Ti**, ***A. Aleksey*** *(A.Yerokhin@sheffield.ac.uk),* University of Sheffield, United Kingdom, *E. Parfenov,* Ufa State Aviation Technological University, Russia, *A. Matthews*, University of Sheffield, United Kingdom

Plasma electrolytic oxidation (PEO) of Ti currently attracts significant interest in the field of functional coatings, especially for catalytic, photovoltaic and biomedical applications. For the latter purposes, the PEO TiO_2 coatings are added with various calcium phosphate compounds that provide intrinsic bioactivity to the coating material. *In-situ* formation of these compounds is possible only if appropriate electrolyte solutions and current regimes of plasma electrolytic oxidation are carefully selected. Exact mechanisms of coating formation and principles of process control however remain unclear. In this paper, the coating formation processes were studied *in-situ* using impedance spectroscopy techniques. The main technical challenge of obtaining a frequency response from the high-voltage plasma-assisted electrochemical process was overcome by application of a frequency sweep of bipolar voltage pulses between 20 Hz and 20 kHz. Characteristic frequency bands were identified corresponding to the coating growth under charge transfer and diffusion control. From impedance spectra, the values of charge transfer resistance and barrier layer capacitance were derived and compared to those obtained using *ex-situ* impedance spectroscopy of resultant coatings. It is shown that under pulsed bipolar conditions of PEO, the critical frequency corresponding to the transition to diffusion control is can be substantially reduced. This indicates that the incorporation of Ca-and P- into PEO coating can be controlled in a wide range of frequencies mainly by electrolyte composition, whereas the current mode can be primarily used to tailor the coating morphology.

12:00pm **H3-13 Tribological Behavior and Corrosion Performance of Nanocomposite Coating Layer of nc-TiN/a-Si_3N_4 Deposited by Sputtering on AISI 316L Stainless Steel Duplex for Biomedical Applications**, ***J. Garcia*** *(jjgarcia@mx1.ibm.com), M. Flores*, Universidad de Guadalajara, Mexico

In this work a nanocomposite coating layer of nc-TiN/a-Si3N4, one of promising nitride coatings to extend the life time of mechanical components due to its high hardness value (>40 GPa), were deposited on AISI 316L stainless steel duplex substrate by a DC reactive magnetron sputtering technique. Tribological and corrosive tests were conducted with the purpose of establish the possibilities to use it as a biomaterial in the body, including: X-ray diffraction to analyze the nanostructure of the film, 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 and scanning electron microscopy (SEM) to evaluate the corrosion susceptibility of the nanocomposite coating. All the results are discussed and compared against the substrate material.

Experimental and Computational Studies of Molecular materials and Thin Films
Room: Sunset - Session TS1

Moderator: A. Amassian, KAUST, J. Rosen, Linköping University

8:00am **TS1-1 Printed Electronic and Photonic Materials for Device Applications**, ***G. Jabbour*** *(ghassan.jabbour@kaust.edu.sa)*, Arizona State University **INVITED**

No Abstract Received

8:40am **TS1-3 Microscopic Characterization of Organic Thin Films for Applications in Organic Electronics**, ***G. Witte*** *(gregor.witte@physik.uni-marburg.de)*, Philipps-University Marburg, Germany **INVITED**

Driven by the recent success of using organic semiconductors as active materials for organic electronic applications detailed microscopic studies on structural and electronic properties of such soft materials have become a focus of scientific interest. Of particular interest are oligoacenes because of their ability to form crystalline phases which reveal remarkable high carrier mobilities and hence constitute well defined model systems. In view of the interrelation between intermolecular packing and electronic properties of such materials there is a fundamental interest in a precise control of the molecular packing and orientation in highly ordered thin films which is also of vital interest for an optimization of thin film devices such as organic field effect transistors (OFETs) where high charge carrier mobility is required.

In this talk I will discuss growth phenomena and structural properties of various organic semiconductor films prepared by molecular beam deposition under vacuum conditions onto different substrates surfaces. By combining various spectroscopic and diffraction techniques with microscopy the evolution of their resulting structure can be traced as a function of film thickness. It is found that the resulting molecular orientation and film morphology depend critically on the roughness and chemical termination of the substrate whereas growth rate and substrate temperature mainly affect the grain size. Films that were grown on differently pre-structured substrate surfaces indicate that the film morphology can be controlled to some extend (*template effect*) whereas the crystalline structure is usually not affected. Moreover, for many metal substrates a pronounced island growth occurs after completion of the first wetting layer or upon post deposition dewetting and result in non-contiguous films. Such dewetting phenomena can be effectively suppressed by first coating the substrate with self-assembled monolayers (SAMs). Possible driving forces for the appearance of the various film structures and strategies for a rational control of the microstructure of such organic films are discussed. Finally I will demonstrate that the concept of specific surface modifications can also be applied to the electrodes in bottom contact OFETs and causes largely improved device characteristics.

9:20am **TS1-5 Controlling Organic Semiconductor Growth for High Performance Organic Transistors**, ***A. Virkar*** *(avirkar@stanford.edu), S. Mansfeld, Y. Ito, Z. Bao*, Stanford University

In organic transistors the interface between the semiconductor and dielectric is extremely important since it is where the vast majority of current flows. To optimize organic electronic devices it is critical to understand how to engineer the ideal dielectric surface. We show record charge carrier mobilities for more than 20 organic semiconductors on a crystalline octadecylsilane (OTS) monolayer surface. Mobilities as high as 5.0 and 3.0 cm2/Vs were achieved for C60 and pentacene transistors, respectively. [1,2] The semiconductor growth mode is the preferred 2D layer-by-layer growth on a crystalline dielectric modification self-assembled monolayer (SAM) whereas on an amorphous SAM the undesirable 3D growth is observed. 2D growth is preferred to 3D growth since less detrimental grain boundaries, which diminish current, are formed. SAM order and organic semiconductor growth mode and nucleation were critically investigated using atomic force microscopy (AFM), grazing incidence X-ray diffraction (GIXD) and Monte Carlo simulations. The interface-semiconductor interaction energy necessary to drive 2D growth was also calculated and important considerations about organic semiconductor nucleation density, stability, and thin film growth on OTS monolayer surfaces are discussed. [1-4]

[1] The Role of OTS Density on Pentacene and C60 Nucleation, Thin Film Growth, and Transistor Performance, Ajay Virkar, Stefan Mannsfeld, Joon Hak Oh, Michael F. Toney, Yih Horng Tan, Gang-yu Liu, J. Campbell Scott, Robert Miller, Zhenan Bao. Adv. Funct. Mater. 2009, 19, 1–9.

[2] Crystalline Ultra Smooth Self-Assembled Monolayers of Alkylsilanes for Organic Field-Effect Transistors, Yutaka Ito, Ajay Virkar, Stefan Mannsfeld, Joon Hak Oh, Michael Toney, and Zhenan Bao. J. Am. Chem. Soc., 2009, 131 (26), pp 9396–9404

[3] Organic Ajay A. Virkar, Stefan Mannsfeld, Zhenan Bao Semiconductor Growth and Morphology Considerations for Organic Thin Film Transistors. Ajay A. Virkar, Stefan Mannsfeld, Zhenan Bao and Natalie Stingelin. Submitted to Advanced Materials

[4] Energetics and Stability of Pentacene Thin Films on Amorphous and Crystalline Octadecylsilane Modified Surfaces. Ajay A. Virkar, Stefan Mannsfeld, and Zhenan Bao. Submitted to Journal of Materials Chemsitry – special issue on Interfaces in Organic and Molecular Electronics

9:40am **TS1-6 Controlling Organic Semiconductor Crystallization and Morphology using Solution Shearing**, ***G. Giri***, Stanford University, *H. Becerril,* Brigham Young University, *E. Verploegen, Z. Bao (zbao@stanford.edu)*, Stanford University

In order to make low cost, large area and flexible organic electronics, solution deposition of organic semiconductors (OSC) is contending to become an important method of producing organic field effect transistors (OFETs). A recently developed solution shearing process has demonstrated better OFET performance compared to simple drop casting or spin casting methods.[1] In this method, OSC solution is sandwiched between two substrates, a non wetting 'shearing substrate' and a wetting 'device substrate' that is heated to a controlled temperature. When the OSC solution is sheared by translating the shearing substrate, semiconductor crystallization occurs on the bottom device substrate. However, this method produced variable films in terms of thickness and electrical performance of OFETs, ranging from non-performing devices to devices with charge carrier mobilities as high as 0.5 cm^{2}V^{-1}s^{-1}.[2] We have fabricated a new machine that can control the gap between the two substrates to an accuracy of tens of microns, control the temperature of the solution from -25°C to 220°C, and control the tilt angle between substrates. We first used the small molecule trimethyl-[2,2';5',2";5",2"] quarter-thiophen-5-yl-silane (4T-TMS) to investigate the thin film formation. Our work explores the changes in thin film morphology due to controlled change in experimental conditions. Changing experimental parameters such as casting temperature, shearing speed, gap width and substrate tilt angles gives rise to different thin film morphologies, which causes differences in carrier charge transport properties. We have shown that there is a local maximum for charge carrier mobility as a function of both gap width and shearing rate. By maintaining control over many variables present during solution shearing and by possessing a theoretical understanding of important parameters, it is now possible to create large, uniform and highly oriented crystalline thin films (~5 cm^2) that show better charge carrier transport properties compared to other solution deposition methods. OSCs with different packing motifs can be used to determine how thin film morphology changes due to crystalline packing. We are looking at molecules that have edge to face, slip stack and brick wall packing motifs. Finally, anisotropy in charge carrier transport as a direct effect of thin film morphology is investigated.

[1] H. A. Becerril, M. E. Roberts, Z. Liu, J. Locklin, and Z. Bao, *Adv. Mater.*, vol. 20, no. 13,pp. 2588–2594, Jul. 2008.

[2] Z. Liu, H. A. Becerril, M. E. Roberts, Y. Nishi, and Z. Bao, *IEEE,* vol. 56, no. 2, pp. 176-185, Feb. 2009.

10:00am **TS1-7 Aligned Growth of Pentacene on Pre-Patterned Substrates**, ***V.A. Pozdin*** *(vap26@cornell.edu), A. Zakhidov, D.-M. Smilgies, G.M. Malliaraas*, Cornell University

Preferential alignment of organic films on a substrate is an important step in achieving high crystallinity and high performance of organic thin film transistors, where high crystallinity is not sufficient for high performance due to strong anisotropy in most organic materials. Therefore registration between grain orientations to contact electrodes becomes an important criterion in device performance. Currently preferential alignment has been achieved through mechanical rubbing of substrates or growth on atomically stepped substrates. Atomic steps present a low energy nucleation side for organic material being deposited on the substrate. In previous work by V. Ignatescu et al. created atomically stepped flat surfaces by annealing miscut silicon or sapphire substrates at high temperatures and have successfully grown pentacene aligned along the step edge. In this work we demonstrate an alternative and more robust method of creating step edged substrate by patterning self assembled monolayers (SAMs) using photolithography in order to achieve the desired step edges. By utilizing SAMs we are able to tune the step height and step edge energy through the length and chemical composition of the SAMs and we are no longer limited in our choice of substrate. As we are using photolithography to define our step edges, we can easily tune the step edge density in order to optimize the organic thin film growth. Pre-patterned substrates are used to grow aligned thin films of pentacene, which are used to make field effect transistors with channel orientation along different crystallographic directions. Additionally we present an AFM and X-Ray study to demonstrate the degree of alignment.

10:20am **TS1-8 Computational Insight Towards Understanding Design Rules for Functional II-Electron Systems**, ***P. Clancy*** *(PQC1@cornell.edu), R.A. Cantrell*, Cornell University **INVITED**

Computational approaches at the level of molecular simulation have made great strides in the past decade to model π–electron-rich systems. We will discuss the role of molecular simulation to predict optimized processing conditions that create ordered thin films of small organic semiconductor molecules, like the acenes and thiophenes. In this talk, we will focus on a model heterojunction, C60-pentaceme, which shows promise as an all-organic *p-n* junction solar cell.

The atomistic modeling of this heterojunction is a computational challenge: A combination of Molecular Dynamics simulation technique and carefully vetted intermolecular models for C60 and Pn can be used to study surface diffusional studies of small C60 clusters on a Pn surface, but not the deposition of many C60 particles. Mesocale Kinetic Monte Carlo (KMC) would allow the study of a monolayer or so, but to conduct such simulations requires an extensive library of energy barriers obtained from static simulations that cover every deposition and diffusion event that can be envisioned. It also requires a new KMC algorithm to capture the multiple lattices involved. If electronic properties are desired, *ab* initio calculations are needed, but computational resource constraints mean that this can only be done for a couple of molecules from a nanoscale part of this structure.

Using a combination of Molecular Dynamics/MM3- intermolecular potential models, molecular statics, KMC and *ab initio* calculations, we will illustrate the effect of two different morphologies for C60-Pn (thin film and bulk) on diffusional characteristics, potential energy surfaces, thin film growth and the final structure of the interface. We will show that the heterostructure is strained and defective compared to the two bulk materials and illustrate the impact of structure on the electronic properties.

11:00am **TS1-10 Architectural Complexity and Tunable Chemical Function in Metal - Organic Coordination Networks at Surfaces**, ***S.L. Tait*** *(tait@indiana.edu)*, Indiana University **INVITED**

Interfaces between organic materials and inorganic supports are critical for the design and function of new organic-based technologies (including OLEDs, organic photovoltaics, and molecular electronics) as well as novel routes to chemical sensors and catalysts. There are vast opportunities for designing structure—function relationships in these systems due to the immense library of organic compounds and metal—organic chemistries available. Molecular self-assembly and two-dimensional coordination chemistry at surfaces are active fields of research, but much remains to be determined with regard to the complex interplay of intermolecular and adsorbate—substrate interactions, chemical and physical, and how these impact both structure and function. Recent studies have led to several new insights into these interactions using a combination of surface analysis experiments on single crystal surfaces and computational studies. We are making progress towards tailored chemical function by rational design of molecular architectures at surfaces and tuning such function through supramolecular design strategies.

11:40am **TS1-12 A Family of High Strength Ternary Titanium and Vanadium Nitride Thin Films**, *D. Sangiovanni,* Linkoping University, Sweden, ***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 Ti-M-N and V-M-N thin films in the B1 (NaCl) structure. The new compounds are obtained by alloying TiN and VN, with Ta, Nb, V, Mo and W, respectively Nb and W, in concentrations of 50 %. We evaluate the elastic moduli and constants for all these ternaries, perform a detailed analysis of their electronic structure, and compare these results with the corresponding properties of TiN and Ti$_{0.5}$Al$_{0.5}$N. Our calculations show that, in terms of hardness, these ternaries compare with TiN and Ti Al N, as we obtain comparable, respectively increased values, for the Young and bulk moduli, in most cases. Significantly, however, these novel compounds exhibit substantially lower values of the C$_{44}$ elastic constant and positive Cauchy pressures, i.e. they are considerably more ductile than TiN and Ti$_{0.5}$Al$_{0.5}$N. This unique combination of increased hardness and ductility, which is in contrast to the hardness/brittleness relationship typically found in hard coatings, is certainly relevant for applications in which high strength thin films/coatings are desired. In terms of electronic structure, our results reveal a layered charge density for all these ternaries, consisting in alternating high and low electron density regions, similar to that reported for MAX phase materials and other nanolaminates. This combination of metallic and ceramic properties is also evident in the density of states analysis we report. In order to fully understand the mechanism responsible for this interleaved arrangement of electrons, we carry out an improved crystal orbital overlap population (COOP) calculation and succeed in resolving energetically the bonding and antibonding contributions, of the first and second neighbors, to the chemical bonds in these compounds. Herein, we present the results of our COOP analysis, and based on this, we explain the observed trend in hardness and ductility as a result of the interaction between the e_g and t_{2g} sets of *d* orbitals characteristic to these ternaries.

Coatings for Use at High Temperature
Room: Sunrise - Session A2

Coatings for Use in Harsh Thermochemical Environments
Moderator: J.R. Nicholls, Cranfield University

1:30pm **A2-1 Hot Corrosion of New HIPIMS Nanostructured and Microstructured Coatings on Gamma-TiAl***, Lasanta, M. Tejero, A. Rey, S. Mato, M.P. Hierro,* ***F.J. Peréz*** *(fjperez@quim.ucm.es),* Universidad Complutense de Madrid, Spain*, P.Eh. Hovsepian, A.P. Ehiasarian*, Sheffield Hallam University, United Kingdom

Molten sulphates are formed in most of the energy production devices, such as gas turbines. There are different attemps in the use of electrochemical techniques in this environments, but the corrosion of the testing samples do not allow to go more than hours of corrosion testing. Based in this problems, and tanking into account the new development of micro and nano-structured coatings for high temperature applications under INNOVATIAL EU project, a new kind of testing sensors with the micro and nano-structured coatings have been develop to monitor their corrosion process in real time. It will allow to know different corrosion mechanism in real time and the expected behaviour in the steady state. Electrochemical impedance spectroscopy is the base analysis for this systems, and the development of reference equivalent circuits for the interpretation of results will be explained in detail. The results will provide a general overview of the oxidation behaviour of each coating and also a semi-quantitative comparative analysis in real time for different nano-structured coatings on γ-TiAl. Some of the coatings developed in this project have shown an excellent result, comparing with some traditional protective systems. Comparative results will be shown

1:50pm **A2-2 The Role of Alkali Compounds in the Corrosion of High Temperature Steels***,* ***L.-G. Johansson*** *(lg@chalmers.se), J.-E. Svensson, M. Halvarsson, J. Pettersson, N. Folkeson,* Chalmers University of Technology, Sweden*, C. Pettersson,* Volvo Powertrain, Sweden*, T. Jonsson, S. Karlsson*, Chalmers University of Technology, Sweden **INVITED**

It is well-known that the fireside environment in biomass- and waste-fired power boilers is considerably more corrosive towards high temperature alloys compared to plants burning fossil fuels. To cope with these corrosion problems, the plants are designed for relatively low maximum steam temperatures, thereby severely limiting the utilization of the fuel. The high corrosivity is often attributed primarily to the high chlorine content of the fuel. The present paper investigates another aspect of these corrosive fireside environments, namely their high alkali content. Thus, the corrosion effects of alkali salts towards austenitic and ferritic high temperature alloys have been investigated, focusing on the mechanisms of corrosion. The work involves isothermal thermobalance and tube furnace exposures in the range 400-800°C. The polished sample coupons are exposed to well-controlled and strongly simplified synthetic environments. A comprehensive analysis of the exposed samples is carried out using ESEM/EDX, FIB, and TEM. *In-situ* ESEM studies of the reaction of KCl on low alloyed steel will also be presented. Additionally, comparisons are made with materials exposed in real plant environments. We find that alkali chlorides and alkali carbonates tends to accelerate the corrosion of chromia-forming steels by reacting with chromia in the protective scale, converting it to alkali chromate (VI), e.g., K_2CrO_4. The resulting iron-rich scale has poor protective properties resulting in a strong increase of oxidation rate. In contrast, the corresponding reaction with alkali sulphate does not occur because it is disallowed thermodynamically. In the case of alkali chloride, the iron-rich oxide scale that results from the reaction is penetrated by chloride ions. The formation of sub-scale chlorides destroys scale adhesion, further accelerating corrosion attack.

2:30pm **A2-4 Effect of Coating Composition on the Protective Behavior of Cr/Cr Oxide Coatings Against Metal Dusting***, L. Melo,* ***D. Melo****,* Instituto Politécnico Nacional, Mexico*, O. Salas (osalas@itesm.mx),* ITESM, Mexico*, V.M. Lopez-Hirata,* Instituto Politécnico Nacional, Mexico*, J. Oseguera*, ITESM, Mexico

The effect of the relative amounts of Cr vs. Cr oxide in coatings deposited on HK40 steel substrates on their protective behavior against metal dusting was investigated. The coatings were produced by reactive magnetron sputtering varying the level of oxygen flow and the power applied. The structure of the coated samples was analyzed by optical microscopy, scanning electron microscopy + energy dispersive microanalysis, and x-ray diffraction. The coated samples were then exposed to a carburizing atmosphere in a thermobalance to evaluate their protective nature through an extensive microstructural analysis. The results indicate that a higher power results in richer Cr-containing coatings, while an increase in the oxygen flow leads to the opposite effect. On the other hand, the analysis of the samples after carburization shows that the coated samples have less carburization products than the uncoated ones and that the protective behavior of the coated samples depends on the microstructure of the coatings.

2:50pm **A2-5 Development of Residual Stresses During Deposition of Protective Coatings Against Metal Dusting***, L.M. López,* ITESM, Mexico*, D. Melo,* Instituto Politécnico Nacional, Mexico*,* ***O. Salas*** *(osalas@itesm.mx),* ITESM, Mexico*, R. Reichelt,* University of Muenster, Germany*, J. Oseguera,* ITESM, Mexico*, J. Muñoz*, CINVESTAV-Qro., Mexico

Residual stresses along with adhesion and density are central features in the performance of protective coatings against metal dusting. In the present study, the development of residuals stresses during deposition of Cr/Cr oxide layers on HK40 steel substrates by reactive magnetron sputtering was investigated. Two series of coatings were obtained: the first one varying the voltage bias applied to the substrate and the second one varying the rate of oxygen feeding. The coatings were characterized by optical microscopy, scanning electron microscopy + energy dispersive microanalysis, x-ray diffraction and atomic force microscopy. The samples were then subjected to nanoindentation experiments to evaluate their mechanical behavior as well as the presence of residual stresses. The results indicate that the processing variables selected do have a clear effect on the type and amount of residual stresses as well as on the coating microstructure. The results of the present study are of great value in the optimization of the coating process required to produce more effective protective layers against metal dusting.

3:10pm **A2-6 Evaluation of the Protective Behavior of Al/Al Oxide Coatings Under Carburizing Atmospheres***,* ***J.D. Alvarez****, O. Salas, J. Oseguera (joseguer@itesm.mx),* ITESM, Mexico*, D. Melo*, Instituto Politécnico Nacional, Mexico

Aluminum oxide thin films on HK40 steel substrates were produced by reactive magnetron sputtering to investigate their response to carburizing conditions. The structure of the films was analyzed as a function of process parameters; power, bias voltage, and oxygen flow as well as the application of an adhesion layer under various deposition conditions. The films were subjected to carburization experiments in a CH_4 atmosphere at 600°C and 800°C in a thermobalance. From the deposition experiments, Al/ amorphous Al oxide films varying in thickness from 200 nm to 1 μm were obtained. Relating the film microstructure to the processing conditions indicated that power and bias voltage seemed to have a stronger effect on the film density and thus on their response to the carburizing atmosphere. In general, the coated substrates showed a better response to carburizing than uncoated ones. In particular, results of carburizing tests performed at 800 °C on aluminum oxide films deposited without the support of an aluminum adhesion layer, showed the effectiveness of the adhesion layer and its impact on the mechanical and protective properties of the film.

3:30pm **A2-8 Microstructure Evolution and Surface Characteristics of Ni-Based Coatings Under Phosphate Glasses Molding Process***,* ***K.-C. Chang****, Y.-C. Hsiao, C.-C. Chang, F.-B. Wu (fbwu@nuu.edu.tw)*, National United University, Taiwan

The Ni-Al, Ni-P, and Ni-P-Al alloy coatings were fabricated by magnetron co-sputtering technique. The phase identification of coatings was characterized by XRD analysis. Interaction between $50P_2O_5$-50ZnO glass and Ni-based coatings was studied. The $50P_2O_5$-50ZnO glass was the candidate for molding process due to its low glass transition temperature, T_g, around 410 °C. However, significant evaporation of phosphate glasses at high temperature was detrimental to the mold coatings. The Ni-based coating/glass assembly was heated to 460 °C and hot pressed for 30 minutes. It was found that the phase transformation of Ni-P coating occurred after hot processing. The precipitated product in Ni-P coating was identified as Ni_3P. On the other hand, the Ni-Al-P coating remained nanocrystalline microstructure after hot pressing. No residual glass and significant degradation on coatings surface were observed. Smooth surface morphology with low roughness number for the Ni-based coatings after hot pressing process was obtained. The surface morphology of Ni-based coatings was suitable for hot pressing of phosphate glasses . As a result, the feasibility of Ni-based coatings for phosphate glass molding was confirmed.

3:50pm **A2-9 High Temperature Properties of Multilayer CrAlSiN Coatings Deposited on Hot Work Tool Steel AISI H11**, *E. Torres (eloy.torres@polito.it), D. Ugues, Z. Brytan,* Politecnico di Torino, Italy, *R. Escobar Galindo,* Instituto de Ciencia de Materiales de Madrid (ICMM - CSIC), Spain, ***F. Cartasegna**, M. Perucca*, Environment Park S.p.A., Italy

Advanced coating concept like nanocomposite coatings become increasingly important for wear protection in elevated temperatures as well as corrosion and oxidation protection. Recently an increasing amount of attention is focused on the nitrides based coatings deposited by cathodic arc evaporation. The addition of silicon to the widely used aluminium/chromium containing transition metal nitrides is promising for the synthesis of hard and thermally stable films with good oxidation resistance.

In this study the nanocomposite $(Cr, Al)_{1-x}N_x/a\text{-}Si_3N_4$ coatings deposited by lateral rotating cathode arc technique (LARC$^{®}$) on hot work tool steel AISI H11 were studied by scanning electron microscopy, glazing incident X-ray diffraction, Atomic Force Microscopy, GDOES spectroscopy and nanoindentation.

The effect of annealing heat treatment in inert atmosphere on the coating crystal structure, surface morphology, hardness and elastic modulus were also investigated. It was found that nanocomposite $(Cr, Al)_{1-x}N_x/a\text{-}Si_3N_4$ coatings undergo phase transformation, above 900°C the hexagonal AlN structure start to precipitate.

The deposited CrAlSiN coatings show an fcc-$Cr_{1-x}Al_xN$ type structure with different aluminium contents that influence mechanical properties and oxidation resistance.

Aluminium rich coating exhibit higher hardness and also shows lower susceptibility to oxidation during heat treatment in temperature range of 400 - 1200°C.

Fundamentals and Technology of Multifunctional Thin Films: Towards Optoelectronic Device Applications
Room: Royal Palm 1-3 - Session C1

Recent Advances in Optical Thin Films
Moderator: J. Bellum, Sandia National Laboratories, R. Sczupak, Reynard Corporation

1:30pm **C1-1 Colloidal Monolayer and Patterned Films Made of Titania Sub-Micron Particles Prepared by Sol-Gel Process**, ***S. Portal** (sabineportal@hotmail.com), C. Corbella, R. Amade, O. Arteaga, M.A. Vallvé, J. Ignés-Mullol, E. Bertran*, University of Barcelona, Spain

In this work we present a new process to produce periodic patterned films and compact monolayers of titania particles. Spherical particles of titania were prepared by sol-gel method from hydrolysis of titanium ethoxide precursor in ethanol. The particle size was centered at around 500 nm with a dispersion of 10%. Langmuir-Blodgett self-assembled monolayers of the synthesized titania particles were deposited on 5 cm^2 –substrates of silicon and glass. Depending on the size distribution, the particle monolayers were characterized by either hexagonal or disordered compact structures. Templates on silicon wafers were realized by Electron Beam Lithography and the grooves were filled with titania particles by spin-coating. Morphological properties (particle roughness, shape) 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. Titania colloidal films can find application in photonics due to titania high refractive index but also as smart surfaces with controllable photo-switched wettability and photocatalytic properties. Titania templates are promissing for applications in bioengineering.

1:50pm **C1-2 Centrifuge Technology: A Breakthrough in Quantitative Adhesion Testing of Optical Coatings**, ***U. Beck** (uwe.beck@bam.de), G. Reiners,* BAM, Germany, *D. Lerche, U. Rietz,* LUM GmbH, Germany, *H. Niederwald*, Carl Zeiss Jena GmbH, Germany

Adhesion testing of coatings is of fundamental interest for quality assurance and still a challenge regarding reliable quantitative results. Because of the huge variety of coating/substrate systems in terms of materials and large thickness range, adhesion tests display the same variety as coating/substrate systems. Almost all tests are qualitative rather than quantitative. Except for the pull-off test (DIN EN 26922), testing is not directly correlated to the adhesive *strength* in terms of force per area.

For optical coatings and films, the standardized tests according to ISO 9211 apply, i.e. abrasion tests (cheese cloth or eraser test) and adhesion tests (tape or cross-hatch test) with different degrees of severity. In fact, instead of the adhesive *strength*, all these tests provide only qualitative information on the abrasion or adhesion *resistance* of a particular coating/substrate system. The adhesive *strength* as physical quantity is not measured and tests are hence not comparable.

In this respect, the patented centrifuge test is a breakthrough in adhesion testing, in particular for optical coatings. It has manifold advantages. First, it can be easily run as multiple-sample test instead of all the other single-sample tests. Second, it is much easier and faster than any other test. Third, adhesive *strength* is measured in absolute numbers (N/mm^2). Fourth, compared to the pull-off test, it is advantageous that sample clamping is one-sided instead of two-sided. The centrifuge technology additionally enables tests under defined climates or hazardous environments. Moreover, versatile test conditions (alternating loads at various load rates) important to fatigue testing can be easily realised by the variation of the number of revolutions.

The desk-top fracture analyser LUMiFrac made by LUM may analyse simultaneously up to eight different samples. For optical layer stacks provided by Carl Zeiss, conventional tests are discussed and compared in detail with the centrifuge test. It could be shown that the centrifuge test has remarkable advantages with regard to accuracy, precision and reproducibility. Hence, comparability is guaranteed. In addition, the centrifuge test was able to discriminate the adhesive *strength* for coating/substrate systems until failure that did not fail in any of the standardized tests. Finally, further activities on the standardization of the centrifuge test are briefly discussed.

The work was partially supported by a grant (IWO 070171) of the Federal Ministry of Economics.

2:10pm **C1-3 Mechanisms of Sub-Picosecond Pulse Laser-Induced Damage to Optical Thin Films**, ***W. Rudolph** (wrudolph@unm.edu), L. Emmert, D. Nguyen,* University of New Mexico, *C.S. Menoni, E. Krous, D. Patel*, Colorado State University **INVITED**

Despite the long history of laser damage studies, this topic has remained of fundamental as well as practical interest for its importance for laser micro- and nano-structuring and the developments of optical components for high power lasers, in particular for sub-ps pulse lasers. Fundamental processes leading to laser breakdown in dielectric thin films are reviewed. In the sub ps laser regime, the damage thresholds are very deterministic and can be related to fundamental film material and film deposition parameters. The effect of native material defects and transient laser-induced defects will be discussed. Scaling laws of the damage threshold with respect to pulse duration, material bandgap, and the number of excitation pulses will be derived and compared to experimental results. Finally, we will describe how the environment (ambient gas and pressure) affects the film's resistance to laser-induced damage.

2:50pm **C1-5 Synthesis, Structure, and Optical Properties of Au-TiO$_2$ and Cu-TiO$_2$ Nanocomposite Thin Films**, ***A.N. Ranade** (a-ranade@northwestern.edu), M.E. Graham, Y.W. Chung*, Northwestern University

Sunlight incident on vehicles such as cars and planes gives rise to two problems. First, absorption of ultraviolet radiation contributes to degradation of fabrics and polymers in vehicles. Second, absorption of visible and infrared radiation results in vehicle heating that typically requires the use of an oversized air conditioning unit for passenger comfort. This in turn reduces the fuel economy. Therefore, it is desirable to develop materials for these vehicles that are transparent to the visible, absorbing to ultraviolet and reflecting to infrared. There are two general approaches to achieving efficient infrared reflection: optical interference and plasma resonance. This talk describes research studies based on the second approach. We start with a titanium dioxide matrix, which is transparent to visible light and absorbs ultraviolet at wavelengths < 400 nm. Incorporation of appropriate metal atoms into this matrix results in a film that acts as a plasma that reflects light in the infrared with wavelength greater than a critical value. The degree of reflectance enhancement is a function of the metal concentration and morphology. In this talk, we will present results of Au-TiO$_2$ and Cu-TiO$_2$ films. These films are made by reactive magnetron sputtering. Their properties are evaluated by transmission and scanning electron microscopy (metal morphology and particle size distribution), atomic force microscopy (surface roughness), x-ray diffraction (structure), and UV-VIS-IR spectroscopy (optical properties). Successful development of thin films with the above desirable attributes will be presented.

3:10pm **C1-6 Persistent Conductivity in Post-Growth Doped ZnO Films Following Pulsed UV Laser Irradiation**, ***G.J. Exarhos*** *(greg.exarhos@pnl.gov),* Pacific Northwest National Laboratory*, L.J. Wang*, Carleton College

Solution and rf sputter deposited doped ZnO films were subjected to multiple 4-nsec pulses of 355 nm or 266 nm light from a Nd:YAG laser at fluences between 5 and 150 mJ/cm^2. Film densification, change in refractive index, and an increase in conductivity were observed following room temperature irradiation in air, a carbon monoxide reducing environment, or under vacuum. At these fluences, films did not damage catastrophically and high visible transmissivity persisted. The increase in conductivity is attributed to formation of oxygen vacancies and subsequent promotion of free carriers into the conduction band. The effects were most pronounced in films irradiated under vacuum. All treated films became insulating again upon equilibration in air at room temperature after several days. Films were characterized by means of ellipsometry, UV-VIS-NIR transmission spectroscopy, visible and UV Raman spectroscopy and Hall measurements. Analysis of interference fringes in measured transmission spectra allowed evaluation of optical properties and confirmed results obtained from ellipsometry measurements. Raman measurements showed an increase in LO mode intensity with respect to TO mode intensity as the films became more conducting in accord with previous work on conducting ZnO films. Results of this study are not only important for the continued development of transparent conducting oxide films that find use in photovoltaic cells and solid state lighting modules, but also provide compelling evidence for the role of free carriers as initiators of the laser damage process in these wide bandgap metal oxide films.

Carbon and Nitride Materials: Synthesis-Structure-Property Relationships
Room: Pacific Salon 3 - Session D1

Boron Nitride, Carbon Nitride-Based Multifunctional Materials and Group-III (Al, Ga, In) Nitride Materials
Moderator: M. Keunecke, Fraunhofer IST, A. Fernandez, Instituto de Ciencia de Materiales de Sevilla

1:30pm **D1-1 A Novel Cubic Boron Nitride Coating Technology: Coating Design, Deposition, Analysis, and Performance in Turning Applications**, *W. Jiang,* Duralor, LLC*,* ***A.P. Malshe*** *(apm2@engr.uark.edu)*, University of Arkansas and NanoMech, LLC **INVITED**

A composite coating series based on nano- and micro-sized cubic born nitride particulates and choice of application-specific binders was developed for turning engineering materials. The coating series were produced via two-step sequential processes: electrostatic spray coating of cubic boron nitride particles with size less than 2 μm for a conformal porous coating preform of designed thickness; chemical vapor infiltration of ceramic binder phase(s) at a temperature of around 1000 oC for a dense and well adherent composite coating. In this paper, the coating design in combination with insert edge preparation for different applications was discussed. As a study case, cubic boron nitride-titanium nitride composite coating was characterized by use of different techniques for coating cross-section, elemental composition, crystal phases, and adhesion strength. Characterization results indicated a composite coating with uniform coating thickness and evenly distributed cubic boron nitride particles in titanium nitride matrix. Additionally, the coating was tested for its machining performance in turning AISI 4340 hardened steels, AISI 4140 pre-hardened steels, and ductile cast iron at representative application conditions, and compared to correspondingly industrial benchmarks. Testing results showed that the composite coating outperforms its industrial counterparts, polycrystalline cubic nitride, titanium aluminum nitride by physical vapor deposition, multi-layer coating by chemical vapor deposition, and aluminum oxide bulk tools, in respective application.

2:10pm **D1-3 Comparative Study of Chemical Bonding Observed for Ion-Implanted BN, B$_4$C and CN$_x$ Films With B-C-N Films**, ***E. Bengu*** *(bengu@fen.bilkent.edu.tr), M.F. Genisel*, Bilkent University, Turkey

The ternary compounds of the B-C-N phase diagram have attracted much attention because it is potentially possible to combine unique properties of different compounds into one and, synthesize new ones. Hence, there is still much effort to synthesize crystalline ternary compounds of B-C-N. However, deposited films were mostly either amorphous or a mixture of h-BN and C/CN$_x$ phases, even though there were numerous claims of hybrid films. In this study, in an effort to investigate chemical bonding and better document phase separation in B-C-N films, we have deposited h-BN, a-B$_4$C and CN$_x$ thin films using reactive magnetron sputtering on Si (100) surfaces. Then, these films were subjected to ion-implantation by 40 keV C$^+$, N$_2^+$ and N$^+$ ions. After implantation, chemical bonding in these films were investigated using X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared (FT-IR) spectroscopy. Local variations in structure for these films were also investigated by high-resolution transmission electron microscopy (HR-TEM) and electron energy loss spectroscopy (EELS) was employed to investigate chemical environment of boron, carbon and nitrogen in these films. Similar data gathered by XPS, FT-IR and TEM studies on sputter deposited B-C-N films were comparatively examined, as well. Results from these studies indicated boron-nitrogen bond to be preferred over carbon-nitrogen or boron-carbon over a wide range of process parameters for B-C-N films. Hence, carbon tends to phase-segregate in to carbon clusters rather than displaying a homogeneous distribution in the both the implanted and deposited films.

2:30pm **D1-4 Challenges in the Industrial-Scale Deposition of Thick Amorphous and Fullerene-Like Carbon Nitride Coatings**, ***E. Broitman*** *(broitman@andrew.cmu.edu),* Carnegie Mellon University*, L. Hultman*, Linköping University **INVITED**

During the last two decades, carbon-nitride (CN$_x$) coatings have enjoyed a growing interest in several disciplines. Amorphous and fullerene-like films exhibit very attractive properties, such as low friction and wear, high hardness, good chemical stability, and high resiliency to deformation, which make them suitable for replacing diamond-like carbon (DLC) films. The first successful industrial application of this material has been the use of very thin (~2 nm) amorphous CN$_x$ films for the protection of hard disk drives. However, commercial use of thicker (1-5 μm) coatings on steel substrates has been difficult because of the development of high compressive intrinsic stresses during deposition, which causes delamination unless the coating/substrate adhesion can be improved.

In 2007, we reported a pretreatment using high power impulse magnetron sputtering (HIPIMS) technology that overcomes the adhesion issue. We thus demonstrated the possibility to deposit thick amorphous CN$_x$ coatings on steel substrates at low temperature (< 200ºC) using an industrial mass-production chamber CemeCon CC800. In this presentation, different strategies to increase the adhesion of carbon-based coatings to steel substrates will be reviewed. Our novel approach, using two HIPIMS power supplies in a master-slave configuration (one to establish the discharge and one to produce a pulsed substrate bias), will be discussed. Plasma processes during our pretreatment leading to the formation of a Cr interface will be described. The structural, mechanical, and tribological properties of amorphous and fullerene-like CN$_x$ coatings deposited in both laboratory and industrial-scale systems will be compared by characterization techniques like HREM, SEM, XPS, ESR, nanoindentation, surface energy drop wetting angle, pin on disk, scratch and Daimler-Benz Rockwell-C tests. Finally, commercial applications of CN$_x$ coatings will be envisioned.

3:10pm **D1-6 Texture Development and Microstructure Characterization of Piezoelectric AlN Thin Films Fabricated by Pulsed Closed FieldUnbalanced Magnetron Sputtering**, ***M. Hasheminiasari*** *(mhashemi@mines.edu), J.J. Moore, B. Mishra*, Colorado School of Mines

Piezoelectric aluminum nitride (AlN) thin films were synthesized by reactive sputtering of Al metal target in different nitrogen-argon gas ratio atmosphere using a pulsed closed field unbalanced magnetron sputtering system on various substrates with thin Cr electrodes. The texture, orientation and the microstructure of AlN films were characterized by means of X-ray diffraction and scanning electron microscopy. The mechanical properties of the coatings were studied using the XP nanoindenter. Impedance analyzer was used to characterize the piezoelectric properties of these films. It was found that reactive gas ratio, the pulsing frequency and the working pressure significantly affected the (002) orientation in AlN films. Strong (002) orientation has been achieved in the AlN thin films under various pulsing conditions, which can be correlated to the high ion energies associated with the pulsed magnetron sputtering.

3:30pm **D1-7 *In-situ* Stress Measurements During Growth of GaN(0001)/Al$_2$O$_3$(0001) by Reactive DC Magnetron Sputter Epitaxy**, ***M. Junaid*** *(junmu@ifm.liu.se), P. Sandström, J. Birch*, Linköping University, Sweden

Growth of GaN by magnetron sputter epitaxy (MSE) has the potential to be used for high quality single crystalline epi-layer synthesis over large substrates at low temperatures. Development of growth stresses is a known issue in GaN epitaxy affect the material properties as well as devices performance and hence need to be controlled.

In-situ stress evolution during growth of GaN(0001) epilayers on (0001)-Al$_2$O$_3$ substrates has been studied during reactive MSE growth of 900 nm thick layers at different growth temperatures. A liquid Ga target was used and a working gas mixture of ultra pure Ar and N$_2$ held at 2.5 and 2 mTorr partial pressures, respectively. The in-situ stress measurements were made by measuring the curvature induced to the substrate by the stress exerted by the growing film. The equipment used was a multi beam optical stress sensor (MOS), based on the deflection of multiple laser beams. The crystalline quality of the films was studied by using x-ray diffraction techniques.

At 750°C , we observed a continuous compressive stress evolution during the film growth, reaching a total film stress of ~200 MPa at the completion of the growth. The FWHM of HR-XRD rocking curves for these films are ~720 arc sec. which is indicates a high crystalline quality. In contrast to this result, a tensile stress of ~150MPa was observed in a film growing at 500°C. This film also has a comparatively low crystalline quality with a rocking curve FWHM of 1200 arc sec. After cooling down to room temperature all films are under compression due to the differences in thermal expansion coefficients between GaN and sapphire.

Our results are in contrast to in-situ stress studies on MOCVD-grown GaN(0001)/Al_2O_3(0001) where a tensile stress evolution to 200-400 MPa was observed during growth at 1000 °C. We attribute the origin of the compressive stresses in our films grown at 750 °C to atomic peening by energetic particle bombardment and/or coherency stresses due to a compressive substrate lattice mismatch. At 500°C, we conclude that tensile stresses due to cohesion over grain boundaries and annihilation of defects (caused by low adatom mobility) dominate over the effect of atomic peening.

Tribology and Mechanical Behavior of Coatings and Thin Films
Room: Pacific Salon 1 - Session E4/G4

Coatings for Machining Advanced Materials and Advanced Manufacturing Methods
Moderator: W. Kalss, OC Oerlikon Balzers, H.G. Fuss, CemeCon

1:30pm **E4/G4-1 A Comparative Study on the Role of Solid Lubricant for Improving Tribological Properties in Turning Process**, *N.S. Kumar Reddy,* BITS-Pilani Hyderabad Campus, INDIA, ***M. Nouari*** *(Mohammed.Nouari@insic.fr)*, Ecole Nationale Supérieure des Mines de Nancy, FRANCE

High speed machining of materials inherently generates large cutting temperatures, which not only reduce tool life but also impair the product quality. Though cutting fluids are widely employed to carry away the heat in metal cutting, they cannot be recommended in the light of ecological and economic manufacture. Hence, there arises a need to identify eco-friendly and user-friendly alternatives to conventional cutting fluids. Modern tribology has facilitated the use of solid lubricants. So, in recent years researchers have started machining with the use of solid lubricants with the aim of improving machining performance and overcome the limitations that arise with the use of cutting fluids or while dry machining. The present work features a specific study of the application of molybdenum disulphide as solid lubricant for improving tribological properties in turning. An experimental setup has been developed to maintain constant flow rate of solid lubricant powder continuously on to the workpiece and tool interface zone. Further, an analytical expression has also been derived for the estimation of motor speed for achieving desired flow rate. The process performance is judged in terms of cutting force, friction coefficient and the surface finish of workpiece, keeping the cutting conditions constant. The results obtained from the experiment show the effectiveness of the use of the solid lubricant as a viable alternative to dry and wet machining. The unique utility of solid lubricant is highlighted.

1:50pm **E4/G4-2 Adaptive PVD Coating for Machining of Hard to Cut Materials**, ***G.S. Fox-Rabinovich*** *(gfox@mcmaster.ca),* McMaster University, Canada, *K. Yamamoto,* Kobe Steel, Ltd., Japan, *B. Beake,* Micro Materials Ltd, United Kingdom, *S. Veldhuis*, McMaster University, Canada **INVITED**

Results of long-term, interdisciplinary research of adaptive nano-structured TiAlCrN-based coatings are presented. A number of novel adaptive hard coatings are developed best suited for specific applications associated with ultra-high speed dry machining of hardened tool steels as well as high performance machining of aerospace materials such as nickel-based superalloys and Ti-based alloy.

Adaptation during cutting is a complex process that is related to generation of the surface tribo-films with unique protective/lubricious ability. The tribo-films are acting in synergy with beneficial transformations within the layer of the coatings as well. If all these parameters work together, as a whole, then the coating possesses emergent properties and presents higher ordered surface engineered tribo-system. As such it is capable to sustain strongly varying and intensifying external impacts with unattainable tool life.

Comprehensive investigation of the structural characteristics of the coating is made using XRD, HRTEM, SEM/EDX. Micro-mechanical properties of the coating such as hardness, plasticity index, impact fatigue fracture resistance, low cycling wear resistance are studied at RT and elevated temperatures using Micro Materials Test System. Tribological characteristics of the coatings are investigated vs. temperature in contact with corresponding materials using custom-made high temperature tribometer. Characteristics of the tribo-films are studied in detail using XPS, and EELFAS methods. Tool life is investigated for specific operating conditions. Cutting forces are measured. Wear patterns are indentified. Chips formation is investigated in details as well.

2:30pm **E4/G4-4 Micro/Nanocrystalline Bilayered CVD Diamond Coated Tools for Hardmetal Machining**, *F.A. Almeida,* University of Aveiro, Portugal, *N. Derkaoui, F. Bénédic,* UPR 1311 CNRS, Université Paris 13, France, ***R.F. Silva*** *(rsilva@ua.pt), F.J. Oliveira*, University of Aveiro, Portugal

Earlier works proved the excellent adhesion of chemically vapour deposited (CVD) microcrystalline diamond (MCD) to silicon nitride (Si_3N_4) ceramics, due to their good thermal expansion match and chemical compatibility. More recently, nanocrystalline diamond (NCD) coatings were developed aiming at a reduced surface roughness and a lower friction coefficient. Promising results have been obtained with NCD in the machining of hardmetals but at the cost of decreased adhesion levels, mostly due to higher graphitic content and lower deposition temperatures that hinder a strong chemical bonding to the substrate. Thus, the superior adhesion of MCD and the surface properties of NCD were combined in the form of MCD/NCD bilayered coatings for cutting tool performance enhancement in turning operations.

2:50pm **E4/G4-7 Dry Stamping Feasibility Test for Various DLC-Cotaed Dies**, ***T. Aizawa*** *(taizawa@sic.shibaura-it.ac.jp),* Shibaura Institute of Technology, Japan, *S. Kataoka,* Shounan Institute of Technology, Japan, *T. Uematsu*, Tokyo Metropolitan Industry Research Institute, Japan

Amorphous carbon (a-C:H) or DLC coatings have been widely utilized in various fields of industries. In particular, DLC-coated tools and dies are utilized in dry stamping with less use of lubricating oils. In this dry tooling, high wear toughness without chipping or cracking is strongly needed for DLC-coated tools in addition to low friction coefficient and specific wear volume. Hence, promising DLC coatings must be selected to satisfy the above requirement for each dry stamping tooling in practice.

In the present paper, nano-laminated coating as well as three different CVD coatings (commercial CVD-DLC, PIG-CVD DLC's with the interlayer of Ti and CrN), are employed to make feasibility test via dry stamping experiment. To be discussed later, through reduction of clearance between die and punch, this dry stamping experiment l becomes equivalent to a process tribological test in extremely severe conditions.

At first, mechanical and tribological properties of these coatings are investigated. Commercial CVD and PIG-CVD coatings have almost the same hardness (H) and friction coefficient (m); e.g. H = 25 – 30 GPa and m = 0.1-0.15. Bimodal thickness (D L) in nano-lamination is varied by D L = 5 nm and 10 nm. The effect of this D L and layer thickness ration in D L on hardness is experimentally evaluated to demonstrate the controllability of mechanical properties via nano-lamination.

Both WC/Co with the grade of V30 punch and die are prepared for dry stamping test and DLC-coated with different thickness in each above coating. These DLC-coated tools are aligned into a die set with the clearance of 2.5% in the sheet material thickness. Increase of burrs in products in dry stamping test is measured with increasing the number of stamping (N). Using the commercial DLC coating, significant increase of burrs is noticed even after N = 10; no significant increase of burrs is noticed in case of nano-laminated and PIG-CVD coated DLC's until N = 500 to 700. Engineering durability is evaluated by residual coating area ratio after dry stamping for N = 1000. High durability is attained by nano-lamination with D L = 5 nm. This is because of high hardness by nano-lamination effect and high toughness from chipping and normal crack propagation by lamination.

3:10pm **E4/G4-9 γ-Al_2O_3 Coatings for Challenging Cutting Operations**, *K. Bobzin, N. Bagcivan,* ***M. Ewering*** *(ewering@iot.rwth-aachen.de)*, RWTH Aachen University, Germany **INVITED**

Crystalline PVD Al_2O_3- coatings offer great potential for their use in cutting operations. They promise high hot hardness and high oxidation resistance at elevated temperatures. Aluminium oxide exists in different crystallographic phases. α-Al_2O_3 appears to be the only thermodynamically stable phase at all common temperatures and pressures. Today there are many efforts to generate α-Al_2O_3 by means of physical vapour deposition. In this regard one problem is the high deposition temperature, which does not allow the deposition on temperature-sensitive materials.

Another promising candidate is γ-Al_2O_3 which is more fine-grained than α-Al_2O_3 and can be deposited at lower temperatures. At high temperatures γ-Al_2O_3 might be transformed into α-Al_2O_3 which could limit the application temperature. But until now it is not clearly proved, up to which temperatures γ-Al_2O_3 thin films are stable and which mechanisms influence the stability. In the present work different (Ti,Al)N/γ-Al_2O_3 are deposited on cemented carbides by means of Magnetron Sputter Ion Plating (MSIP). The (Ti,Al)N bond coat was employed to improve adhesion of γ-Al_2O_3 on the substrate. It could be shown that the γ-phase is stable in vacuum up to 1200°C. In atmosphere the formation of α-Al_2O_3 begins at 900°C and it is influenced by the choice of transition zone between (Ti,Al)N interlayer and γ-Al_2O_3. The results show that the thermal stability of the g-phase and therefore the application temperature of the coating can be enhanced by the choice of interlayer.

The examinations show that γ-Al_2O_3 seems to be suitable for cutting of difficult to machine materials like Inconel or austenitic stainless steel, because high cutting temperatures but also adhesion related sticking of the workpiece material are expected. To prove this several cutting experiments have been done which show (also in comparison to nitride coatings) promising results.

3:50pm **E4/G4-11 Factors Controlling the Behavior of Coatings Under Extreme Contact Loading in Dry Machining Processes**, *F. Kone (fousseny.kone@insic.fr)*, ***C. Czarnota***, *B. Haddag*, *M. Lazard*, *M. Nouari*, Ecole des Mines de Nancy, France

Generation of wear during metal cutting processes affects productivity and manufacturing efficiency, and strongly influences the cutting tool life. Thin hard coatings, synthesized by physical or chemical vapor deposition (PVD and CVD) methods, are then often used in machining processes to enhance wear resistance at the tool-chip interface. The current study investigates the relationship between wear and conditions of the tool-chip contact. In this work, we team numerical simulations to SEM imagery in order to map the tribological parameters such as temperature, contact pressure and friction coefficient within the zone of action of a coated carbide (WC-Co) tool. Several experiments have been conducted on carbide tools with two types of coatings. The first one is made of three layers namely TiN, Al_2O_3 and MT-TiCN, and the second has two layers which are Al_2O_3 and TiCN. For these tests, different cutting speeds and feed rates have been used to investigate the influence of the interface parameters on the chip morphology and wear mechanisms. The cutting speed was taken between 30m/mn and 100m/mn, the speed rate between 0.1mm and 1mm. The analysis shows the effects of tribological parameters (friction, temperature, and contact pressure) on the performance and behavior of coatings under dry contact condition of machining processes.

4:10pm **E4/G4-12 A New Hybrid Tribological Characterisation of Coating Delamination Process in Cutting Tools Wear**, ***S. Bahi*** *(slim.bahi@insic.fr)*, GIP-INSIC, France, *M. Nouari*, Ecole des Mines de Nancy, France, *A. Moufki*, LPMM, France, *M. El Mansori*, Arts et Métiers ParisTech, France, *A. Molinari*, LPMM, France

To minimize tool wear and coating delamination processes, it is necessary to understand the nature of interactions between chip flow, tool and coating materials. In this paper, a hybrid analytical-numerical approach is performed for the orthogonal cutting process. The modelling of the thermomechanical material flow in the primary shear zone, the tool-chip contact length and the sliding-sticking zones is obtained from an analytical approach. In addition, the Finite Element method is used to solve the non linear thermal problem in the chip. At the chip-tool interface, the friction condition can be affected by the important heating induced by the large values of pressure and sliding velocity. In spite of the complexity of phenomena governing the friction law in machining, a reasonable assumption is to consider that at the sliding zone the local friction coefficient is primarily function of the temperature and mechanical parameters (strain, strain rate, stress) at the tool-chip interface.

The objective is to propose an approach which can easily be used to identify the main parameters governing tool wear and to explain the experimental trends. The effects of cutting conditions and material behaviour on the sliding-sticking zones and on the temperature distribution along the tool-chip interface are evaluated. It has been found that the sliding-sticking zones at the tool chip interface strongly control the local conditions of stress, velocity and temperature. Experimental analyses of the sticking-sliding zones and their evolution at the tool-chip interface have been used to identify tool wear modes and coating delamination process for different cutting conditions. A qualitative comparison between the model and the experimental results is also provided.

Tribology and Mechanical Behavior of Coatings and Thin Films
Room: Sunset - Session E5

Nano- and Microtribology
Moderator: N. Randall, CSM Instruments, USA, J.H. Hahn, Korea Research Institute of Standards and Science

1:30pm **E5-1 Applications of Nano-Scale Coatings in Tribological Systems**, ***D.-E. Kim*** *(kimde@yonsei.ac.kr)*, Yonsei University, Korea **INVITED**

Thin film coatings are utilized extensively to modify or functionalize solid surfaces in various technologies. In tribological applications, coatings are typically used to control friction and minimize surface damage due to contact against a counter surface. Particularly in ultra-precision systems such as micro-electro-mechanical-systems (MEMS) and in applications where extremely smooth surfaces are used such as in hard disk drives (HDD), the surface forces that exist at the contact interface of two components can cause significant problems in operation of the device. Thus, it is essential to apply surface coatings to minimize the surface forces. Since these systems require tight tolerances coatings with thickness in the nano-scale range such as self-assembled-monolayer (SAM) and perfluoropolyether (PFPE) are utilized. These coatings, with a thickness in the range of a few nanometers, have been effectively implemented in reducing stiction of MEMS components and head sliders of HDD.

In this presentation an overview of the tribological behavior and characteristics of such ultra-thin films for microsystems applications will be provided. Specifically, the effectiveness of SAM and PFPE based lubricant coatings on wear reduction of silicon based materials will be assessed. Another application where tribological behavior of SAM coating needs to be clearly understood is in probe based lithography where SAM coating is used as a resist layer. The SAM resist layer is preferentially removed by the probe tip to fabricate patterns on the substrate surface. In addition to the general tribological behavior of SAM coating, the physical interaction between SAM coating and a probe tip in probe based lithography will be presented.

Acknowledgement: This work was supported by Ministry of Knowledge Economy (2008-N-PV08-P-06-0-000).

2:10pm **E5-3 Evaluation of Thin PVD Coatings using Rooms and High Temperature Nano-Testing**, ***N.M. Renevier*** *(nrenevier@uclan.ac.uk)*, University of Central Lancashire, United Kingdom, *B. Beake*, Micromaterials Ltd, United Kingdom

There is an increasing demand for understanding nanostructured coatings properties not only at room temperature but also at high temperature near real application condictions. Recent developments in high-temperature nanoindentation[1] have shown increased interest amongst the research community as a step to get closer to real problems or modelling. Measurement methods have been developed for evaluating the hardness and modulus of Physical Vapour Deposited (magnetron sputtering and cathodic arc) coatings when the temperature is raised from room temperature to 400 degrees. Additional nano-testing capabilities have been used to characterise nano-structured properties, this includes nano-scratch, nano-impact, nano-wear. Atomic Force Microscopy and Scanning Probe Microscopy have been used as a mean of surface analysis. Additional techniques such as Scanning Electron Microscopy, Energy Dispersive Spectroscopy and X-Ray Diffraction techniques have been used to complement the analysis. Physical parameters including temperature or loading curve, coatings deposition technique, coating composition and microstructure have been investigated and a comprehensive database has been produced and some results are reported in this paper.

[1] B. Beake, J.F. Smith, Philosophical Magazine A, Volume 82, Number 10, 1 July 2002 , pp. 2179-2186(8).

2:30pm **E5-5 Micro-Tribological Performance of Au-MoS_2 Nanocomposite and Au/MoS_2 Bilayer Coatings**, ***P. Stoyanov*** *(pantcho.stoyanov@mail.mcgill.ca)*, *S. Gupta*, McGill University, Canada, *J.R. Lince*, The Aerospace Corporation, *R. Chromik*, McGill University, Canada

Gold is a noble material that has been known for its excellent corrosion resistance, great electrical conductivity, and thermal properties. Therefore, gold is widely used as an electrical conductor in microcomponents/microswitches. Common failure mechanisms, however, when using Au in these components are adhesion, melting, and increase in electrical resistivity due to wear of the coating. Typical strategies to overcome these issues are solid-solution alloying to increase strength and modification of operation conditions of the device. A potential alternative to these strategies has been explored by examining the mechanical properties and microtribology of Au thin films as nanocomposites with small additions of MoS_2 and bilayers with a sacrificial MoS_2 top layer. Results in the literature for macroscopic tribocontacts show that the co-sputtering of MoS_2 with Au increases the wear resistance and the endurance life, but also increases the electrical resistivity significantly when the at% Au falls below roughly 80%. For this study, microtribological properties of bilayered Au/MoS_2 lubricants, with varying thickness of the MoS_2 layer on top of Au, were studied with the purpose to improve the wear resistance. Reciprocating microscratch tests were performed using a nanoindentation instrument with varying the tip radius, contact pressures, and sliding cycles. Single scratch tests with increasing normal load were also performed in order to investigate the adhesion between the different layers. Characterization of the wear track was performed using a micro-Raman spectrometer and an atomic force microscope. The results showed that the nanocomposite Au-MoS_2 coatings had increased the wear resistance compared to pure Au films. Similarly for bilayer Au/MoS_2 samples, the wear resistance of the Au film was enhanced by the MoS_2 top layer, which behaved as a sacrificial layer protecting the Au. The mechanism for this wear resistance was explored by ex situ examination of MoS_2 transfer films and wear debris at specific sliding cycles. Future work will focus on the effect that these modification to the electrode material and structure have on the electrical properties at similar length scales to a MEMS contact.

2:50pm **E5-6 Micro-Tribology Experiments on Low Friction Coatings**, ***M. Gee*** *(Mark.Gee@npl.co.uk), J.W. Nunn*, National Physical Laboratory, United Kingdom

A new tribometer has been designed to carry out micro and nanoscale tribological experiments. The system has been designed for both use on the laboratory bench and in-situ in a scanning electron microscope. The main requirement that the system addresses is to evaluate the tribological response that occurs at the asperity level in macroscale tribological contacts so that a better understanding can be developed so that reliable prediction of performance for engineered sur-faces can be made.through improved modelling. A secondary aim is to evaluate the tribological response of system elements in MEMS and NEMS devices. Experiments have been carried out under a range of coatings to examine the frictional performance and durability of the coatings. The damage to the coatings that was caused by single and multiple pass experiments using blunt and sharp probes under a range of different laoding conditions was evaluated using confocal microscopy, AFM topography measurement, and in some cases SEM stereo reconstruction, as well as high resolution SEM. For crystalline coatings that were tested, the plastic strain in the worn areas was evaluated using EBSD. The implications for the use of these coatings in wear resistant applications is discussed.

3:10pm **E5-7 In Situ Accelerated Nano-Wear - a New Technique to Fill the Measurement Gap**, ***B. Beake*** *(ben@micromaterials.co.uk)*, Micro Materials Ltd, United Kingdom, *T. Liskiewicz*, Leeds University, United Kingdom

A new nanotribological testing technique is introduced. It fills a key measurement gap in terms of pressures, forces, contact areas and sliding speed between AFM based wear testing and micro-/macrotribometers and hence more directly maps onto contact conditions in a range of applications including MEMS devices, automotive engines and biomedical devices.

In situ (during the test) measurements of both true nano-scale fretting wear (nano-fretting) or nano-/microscale reciprocating wear are possible over several hours (up to 1000000 wear cycles or more).

The large number of cycles possible in the accelerated nano-wear test - compared to existing nanotribology tools - is due to the inherent stability of the instrumentation (typical signal drift <0.005 nm/s; NanoTest platform, Micro Materials Ltd). The in situ monitoring of nano-wear over such long periods enables tests to be usefully run for greater duration and at lower contact pressures than is typical in previous nanotribological tests. Results are presented on a wide range of hard and soft thin films and are used to optimise coatings for enhanced durability.

3:30pm **E5-8 Advancement in Nano Tribology with the Use of the Single Point Nanoscratching Technique**, ***E. Poiré*** *(epoire@ep-labs.com)*, EP Laboratories Inc

The fact that devices are getting smaller and coatings thinner has led to the need of performing tribology studies at a smaller scale. Single point nanoscratching instrument is a tool of choice that allows the study of wear and friction properties at the micron and nanometer scales. The instrument and software capabilities provide a wide range of possible test configurations that include measuring the friction and depth for uni-directional and bi-directional multipasses. This paper will present results of nano wear and friction obtained with a nanoscratching instrument.

3:50pm **E5-9 Designing Robust Hydrophobic Surfaces**, ***M.M. Gentleman*** *(mgentleman@tamu.edu)*, Texas A&M University, *J.A. Ruud*, GE Global Research

Oxides are believed to be hydrophilic because of the strong affinity for hydroxylation at their surfaces. This paper explores the relationship between hydroxylation of oxide surfaces and their resulting wettability. Here we demonstrate that hydroxyls increase the hydrophobicity, or reduce the wettability, of oxide surfaces by reducing the polar component of surface free energy. Using alumina as a model material, increased hydrophobicity with hydroxylation was confirmed experimentally and a correlation between the strength of the hydroxyl-driven hydrophobic response and surface treatment was demonstrated.

New Horizons in Coatings and Thin Films
Room: Royal Palm 4-6 - Session H2-1

High Power Impulse Magnetron Sputtering

Moderator: R. Bandorf, Fraunhofer IST, J.-E. Klemberg-Sapieha, Ecole Polytechnique de Montreal

1:30pm **H2-1-1 Diagnostics of HPPMS Discharges; Sputtered Vapor Ionization, Transport and Transfer of Sputtered particles and Active Species**, ***J. Bretagne*** *(jean.bretagne@u-psud.fr), D. Benzeggouta, C. Boisse-Laporte,* Université Paris Sud, France, *L. de Poucques,* Université Henri Poincaré, France, *M. Ganciu,* National Insitute of Laser, Romaina, *M.-C. Hugon, J.-C. Imbert, T. Minea,* Université Paris Sud, France, *P. Vasina,* Masaryk University, Czech Republic, *C. Vitelaru*, Université Paris Sud, France & Cuza University, Romania **INVITED**

HPPMS is actively studied for material etching and deposition. Due to the conjunction of the specific magnetic geometry and the high pulse currents which are achieved, HPPMS discharge is complex. The understanding of fundamental processes governing its behavior helps their optimization in terms of deposition process and challenges in HPPMS require a joint effort of plasma and material physicists. It is particularly important to control the creation and the transport of all gas phase species to correlate the discharge characteristics with deposited thin films properties.

Present contribution highlights the discharge and the plasma phase characterization performed in our group. Various diagnostic methods have been used depending on the discharge conditions.

Optical emission spectroscopy (OES) technique is used to study the time dependent variations of characteristic buffer gas and sputtered vapor spectral lines. Line intensity variations and their overall changes versus discharge conditions yield information about the sputtering process and its evolution during the pulse. Moreover, especially in reactive HPPMS discharges, the use of short pulses permits to separate surface processes and volume kinetics and is very useful. However, from OES technique it is difficult to deduce quantitative measurements on the plasma species.

HPPMS plasmas can be spatially and temporally characterized using optical absorption spectroscopy (OAS) and Langmuir probe measurements. OAS is used to evaluate densities of the most populated species (ground neutral and ionic states, metastable states) of the sputtered vapor. It permits to determine the vapor ionization ratio in the HPPMS plasma and consequently the discharge conditions which optimize this ratio. However, the OAS effectiveness is limited to process conditions in which the sputtered particles are thermalized. Therefore, OAS fails when used to probe the plasma close to the target or at too low pressure.

The most interesting parameters for layer deposition are fluxes and energy distributions of sputtered particles hitting the substrate. This can be tackled by using time and energy revolved mass spectroscopy. As well, the recently developed Tunable Diode-Laser Induced Fluorescence (TD-LIF) technique, taking advantage of the newly available laser diodes and applied to conventional magnetron discharges, permits to get local information on the 2D particle velocity distributions, even in the intense magnetized plasma. Moreover, it gives access to relative fluxes and densities of particles near the substrate. The use of this technique for HPPMS conditions, with sufficient temporal resolution, is under development.

2:10pm **H2-1-3 High Rate Copper Deposition by Gasless High Power Impulse Magnetron Sputtering**, ***J. Andersson*** *(joakim.andersson@angstrom.uu.se),* Uppsala University, Sweden*, A. Anders*, Lawrence Berkeley National Laboratory

The high density of ionic species in high power impulse magnetron sputtering allows for dense films, interface tailoring and coating of complex geometries. The major issue of the technique is the usually reduced deposition rate compared to DC magnetron sputtering. However, utilizing gasless sputtering of copper [APL 92 (2008) 2215030], it is shown that the deposition rate is increased by a factor of 3 compared to sputtering at 2.0 Pa of argon with typical pulse lengths of 100 microseconds. With longer pulses of 1 millisecond, the difference is less but still significant. Another effect that has been quantified is the role of sputter erosion of the target on the rate of deposition as well as on discharge characteristics. New experimental data will be discussed in terms of the local magnetic field strength, particle transport in the plasma, power efficiency and sputter yield. Gasless sputtering is shown to be a useful tool to experimentally illustrate the effects of self-sputtering versus gas in the sputter process, as well as to increase the deposition rate of copper.

2:30pm **H2-1-4 Spatial and Temporal Investigation of High Power Pulsed Magnetron Discharges by Optical 2D-Imaging**, ***B. Liebig*** *(b.liebig@liv.ac.uk),* University of Liverpool, United Kingdom*, N.S. Braithwaite,* The Open University, United Kingdom*, J.W. Bradley,* University of Liverpool, United Kingdom*, P. Kelly*, Manchester Metropolitan University, United Kingdom

Optical 2D-imaging in combination with Abel inversion was used to study the spatial and temporal evolution of plasma-induced emission of HIPIMS discharges. Two different discharges with titanium and aluminium-doped zinc target in an argon atmosphere were observed optically. Several wavelength filters were employed to investigate the development of selected species, namely argon and titanium neutrals, as well as argon and zinc neutrals and ions.

Titanium neutrals mainly emit light in a region above the racetrack close to the target surface, whose radial position and width alters within the pulse. The emission of argon neutrals, observed at 750 nm and 810 nm, starts earlier in the pulse and undergoes a significant development during the pulse, including two maxima which correspond to maxima in the electron density. From the emission's spatial distribution at the discharge current maximum it is concluded that gas rarefaction of argon occurred.

Investigating the intensity emitted by neutrals in the discharge with aluminium-doped zinc target, the findings for the titanium discharge could be proved. In addition, the spatial and temporal development of argon and zinc ions has been recorded. The distribution of zinc and argon ions is still part of on-going experiments to provide a better understanding of the sputtering process in HIPIMS discharges, but from recent experiments it could be concluded that the emission profile revealed much wider maxima close to the target surface than for neutral species. Furthermore, almost no light is emitted by argon ions at the end of the "off"-phase, whereas a residual intensity for all neutrals could be detected which in addition to the extraordinarily long decay times indicates that Penning excitation by metastable atoms rather than electron impact excitation is the dominating effect in the late "off"-time of the discharge.

2:50pm **H2-1-5 Characterization and Simulation of HIPIMS Discharges in Gas Mixtures***,* ***M.A. Lange*** *(matthew.lange.ctr@wpafb.af.mil), A.N. Reed,* Air Force Research Laboratory / Universal Technology Corporation*, J. Jones, C. Muratore, A.A. Voevodin*, Air Force Research Laboratory

High power impulse magnetron sputtering, HiPIMS, is broadly recognized as a physical vapor deposition process having advantages over conventional dc sputtering. The advantage of HiPIMS is that the orientation and relative density of thin films can be controlled by manipulating the flux and kinetic energy of incident film material. Film structures exhibit a strong dependence on voltage and current waveforms to the target as well as gas pressure. Plasma characterization techniques were used to correlate processing parameters to the structure and properties elemental and binary thin film materials. For example deposition rates and orientations of hafnium films demonstrated marked changes at pulse durations beyond a critical value (50-100 m s) at a constant duty factor. Plasma mass spectrometry allowed correlation of these changes to the dependence of neutral flux on pulse duration. Background pressure also affected deposition rate and crystal structure of thin film materials. Modeling and probe measurements were used to identify the effects of background pressure on electron temperature. Ion energy distributions were also measured for qualitative model validation. Finally, pulse frequency and duration were found to affect the orientation of compound films processed in gas mixtures. These structural changes were compared to temporally-resolved measurements of plasma composition, especially the concentration of atomic species between pulses.

3:10pm **H2-1-6 Density Measurement of Films Deposited by High Power Impulse Magnetron Sputtering***, M. Samuelsson, D. Lundin (danlu@ifm.liu.se),* ***D. Magnfält****, J. Jensen, U. Helmersson*, Linköping University, Sweden

The densification process of thin films using high power impulse magnetron sputtering (HiPIMS) has been investigated for eight different target materials (Al, Ag, Cr, Cu, Pt, Ta, Ti and Zr). The density values as well as deposition rates have been compared to results from thin films grown by direct current magnetron sputtering (DCMS) grown under the same experimental conditions. Overall, it was found that the HiPIMS coatings were approximately 10 % denser compared to the DCMS coatings. This could be attributed to the increased ion bombardment commonly seen in HiPIMS discharges leading to a less pronounced columnar microstructure, where the momentum transfer between the growing film and the incoming ions is very efficient due to the equal mass of film and bombarding species. As expected the deposition rates were found to be lower for HiPIMS compared to DCMS, but much less so in the case of Ta, Pt and Ag with $\text{rate}_{\text{HiPIMS}}/\text{rate}_{\text{DCMS}} \sim 70$ % - 85 % while still achieving denser coatings. A global plasma model for explaining the increase in density, based on metal ion flux ratios for different target materials, is proposed, which is in agreement with the experimental results.

3:30pm **H2-1-7 Time-Resolved Characteristics of Reactive HIPIMS Plasmas***, M. Hala,* ***J.-E. Klemberg-Sapieha*** *(jsapieha@polymtl.ca), J. Capek, L. Martinu*, Ecole Polytechnique de Montreal, Canada

We performed a comparison of HIPIMS discharges ignited in the same sputtering reactor using different commercially available power supplies. Each power supply offers, different possibilities to increase power, specifically higher voltage for square pulse generator with a few hundreds of microseconds in duration and longer, custom-shaped pulses for the arbitrary pulse generator with lower maximum voltage capabilities.

We discuss the consequences of these differences on the discharge dynamics and their possible influence on the deposition process. We investigated time- and space-resolved optical emission spectroscopy (OES) in conjunction with fast imaging of plasma dynamics of HiPIMS discharges using Cr cathode and Ar, N_2 and O_2 gases in the pressure range from 0.7 to 2.6 Pa.

3:50pm **H2-1-8 Influence of HIPIMS Plasma Ionization on the Microstructure and Texture of TiN Thin Films***,* ***A.P. Ehiasarian*** *(a.ehiasarian@shu.ac.uk), A. Vetushka,* Sheffield Hallam University, United Kingdom*, Y. Aranda Gonzalvo,* Hiden Analytical Ltd., United Kingdom*, G. Sáfrán, P.B. Barna*, Hungarian Academy of Sciences, Hungary

HIPIMS (High Power Impulse Magnetron Sputtering) discharge is a new PVD technology for the deposition of high-quality thin films. In this method, a high power density is applied at the cathode yielding a higher degree of plasma and sputtered species ionization than in standard magnetron sputtering.

In this study, the operation of HIPIMS in an Ar and N_2 atmosphere with a Ti target was investigated. Plasma was operated at a pressure of 0.24 Pa at the metallic-to-poisoned transition point. Plasma ionization was regulated by varying the peak discharge current from 5 to 30 A. The frequency was adjusted between 200 and 1000 Hz to maintain a constant average power of 0.4 kW.

Time-resolved Langmuir probe (LP) measurements of the plasma density showed a linear increase to 3×10^{16} m^{-3} with peak current and constant electron temperature. The influence of the gas-metal ion ratio, plasma composition and plasma density on film structure was investigated.

Energy-resolved mass spectrometry measurements showed that the reactive HIPIMS discharge produced a deposition flux with a significantly increased content of ionised film-forming species, such as Ti^+, Ti^{2+} and N^+. Increasing the discharge current from 5 to 30 A resulted in an enhanced activation of nitrogen and the density of the atomic ions N^+ was factor 1.5 higher than molecular ion N_2^+. Ti^{2+} : Ti^+ ratio increased by factor of 20 with discharge current.

The microstructure of TiN films was strongly influenced on HIPIMS peak current as shown in the Figure. At low currents, the structure was voided, columnar with rough surface and faceted column tops. At high currents the structure was fully dense with low roughness and flat column tops. The texture of all films deposited at all currents was high and changed from (111) to (200) as current increased.

The effects of increased high amount of nitrogen atomic ions and enhanced ionization of sputtered metal species on the development of texture and microstructure are discussed.

4:10pm **H2-1-9 HPPMS (Cr,Al,V)N and (Cr,Al,W)N Thin Films for Friction Reduction Through High Temperature Activation**, *K. Bobzin, N. Bagcivan,* ***S. Theiß*** *(theiss@iot.rwth-aachen.de), R.H. Brugnara*, RWTH Aachen University, Germany

Steel forming processes like hot forging and extrusion request excellent mechanical properties and good friction behavior of surfaces. In the temperature range of these processes (600°C – 800°C) self-lubricant hard coatings deposited by PVD suggest a possibility to meet these challenges. In this work the transition metals vanadium and tungsten were embedded in a (Cr,Al)N hard matrix. The coatings were deposited by HPPMS PVD technology on 1.2999 hot working steel. The transition metals are known to generate friction reducing oxide phases at high temperatures. These so called Magnéli phases offer a wide range of structures with disordering effects. The effects lead to crystallographic shear planes resulting in lower friction at application temperature. The in-situ formation of different oxide phases in the tribocontact zone offer advantages like high wear resistance and low friction.

The deposited coatings were analyzed with common thin film characterization methods revealing hardness, Young's modulus and adhesion. Furthermore, room temperature and high temperature Pin-on-Disk (PoD) tribometer measurements (25°C, 600°C and 800°C) and high resolution analysis like SEM, XRD, TEM and EDX were carried out. The phase analysis of XRD were carried out with specimens, which where annealed for 4 h (25°C, 600°C, 800 °C and 1000°C) in an oxygen containing atmosphere.

The analyses show a reduction of the friction coefficient from 0.60 (25°C) to 0.20 (600°C) and 0.05 (800°C) for the (Cr,Al,V)N coating. Here a formation of VO_2 and V_2O_3 at the surface can be obtained. Furthermore, TEM and EDX measurements show the formation of an alumina interlayer and a diffusion of the V atoms to the surface. A reduction of the friction coefficient for (Cr,Al,W)N (RT: 0.50) can not be obtained at 600°C (0.61). But at 800°C the friction coefficient drops to 0.38.

4:30pm **H2-1-10 Low Temperature Synthesis of α-Al_2O_3 Films by High-Power Pulsed Plasma Chemical Vapor Deposition**, ***K. Jiang*** *(jiang@mch.rwth-aachen.de), K. Sarakinos,* RWTH Aachen University, Germany, *S. Konstantinidis,* Université de Mons, France, *J.M. Schneider*, RWTH Aachen University, Germany

α-Al_2O_3 films are widely employed in surface protection and microelectronics applications due to their exceptional physical and chemical properties. In the industrial practice, α-Al_2O_3 is grown by chemical vapor deposition (CVD) at substrate temperatures in excess of 1000°C to provide the film forming species with sufficient energy to form this phase. Plasma assisted physical and chemical vapor deposition techniques provide an alternative source of energy to the growing film surface, i.e. the bombardment by energetic species. The use of energetic bombardment has been shown to facilitate growth of α-Al_2O_3 films at temperatures from 550 ~ 750°C [1-3]. However these films frequently exhibit high porosity, low values of hardness and Young's modulus compared to bulk, as well as poor performance. It is therefore evident that the low temperature growth of dense α-Al_2O_3 films is still a challenge. In the particular case of plasma assisted chemical vapor deposition (PACVD) films, the porosity may primarily be attributed to Cl incorporation due to the incomplete disassociation of the $AlCl_3$ precursor used for film deposition [4].

A decrease of the Cl incorporation can be facilitated by an increase of efficiency of the $AlCl_3$ dissociation in the gas phase as well as by a more intense energetic bombardment of the growing film. These can be achieved by employing a high density plasma. In order to create this high density plasma, we implement a novel generator that is able to deliver a 4 folder times higher peak power densities compared to the conventional generator employed at this semi-industrial PACVD chamber. We show that these conditions allow the growth of dense α-Al_2O_3 films with negligible Cl incorporation at a temperature of 560 ±10 °C. Films deposited at a pulse voltage of 1.3 kV, pulse length of 100 µs and frequency of 5 kHz exhibit elastic modulus and hardness values close to bulk values.

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[2] O. Zywitzki, G. Hoetzsch, F. Fietzke, et al., Surface & Coatings Technology **82**, 169 (1996).

[3] E. Wallin, T. I. Selinder, M. Elfwing, et al., Epl **82** (2008).

[4] R. Snyders, K. Jiang, D. Music, et al., Surface & Coatings Technology **204**, 215 (2009).

4:50pm **H2-1-11 Tribological Properties of Cr_2AlC Coatings Manufactured via DCUMS and HPPMS**, ***A. Flores Renteria*** *(floresre@tu-cottbus.de), C. Leyens,* BTU Cottbus, Germany, *M. to Baben,* RWTH Aachen, Germany, *J.M. Schneider*, RWTH Aachen University, Germany

This research work reports on some tribological properties of Cr_2AlC coatings manufactured in an industrial-sized coater via Direct Current Unbalanced Magnetron Sputtering (DCUMS) and High Power Pulsed Magnetron Sputtering (HPPMS). The coatings were tested using a scratch tester and a ball-on-disc tribometer. The scratch tests were applied using the EN 1071 norm conditions (load rate 100 N.min^{-1}, and speed of 10 mm.min^{-1}). The tribo tests were carried out at room temperature conditions using a 100Cr6 ball with 6 mm diameter applied with a 5 N force and a linear speed of 10 cm.sec^{-1} for 500 m. The results indicate that the friction coefficient and the wear rate of the HPPMS Cr_2AlC coating is 1.75 and 3 times that of DCUMS coating, respectively. XRD results confirm that the coatings contain a single phase (Cr_2AlC), with a strong texture in the case of HPPMS. Moreover, SEM micrographs of the cross section show a denser microstructure in the case of the HPPMS coating, which could be assumed to improve its wear resistance. Nevertheless, it seems that in this case, the influence of the texture dominates over the microstructure on the tribological properties of the manufactured Cr_2AlC coatings. This effect could be correlated to the anisotropic hexagonal crystal structure of these ternary alloys, which has been previously reported in the case of bulk MAX phases.

5:10pm **H2-1-12 Exploring the Potential of High Power Pulsed Magnetron Sputtering for the Deposition of Diamond Like Carbon Films**, ***K. Sarakinos*** *(sarakinos@mch.rwth-aachen.de), A. Braun, C. Zilkens, S. Mráz, J.M. Schneider,* RWTH Aachen University, Germany, *H. Zoubos, P.A. Patsalas*, University of Ioannina, Greece

The fraction of sp^3 bonds in diamond like carbon (DLC) films is important for their properties and their functionality in technological applications. The formation of sp^3 bonds in DLC films grown by plasma assisted physical vapor deposition (PVD) is known to be promoted by subsurface densification generated by the subplantation of energetic inert gas (Ar^+) and C^+ ions. High sp^3 content (more than 50% at.) and high density are prerequisites in order the films to be hard, dielectric, and optically transparent . State of the art ionized PVD techniques, such as pulsed laser deposition and cathodic arc, are able to provide high fluxes of ions allowing for the efficient control the sp^3 fraction. However, these techniques suffer from drawbacks, such as macroparticle formation and inhomogeneity, which complicate their implementation on an industrial scale. Magnetron sputtering (MS) techniques (both in dc and rf configuration), despite being the industrial standards, are characterized by a relatively low degree of ionization which results in the deposition of carbon films with low sp^3 fractions. It is therefore evident that there is a need for an industrial relevant highly ionized PVD technique that would enable deposition of DLC films both on laboratorial and on industrial scales. High power pulsed magnetron sputtering (HPPMS) is a novel PVD technique which has been shown to allow for the generation of ultra dense highly ionized plasmas. In the current study, we explore the feasibility of HPPMS for the synthesis of DLC films. Depositions are performed using HPPMS and dcMS, for reference, using constant average target power values of 60 and 100 W. For the HPPMS experiments unipolar pulses with a width of 50 µs and a period ranging from 1000 to 4000 µs are applied to the target. The increase of the pulsing period results in an increase of the peak target power density from 80 to 300 Wcm^{-2}. In order to tune the energy of the bombarding ionized species negative unipolar bias voltage (V_b) is applied to the substrate with values ranging from that of a floating substrate up to 250 V. The effect of the plasma conditions on the bonding state and the density of the films is investigated by means of Auger Electron Spectroscopy (AES) and X-ray reflectometry (XRR). It is found that at all deposition configurations the increase of the negative unipolar bias voltage up to a value of 130 V leads to an increase of the sp^3 fraction. Depending on the pulse configuration and the bias voltage, HPPMS results in up to 60% larger sp^3 fractions than those obtained by conventional dcMS.

5:30pm **H2-1-13 HPPMS – The Next Generation of Dedicated Coatings for High Precision Cutting Tools**, ***T. Leyendecker***, *W. Reichert, S. Bolz, C. Schiffers (christoph.schiffers@cemecon.de)*, CemeCon AG, Germany

Dedicated coatings for high precision cutting tools are a successful approach for meeting the increasing demands in metal cutting. PVD sputter coatings have taken the lead in a wide range of applications due to their super smooth surface without any marco-particles or droplets in the film. HPPMS has been widely discussed in the scientific community as the most promising development to push ahead coating technology.

CemeCon refined HPPMS to the point that the very first commercial job coating production using this technology has started. This talk will focus on how the advantages of HPPMS add new options to the coating designer's tool box when adapting and tailoring films to the specific and very different requirements of machining operations like drilling, turning, milling, reaming, threading, gear cutting or grooving. This next generation of dedicated coatings targets growing market segments as hard milling and energy generation with the need of the machining of high temperature materials.

Thursday Morning, April 29, 2010

Coatings for Use at High Temperature
Room: Sunrise - Session A3-1

Thermal Barrier Coatings
Moderator: A. Bolcavage, Rolls-Royce Corporation, R.G. Wellman, Cranfield University, B.T. Hazel, General Electric

8:00am **A3-1-1 Models for Foreign Object Damage to Columnar Zirconia Thermal Barrier Coatings**, *M.W. Crowell,* University of California, Santa Barbara (now at Los Alamos National Lab), ***R. McMeeking*** *(rmcm@engineering.ucsb.edu), A.G. Evans*, University of California, Santa Barbara **INVITED**

The columnar thermal barrier oxides typically relied upon to protect critical hot-section rotating parts from extreme temperatures in modern aero-turbines suffer from a number of damage mechanisms. These include thermal, chemical, and mechanical attack, each of which can limit the functional life of the thermal barrier coating (TBC), and hence the underlying component and the entire engine. Mechanical attack in the form of impacts due to particulates ingested in the engine's hot gas path have proven to be particularly unpredictable. Engine designers are often forced to assume TBCs subject to these impacts will immediately spall and provide no thermal protection. However, there exists both engine and experimental evidence suggesting variations in the TBC's columnar microstructure can help in resisting such foreign object damage (FOD). The engine operating environment is extremely complex and difficult to accurately reproduce experimentally, so dynamic finite element modeling has been employed, as well as model experiments. Automated parameter variation and 2-D modeling in ABAQUS have enabled high resolution parametric studies of varying FOD scenarios and TBC microstructures. Various figures of merit concerning simulated resistance to spallation have been explored via postprocessing in MATLAB, and validation has been obtained through the experiments. Such methods and results will be presented.

8:40am **A3-1-3 Lifetime of Thermal Barrier Coatings With MCrAlY-Bondcoats: Effects of Testing Procedure and Coatings Microstructure**, ***D. Naumenko*** *(d.naumenko@fz-juelich.de), P. Song, L. Singheiser, W. Quadakkers*, Forschungszentrum Jülich GmbH, Germany

Yttria stabilized zirconia thermal barrier coatings (TBCs) produced by air plasma spraying on Ni-based superalloys with MCrAlY (M = Ni, Co) bondcoats were studied. The specimens were subjected to cyclic oxidation testing in laboratory air at temperatures between 1000 and 1100°C under various cyclic conditions. It was observed that the lifetime of the TBC-system was about 30% shorter when tested with hot-dwell times in the order of 2 hours than when tested with hot-dwells in the order of 20 hours. Analytical studies of the polished cross-sections of the exposed specimens by optical metallography and scanning electron microscopy (SEM) indicated that TBC-failure was initiated by delaminations at the alumina scale/bondcoat interface in the convex regions of the rough bondcoat surfaces, which then propagated through the TBC. Independent of the testing procedure the absolute values of the TBC lifetime were found to depend strongly on the TBC-microstructure and especially the morphology of the TBC/bondcoat interface. Comparison of two TBC systems with nominally the same base material, bondcoat and TBC chemical compositions revealed that these properties crucially determine the rate of crack propagation through the TBC.

9:00am **A3-1-5 Suspension Plasma Spray as a Route for Microstructural Design of New Thermal Barrier Coatings**, ***R.W. Trice*** *(rtrice@purdue.edu)*, Purdue University **INVITED**

Suspension plasma spray is an emerging injection technology that adapts to existing plasma spray equipment; it affords the capability to form new coating microstructures for thermal barrier and other applications. In suspension plasma spray, powders are first dispersed in a solvent to form a stable suspension, then fed through a small nozzle into the plume. The enthalpy of the plume evaporates or combusts the solvent, and the powders are melted and propelled towards the substrate where they flatten to form lamella. Coatings are composed of stacked lamella, similar to conventional plasma spray with some important differences. First, powders as small as 50 nm have been plasma sprayed using this approach, much smaller than the 10 micron lower limit associated with conventional powder feed techniques. Also, it has recently been demonstrated that by changing the composition of the suspension the final composition of the coating can be varied. In this paper we will present some recent recent results that establish processing-property-microstructure relationships, with a focus on how porosity distribution and shape relate to thermal conductivity. Finally, we will present results that show that suspension plasma spray can be combined with a defect oxide clustering approach to fabricate ultralow thermal conductivity coatings that possess conductivities of 0.8 W/m/K after 50 hours at 1200^{o}C.

9:40am **A3-1-7 Proto-TGO Formation in TBC Systems Fabricated by Spark Plasma Sintering**, ***M. Boidot****, S. Selezneff, D. Monceau (daniel.monceau@ensiacet.fr), D. Oquab, C. Estournès*, CIRIMAT, France

Complete thermal barrier systems were fabricated on single crystal Ni-based superalloy (AM1) in a one-step Spark Plasma Sintering process (SPS). The lifetime of such systems is highly dependent on its ability to form a dense, continuous, slow growing alumina layer (usually called Thermally Grown Oxide, TGO) between an underlying bond coat and a ceramic top coat. Then, TEM-EDS and Raman spectroscopy were used to determine the nature of the proto-TGO phases in the as-fabricated systems. The proto-TGO is determined as being amorphous-Al_2O_3 in the as-fabricated samples, transforming to α-Al_2O_3 during thermal treatment or cyclic oxidation under laboratory air at 1100°C. Oxidation kinetics calculations are presented and demonstrate the phase transformation from amorphous alumina to alpha alumina during thermal treatment. This paper investigates the mechanisms that lead to both the formation of the amorphous-alumina called proto-TGO and the reactive elements doping of the bond coat (Zr in the present case) during TBC processing.

10:00am **A3-1-8 Effect of Superalloy Substrate and Bond Coating on TBC Lifetime**, ***B.A. Pint*** *(pintba@ornl.gov), J.A. Haynes,* Oak Ridge National Laboratory, *Y. Zhang*, Tennessee Technological University

Several different single-crystal superalloys were coated with different bond coatings to study the effect of composition on the cyclic oxidation lifetime of an yttria-stabilized zirconia (YSZ) top coating. Three different superalloys were coated with a 7µm Pt layer that was diffused into the surface prior to YSZ deposition by physical vapor deposition from a commercial source. One of the superalloys was coated with a standard Pt-modified aluminide coating and Pt-diffusion coatings with 3 or 7µm of Pt. Three coatings of each type were cycled to failure in 1h cycles at 1150°C to get an average coating lifetime. The Pt-diffusion bond coating on the superalloy containing Ti exhibited the shortest YSZ coating lifetime. Initial characterization has been conducted to understand the role of Ti in the coating system.

10:20am **A3-1-9 On The Design of Industrial Sensor Thermal Barrier Coating Systems**, ***J.P. Feist*** *(j.feist@stscience.com),* Southside Thermal Sciences, *A.L. Heyes,* Imperial College London, United Kingdom, *R. Vaßen,* Forschungszentrum Jülich GmbH, Germany, *J.R. Nicholls*, Cranfield University, United Kingdom **INVITED**

This paper will review the development and design aspects of Thermal Barrier Coating (TBC) Systems with intrinsic sensor properties. The sensor properties are introduced by embedding rare earth elements into the coatings which make these coatings phosphores. The concept of thermal–sensing and of phase detection utilising luminescence effects in TBCs was first introduced by Choy, Feist, Heyes et al. in 1998 (Choy et al US6974641; US2009226326).

TBCs are ceramic protective coatings designed to withstand extreme environmental conditions such as high temperatures, thermal shock and possibly corrosion attack. Over the past decades a tremendous effort has been put into the development and understanding of thermal barrier coatings as their application in the gas turbine industry promises higher operational efficiency, longer life of components and hence lower fuel bills and maintenance bills. As the effort of the turbine industry is focused on lowering carbon emissions a drive for even higher operating temperatures is foreseen. This will require new approaches in regard to component monitoring to reduce maintenance costs and to permit maximum utilisation of engine components in the hot section.

The paper looks into the design of materials suitable to manufacture EBPVD and APS sensor coating systems. Different aspect will be highlighted such as suitable dopants, two phase systems and layered coatings. Selected systems were manufactured and characterised using industrial standard coating techniques. These systems were studied on luminescence from room temperature to temperatures in excess of 1400oC. Further, some systems have shown very promising durability properties when tested alongside standard thermal barrier coatings.

In addition to the thermal sensing properties the paper will demonstrate the potential to measure other properties such as ageing of the material or hot corrosion effects.

11:00am **A3-1-11 Microstructure Design and Mechanical Properties of Thermal Barrier Coatings with Layered Top and Bond Coats**, *Y.-G. Jung (jungyg@changwon.ac.kr),* ***S.-W. Myoung****, J.-H. Kim, W.-R. Lee,* Changwon National University, Republic of Korea*, U.G. Paik,* Hanyang University, Republic of Korea*, K.-S. Lee*, Kookmin Universiy, Republic of Korea

Thermal properties and failure mechanisms of thermal barrier coatings (TBCs) are closely related with its microstructure. Numerous factors, besides the thermo-mechanical properties, have to be considered in practical applications of TBCs, such as erosion and wear resistance. There is therefore a need to improve the adhesive strength and mechanical characteristics, which are essential to improving the reliability and lifetime performance of the air-plasma sprayed (APS) TBC system. In this study, the microstructures in the top and bond coats of TBCs have been designed as a new strategy for the advanced coatings, and we prepared the layered TBC with three coating layers in both the top and coats using a specialized coating system (TriplexPro-200). In order to determine and to understand the effects of the microstructure design on the fracture behavior and the mechanical properties, the adhesive strength and sharp indentation tests were conducted. Results were compared with the common TBC systems with single layer in each coat. In the layered TBCs, more dense coating could be possible due to an higher flame velocity compared to a conventional APS system (9MB), and semi-graded coating also possible using a multi-hopper system. The bond and top coats were coated with 100 and 200 mm for each feedstock, resulting in 300 and 600 mm in the bond and top coats, respectively. The microstructure of the top coat could be controlled by changing the feedstock—dense/intermediate/porous layers from surface to interface or reverse microstructure. The adhesive strength values of the bond and top coats were about 80 and 10 MPa, respectively, independent of microstructure, which are higher values than those of TBC system prepared by the 9MB system. The hardness and toughness values were gradually changed from surface to interface, indicating that the mechanical properties are well corresponded with the microstructure of TBCs.

Hard Coatings and Vapor Deposition Technology Room: Town & Country - Session B5-1

Properties and Characterization of Hard Coatings and Surfaces

Moderator: M. Fenker, FEM Research Institute, Y.W. Chung, Northwestern University, G. Abadias, University of Poitiers

8:00am **B5-1-1 Determination of Mechanical Properties of FIB-Based Cantilever Bending Technique**, ***R. Pippan*** *(reinhard.pippan@oeaw.ac.at), K. Matoy, St. Massl, C. Motz, M. Rester*, Austrian Academy of Sciences, Austria **INVITED**

The strength and ductility of thin films are important material parameters owing to their significant influence on lifetime and structural integrity of components. Such intrinsic parameters of the coatings are difficult to determine due to the small dimension, the defects, the brittleness, the residual stress, etc.

The purpose of this presentation is to present a new technique for the evaluation of intrinsic strength and intrinsic mode I fracture toughness of thin films based on the fabrication of microcantilevers by means of a focused ion beam workstation and the subsequent testing of these cantilever beams in an in situ microindenter mounted in a scanning electron microscope. The advantages and the limitations of the method will be presented. The measured strength and fracture toughness of a TiN coating and different types of interfaces are analysed. Besides the determination of strength and toughness, the residual stress distribution can be evaluated and the effect on fracture behaviour is investigated.

8:40am **B5-1-3 Characterization of Nanoindented TiAlN/CrN Nano-Multilayer Films by Transmission Electron Microscopy**, ***P.-L. Sun*** *(plsun@fcu.edu.tw),* Feng Chia University, Taiwan*, C.-H. Hsu, S.-H. Liu,* Tatung University, Taiwan*, C.-Y. Su,* National Taipei University of Technology, Taiwan*, C.-K. Lin*, Feng Chia University, Taiwan

In this work, TiAlN/CrN multilayer thin films were deposited on an AISI 403 stainless steel substrate by cathodic arc deposition (CAD). The effect of substrate orientation (vertical or horizontal to the arc) and substrate rotational speed were investigated in detail. Microstructure characterizations of the as-deposited thin films were done by X-ray diffraction, X-ray photoelectron spectroscopy, scanning electron microscopy and transmission electron microscopy. Additionally, nanoindentation was conducted on the thin film multilayers. The experimental results indicate that the TiAlN/CrN multilayer films prepared with a vertical substrate orientation and a substrate rotational speed of 4 rpm possessed superior coating hardness and hardness/elastic modulus (H/E) ratio. The microstructure and interfacial structure of the indented TiAlN/CrN multilayer thin films were investigated by transmission electron microscopy and the deformation mechanism will be discussed.

9:00am **B5-1-4 Influences of Annealing on the Microstructures and Mechanical Properties of Cr_2N/Cu Multilayered Thin Films**, *C.-L. Li,* Tungnan University, Taiwan*,* ***H.-M. Lin****,* National Tsing Hua University, Taiwan*, J.-W. Lee (jefflee@mail.mcut.edu.tw),* Mingchi University of Technology, Taiwan*, J-.G. Duh,* National Tsing Hua University, Taiwan*, L.-C. Chang*, Mingchi University of Technology, Taiwan

Nanostructured Cr_2N/Cu multilayer coatings with bilayer thickness ranges from 5 nm to 40 nm were deposited periodically by a bipolar asymmetric pulsed DC reactive magnetron sputtering technique. A rapid thermal annealing at 400C for 2, 4 and 8 min were further applied, respectively. The structures of annealed multilayer coatings were characterized by an X-ray diffractometer. The surface and cross sectional morphologies of annealed thin films were examined by a scanning electron microscopy (SEM) and transmission electron microscopy (TEM), respectively. The surface roughness of thin films after annealing was explored by an atomic force microscopy (AFM). The nanohardness and elastic modulus of annealed multilayer coatings were investigated by means of a nanoindenter . The fracture toughness values of annealed coatings were further evaluated by microhardness tests. The coalescence of Cu nano layers into Cu particles was observed after annealing. It is found that hardness and toughness of coatings were influenced effectively by the annealing time. A hardness enhancement was found on the coating with a critical bilayer thickness of 10 nm. The possible strengthening mechanism was also proposed in this work.

9:20am **B5-1-5 Microstructural and Mechanical Properties of TiN/VN Nano-Structured UMS Coatings**, ***Q. Yang****, M. Bielawski (mariusz.bielawski@nrc.gc.ca), R.C. McKellar*, National Research Council Canada

Erosion-resistant coatings are used to protect compressor components of land and airborne gas turbines from destructive effects of hard particles suspended in the inflowing air. To meet demands of the aerospace industry, new high performance erosion-resistant coatings are being developed. In particular, nano-structured Physical Vapour Deposition (PVD) coatings are among the most promising materials for this application. Nano-structured TiN/VN coatings with a range of bilayer periods were deposited on Ti-6Al-4V alloy and 410 stainless steel substrates by Unbalanced Magnetron Sputtering (UMS) and evaluated for microstructural and mechanical properties. A nanomechanical indentation technique was used to determine hardness H, Young's modulus E and H^3/E^2 ratio. The H^3/E^2 ratio was used to evaluate potential erosion-resistance properties of the TiN/VN coatings. It was found that the obtained values of hardness and H^3/E^2 ratio varied widely with deposition conditions and appeared to be dependent on the substrate material. Further investigations were carried out using an XRD technique to evaluate bilayer period (from satellite peak position) and preferred orientation of the coatings. The XRD measurements were complemented by texture evaluation through pole figures. It was concluded that the preferred orientations of the coatings on different substrates evolved differently with rotation speeds, which might be caused by the difference in magnetic properties of the substrate materials. Contrary to 410 stainless steel which is martensitic, titanium alloy Ti-6Al-4V is non-magnetic, and thus the ion bombardment during the UMS deposition process was different in both cases. The bi-layer period of the TiN/VN coatings varied between 2.47 and 11.4 nm and was practically independent of the substrate materials. Thus, the hardness variations of the coatings on different substrates could not be attributed to the bilayer period. In the next step, the effect of preferred orientation on hardness enhancement was analysed and positively linked with observed hardness changes in tested coatings. It was found that for the 410 stainless steel substrate, coatings with the (111) preferred orientation had the lowest hardness in the series as opposed to coatings with a (200) or (220) orientation that showed higher hardness. For the Ti-6Al-4V substrate, the hardest coatings were those with a strong (220) orientation. However, these observations did not explain all variations in the coatings' hardness, and the differences were attributed to residual stress in the coating/substrate systems. Further investigations will be carried out in this direction.

9:40am **B5-1-6 Co-development of Stress and Texture in TiN Films, Revealed by In-Situ Film Stress Measurments**, *R. Machunze (r.machunze@tudelft.nl)*, ***G.C.A.M. Janssen***, Delft University of Technology, The Netherlands

Titanium nitride coatings (TiN) are used amongst other applications as wear-protective coatings or as diffusion barriers in IC technology. In these applications the film stress is a key factor determining the performance of the coating.

Two series of TiN films with thickness up to 100 nm have been deposited on Si wafers by reactive DC magnetron sputtering from a Ti target in an AJA sputtering system at a temperature of 360 °C and a RF substrate bias voltage of -150 V. The deposition rate was approximately 100 nm/h. The nitrogen flow was kept constant; the argon flow was varied to obtain deposition pressures of 0.4 and 0.6 Pa, respectively. With a two-laser beam set-up we measured the change in wafer curvature and hence the film force during film growth. From the film force the average stress and the instantaneous stress are derived.

We found a distinctly different film force development for the films grown at different deposition pressures. At equal total thickness the 0.6 Pa film shows a small average film stress of -0.6 GPa, the 0.4 Pa film a more compressive film stress of -5.6 GPa. The 0.6 Pa film revealed a linear increase of film force for the first 30 nm; then the film force remains constant, indicating no stress in the higher up parts of the film. In contrast, the film force of the 0.4 Pa film showed linear increase over the whole film thickness. X-ray diffraction on both series revealed a different texture evolution as the films grow thicker: the 0.6 Pa film has a 111 texture, the 0.4 Pa film a 001 texture.

At 0.6 Pa the bombardment of the growing film with energetic particles will be less intense than at 0.4 Pa. An intense film bombardment will lead to 001 texture [Greene et al. APL **67** (1995) 2928]. By this mechanism we explain the difference in texture. The difference in stress we explain by a difference in the susceptibility to compressive stress generation by energetic particle bombardment. Crystals with their 001 direction parallel to the growth direction are more open than crystals with their 111 direction parallel to the growth direction.

With our in-situ measurements we are able to correlate film stress and film texture development of TiN films. We show that for TiN the film texture is an important parameter for controlling film stress, energetic particle bombardment generating more compressive stress in crystals with their 001 direction parallel to growth direction than crystals with their 111 direction parallel to growth direction.

10:00am **B5-1-7 Effect of Grain Size on the Residual Stress State and Thermal Expansion in Magnetron Sputtered Thin Films**, ***R. Daniel*** *(Rostislav.Daniel@unileoben.ac.at), D. Holec, J. Keckes, C. Mitterer*, Montanuniversität Leoben, Austria

The thickness dependent residual stress state in thin films is analyzed in magnetron sputtered Cr and CrN zone-T structured layers with thicknesses ranging from 100 nm to 3 µm. The relationship between layer thickness on silicon (100) substrates and both intrinsic and thermal stresses was investigated in detail by means of X-ray diffraction and substrate curvature methods and correlated with the film microstructure. Due to competitive growth, the grain size was found to increase with increasing layer thickness. The development of both stress components strongly depends on the grain size. The ion-irradiation induced compressive stresses were observed to increase with decreasing grain size, whereas the thermal stresses were tensile and highest for small grain sizes. The thus conclusive relation between the thermal expansion coefficient and grain size results from a more pronounced volume expansion of fine grained structures when compared with coarser ones. This is related to the increasing volume fraction of disordered grain boundaries with decreasing layer thickness, representing the interface between mutually misorientated crystallites where the thermal stress is redistributed. This phenomenon is described by a model that explains the size effect of the thermal expansion and the origin of internal stresses in thin polycrystalline films. The model is further extended for a CrN/Cr dual-layer system where a 100 nm to 2.9 µm thick CrN toplayer is epitaxially aligned with the underlying highly (200)-oriented Cr interlayer.

10:20am **B5-1-8 Influence of Multilayer Designs on their Residual Stresses and Mechanical Properties**, *W. Tillmann*, ***E. Vogli*** *(evelina.vogli@udo.edu), H.-A. Crostack, G. Fischer, U. Selvadurai-Lassl, J. Herper*, TU Dortmund, Germany

Thin films are applied in many industry areas to increase the hardness, the abrasion resistance, the chemical and thermal stability of surface components. The hardness and toughness of thin films and thereby their lifetime are mostly determined by the level of residual stresses. Therefore the determination of residual stresses plays an important function by optimization and selection of thin films. The residual stresses can be modified and adjusted by designing thin films to increase the lifetime.

In this research work different designs of Ti- and Cr-based multilayers were deposited onto substrates pretreated by polishing and different etching. The influence of multilayer design and substrate pretreatment on residual stress of these multilayers and the subsurface substrate were analyzed by means of synchrotron X-ray diffraction. Furthermore multilayers adhesion and hardness were systematically analyzed and correlated with residual stresses and designs. Tribological tests were carried out to study the effect of residual stresses on wear and friction of the multilayers.

10:40am **B5-1-9 Thermal Decomposition of Epitaxial Al-Cr-N Hard Coatings: Crystallography and Mechanical State of Individual Phases**, ***M. Bartosik*** *(matthias.bartosik@stud.unileoben.ac.at), R. Daniel, C. Mitterer, J. Keckes*, Montanuniversität Leoben, Austria

Epitaxial Al-Cr-N thin films are deposited on c-cut sapphire substrates using reactive magnetron sputtering in Ar and N_2 gas mixture at 500°C. The samples are annealed in the temperature range of 900-1100°C for 2 hours in order to induce thermal decomposition of cubic Al-Cr-N. X-ray diffraction and transmission electron microscopy are used to characterize the influence of the heat treatment on phase composition, epitaxial orientation relationships and mechanical state of individual phases with respect to the substrate. The pole figure analysis shows that cubic (111) oriented Al-Cr-N turns into hexagonal (0002) AlN and cubic (111) CrN whereby the in-plane orientation can be correlated with the substrate. The cubic phases show always two variants. The residual stresses in the phases are quantified using $\sin^2\psi$ method.

11:00am **B5-1-10 Plasma Sprayed Ceramic-Carbon Nanotube Coatings with Tailored Mechanical Properties**, ***S. Seal*** *(sseal@mail.ucf.edu)*, University of Central Florida, *A. Agarwal*, Florida International University **INVITED**

Carbon nanotubes (CNT) are potential reinforcements for producing metal-ceramic matrix composites and coatings with high strength and toughness. However, the critical issue of avoiding CNT agglomeration and introducing CNT-matrix anchoring has challenged many researchers to improve the mechanical properties of the CNT reinforced nanocomposite. In the current work, dispersed CNTs are grown on or mixed with ceramic and metal powder particles by a variety of techniques. Consequently, these CNT powder mix were successfully plasma sprayed to obtain a thick coating on the steel substrate for detailed chemical and mechanical characterization. These CNT reinforced coating and composites show a promising enhancement in hardness and fracture toughness of the plasma-sprayed coating attributed to the existence of strong metallurgical bonding between metal ceramic particles and CNTs. In addition, CNT tentacles have imparted multi-directional reinforcement in securing the splats. High-resolution transmission electron microscopy shows interfacial fusion between metal-ceramic and CNT and the formation of Y-junction nanotubes. Various strengthening mechanisms are discussed.

11:40am **B5-1-12 Elemental Characterization of Metallurgical Coatings and Films using Glow Discharge OES and Laser Ablation ICP-MS**, ***F. Li***, *S. Anderson (scott.anderson@balazs.com)*, Air Liquide Balazs NanoAnalysis

New material analysis strategies using radio frequency (RF) plasma source atomic spectroscopy and mass spectrometry have been developed to address the increasingly complex characterization needs from the semiconductor, solar, disk drive, and metallurgical industries. The specific techniques that were studied include glow discharge optical emission spectroscopy (RF GD-OES) and laser ablation ICP mass spectrometry (LA ICP-MS). The findings reveal that these techniques provide distinct applications and data where traditional analyses incorporating electron beam, ion beam, and x-ray techniques are not sufficient. By using RF plasma or laser ablation for material sputtering, excitation or ionization, many intrinsic limitations associated with traditional techniques are avoided.

RF GD-OES has been used to examine surface stoichiometry of metallurgical coatings and assist advanced surface modification processes designed for chemical corrosion and mechanical wear resistance. Its excellent depth resolution and simultaneous multi-element profiling capability also enable the examination of both physical and chemical deposition processes by studying the vertical elemental distributions in coatings from the surface to the interface region. LA ICP-MS has been used for microscopic defect identification and determination of trace impurities in sputtering targets, hard coatings and multi-layer thin films. These experiments and data collection is unaffected by any surface equilibrium issues or changes in ion yield at the film interface regions as with other techniques. Examples of the materials analyzed to date include anodized alumina, ceramic, quartz, polymer, diamond and diamond like carbon (DLC), various metal and alloy films, silicon carbide (SiC), silicon nitride

(Si_3N_4) and a wide range of thin film materials used in the semiconductor and photovoltaic manufacturing process. The signal intensities produced by these techniques all have simple and well-defined mathematical (linear) relationships with elemental concentrations in metallurgical materials. Their wide linear dynamic ranges coupled with various NIST traceable material standards developed in our laboratory have made accurate and precise analysis possible, especially for those challenging and difficult advanced metallurgical materials and multifunctional thin films emerging from high-tech manufacturing processes.

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

Room: Royal Palm 1-3 - Session C2-1

Thin Films for Active Devices and Microstystems

Moderator: T. Miyata, Kanazawa Institute of Technology, N. Drolet, Konarka

8:00am **C2-1-1 Organic Semiconductor Lasers, Optical Amplifiers and Detectors**, *Y. Yang, D. Amarasinghe, G. Tsiminis, J.W. Levell, M.E. Giardini, A. Ruseckas, G.A. Turnbull,* ***I.D.W. Samuel*** *(idws@st-andrews.ac.uk)*, University of St. Andrews, United Kingdom **INVITED**

The attractive properties of organic semiconductors such as simple fabrication and scope for tuning properties make these materials appealing for thin film devices with a wide range of applications in electronics and optoelectronics. The great progress made in materials for organic light-emitting diodes has led to a newer field of organic semiconductor lasers. In addition to simple processing and tuneability, the strong absorption, high gain cross section, broad spectra and high solid state fluorescence quantum yields of organic semiconductors are attractive for applications as lasers. The high chromophore density in neat films enables high gain to be obtained, and distributed feedback lasers in which lateral corrugation of the film provides feedback are commonly used.

The development of practical polymer lasers requires progress in reducing the threshold for lasing so that convenient pump sources can be made. Pump lasers have been steadily reduced in size from large frame lasers to a microchip laser and more recently a gallium nitride laser diode. The need for another pump laser has limited the development of polymer lasers. We have overcome this problem by matching an InGaN LED as pump source to a fluorene copolymer laser. The LED is a convenient low cost electrical pump source and the polymer gives tuneable emission at wavelengths not readily accessible by inorganic semiconductors. Hence this hybrid optoelectronic device provides the key advantages of electrical pumping and simple fabrication expected from an electrically pumped polymer laser.

Another hybrid optoelectronic device will also be shown – a photodiode using a combination of silicon and an organic semiconductor thin film to give greatly enhanced ultraviolet response.

The presence of gain in organic semiconductors can also be used to make optical amplifiers. These give broadband amplification of ultrafast optical pulses in the visible region of the spectrum. Finally, we will also show how organic thin films can be conveniently patterned by soft lithographic techniques.

8:40am **C2-1-3 Concepts for the Material Development for Solution Processable Phosphorescent Polymers and their Application in PLEDs**, ***S.J. Janietz*** *(silvia.janietz@iap.fraunhofer.de), H.K. Krueger, M.T. Thesen, A.W. Wedel*, FhG-IAP, Germany

Organic electronics is based on new conductive and semiconductive materials which, when put in solution, can be processed using manufacturing methods. By adapting established printing and other structuring processes, such as laser patterning, it is possible to mass produce very cost-effective electronics on large area, flexible substrates. A big advantage of organic electronics is that it allows the combining of a large number of different plastic electronic components and their production in one integrated manufacturing process.

One example of organic electronics is the application of polymer based light emitting devices (PLEDs). PLEDs are very attractive for large area and fine-pixel displays, lighting and signage. The polymers are more amenable to solution processing by printing techniques which are favourable for low cost production in large areas. With phosphorescent emitters like Ir - complexes higher quantum efficiencies were obtained than with fluorescent systems, especially if multilayer stack systems with separated charge transport and emitting layers were applied in the case of small molecules. But polymers exhibit the ability to integrate all the active components like the hole-, electron-transport and phosphorescent molecules in only one or maximal 3 layers. Therefore this concept is very attractive for an alternative technology processing in comparison to the more complicated multilayer stack systems based on the evaporation of small molecules. Two different synthetic routes were developed . In one case, structure optimized and energy-level adapted hole-, electron- transport and phosphorescent molecules were selected and modified with polymerizable groups. Terpolymers were synthesized containing optimized ratio of the 3 selected components. The results of the OLED characterization will be discussed in detail in com parison with the chosen structure of the molecules. Another approach is to separate the transport molecules in two different layers. For this reason cross linkable polymer layers have to be applied to realize the multi layer structure stability during wet processing .

9:00am **C2-1-5 Light Emission from Organic Field-Effect Transistors**, *E. Feldmeier, M. Schidleja, C. Siol, C. Melzer,* ***H. von Seggern*** *(seggern@e-mat.tu-darmstadt.de)*, Technical University of Darmstadt, Germany **INVITED**

The discovery of light emission from organic field-effect transistors (OFETs) in 2003 by Hepp et al. [1] and Ahles et al. [2] has opened an interesting field of research for the investigation of ambipolar charge transport in inorganic devices. The history and latest progress on organic light-emitting field-effect transistors will be presented. Based on the finding that ambipolar transport is possible for a variety of polymers and small molecules on electron-trap-free gate insulators, light emitting OFETs utilizing PMMA (poly(methyl methacrylate) and PS (polystyrene) as gate dielectrics and F8BT (poly(9,9-di-n-octylfluorene-alt-benzothiadiazole) and different polyacences like teracene, ditetracene and pentacene as organic semiconductors [3] will be demonstrated. It will be investigated how electron and hole transport are initiated and finally result in recombination, which leads to a spatially controllable emission zone [3,4]. The influence of injection barriers from different source and drain metals is also addressed. It will be demonstrated that by selecting ohmic contacts strong light emission is already observable in pure electron and hole accumulation indicating strong thermal injection of charge carriers at the contacts. Some of the experimental results are compared to theoretical derived OFET characteristics from an OFET model by Schmechel et al. [5] generalized through the inclusion if charge carrier injection by a model proposed by Scott and Malliaras [6].

[1] A. Hepp, H. Heil, W. Weise, M. Ahles, R. Schmechel, H. von Seggern, "Light-emitting field-effect transistor based on a tetracene thin film", *Phys. Rev. Let.* **91**, 157406-1 (2003)

[2] M. Ahles, A. Hepp, R. Schmechel, H. von Seggern, "Light emission from a polymer transistor", *Appl. Phys. Lett.* **84**, 428 (2004)

[3] J. Zaumseil, R. H. Friend, and H. Sirringhaus, "Spatial control of the recombination zone in an ambipolar light-emitting organic transistor", *Nat. Mater.* **5**, 69 (2006)

[4] M. Schidleja, C. Melzer, H. von Seggern "The organic light-emitting field-effect transistor" submitted to *Frequenz*

[5] R. Schmechel, M. Ahles, H. von Seggern, „A pentacene ambipolar transistor: Experiment and theory" *J. Appl. Phys.* **98**, 084511 (2005)

[6] J. C. Scott, G.G. Malliaras, Chem. Phys. Lett. 299, 115 (1999)

9:40am **C2-1-7 Polythiophene Thin Films Electrochemically Deposited on Sol-Gel Based TiO_2 for Photovoltaic Applications**, *R. Valaski,* Inmetro*, N. Yamamoto, R. Mello, M. Oliveira, L. Roman,* UFPR, Brazil*, C. Legnani, W. Quirino,* Inmetro, Brazil*,* ***M. Cremona*** *(cremona@fis.puc-rio.br)*, PUC-Rio, Brazil

Due to its higher stability in environmental conditions and its high absorption coefficient in the visible range of spectrum, polythiophene (PT) is one of the most promising organic semiconductors for photovoltaic applications. The electrochemical methods for organic films production present some interesting features as simultaneous organic synthesis and film deposition and the possibility of thickness control by the time deposition. Moreover, the overcoming of some intrinsic difficulties of the electrochemical method allows the development of efficient devices and has strategic importance due to the easiness and the lower costs of production. In this context the electrochemical deposition of PT on titanium dioxide (TiO_2) films has being a feasible alternative towards more efficient and more durable devices. TiO_2 is an n-type semiconductor with a large gap and it has been demonstrated that it is able to improve drastically the efficiency of organic photovoltaic cells. Among the different experimental techniques to produce TiO_2 layers the sol-gel method stands out due to be an easier way of production large area films without controlled atmosphere or considerably changes in the process. As most of organic semiconductors are p-type a TiO_2 intermediate layer between the electrode and the organic active layer produces a p-n junction. Furthermore, the difference between the material gaps produces energy steps which improve the dissociation of the excitons generated in organic layer by the radiation absorption. In this work, TiO_2 films produced by sol-gel technique were structurally, morphologically and electrically characterized by X-ray diffraction, AFM and Four Probe method . X-ray diffraction results lead to the conclusion that sol-gel TiO_2 films are predominantly composed by the anatase phase with electron mobility of 10^1 $cm^2/V.s$, which is coherent with the values present in the literature. TiO_2 resistivity also varies in a range between 10^6 and 10^4 Ω.cm depending on temperature treatment.. Using a three electrode cell controlled by a potentiostat, PT films were electrochemically deposited under 3 V/Ag/AgCl and dedoped with a potential of 0.2V/Ag/AgCl. The electrolyte was a 0.02 M of $(CH_3)_4NBF_4$ in acetonitrile with 0.1 M of thiophene monomer. In order to study the influence of PT/TiO_2 bi-layer on the photovoltaic efficiency, *IPCE* (dynamic spectra under short-circuit condition) and *J(V)* curves were also measured in dark and under illumination for some organic photovoltaic devices (OPV).

10:00am **C2-1-9 Microstructural and Optical Properties of Ga-Doped ZnO Semiconductor Thin Films Prepared by the Sol-Gel Process**, ***C.-Y. Tsay*** *(cytsay@fcu.edu.tw), C.-W. Wu,* Feng Chia University, Taiwan*, C.-M. Lei,* Chinese Culture University, Taiwan*, F.-S. Chen,* Tatung University, Taiwan*, C.-K. Lin*, Feng Chia University, Taian

ZnO-based semiconductor thin films attract considerable interest as an active channel layer in thin film transistors. In this study, transparent semiconductor thin films of Ga-doped ZnO (GZO), Ga dopant varying from 0 to 7 at.%, were deposited onto alkali-free glass substrates by the sol-gel process. The effect of Ga doping on crystallinity, microstructure, optical properties and electrical resistivity of ZnO thin films were systematically investigated. Moreover, chemical compositions and photoluminescence spectra of GZO thin films were examined. Each spin-coated film was dried at 300°C for 10 min, and then annealed at 500°C for 1 h in air ambiance. XRD results revealed that the undoped ZnO thin film exhibited preferential orientation along the (002) plane and ZnO thin films doped with Ga degraded the crystallinity. Both optical transmittances in the visible range and electrical resistivity of GZO thin films increased with increasing the dopant. In the present study, the 7 at.% Ga-doped ZnO thin film exhibited the best average transmittance of 90.5% and a resistivity of 2.0×10^3 Ω-cm.

10:20am **C2-1-10 Characteristics of Highly Transparent Conductive Ga-Doped ZnO on Polymer Substrates Prepared by Ion-Plating Deposition with DC Arc Discharge**, ***T. Yamamoto*** *(yamamoto.tetsuya@kochi-tech.ac.jp), A. Miyake, T. Yamada, H. Makino, N. Yamamoto*, Kochi University of Technology, Japan

Highly transparent conductive polycrystalline Ga-doped ZnO (GZO) films with a thickness of about 100nm prepared on cyclo-olefin polymer (COP) or glass substrates at various substrate temperatures below 90°C by ion plating with DC-arc discharge were investigated. A systematic study has been made of the influence of substrate temperature T_s. An increase in T_s resulted in a beneficial effect on the crystallinity, electrical conductivity and absorption coefficient in the visible (VIS) range regardless of the type of substrate. The analysis of the XRD patterns of the films showed that all polycrystalline GZO films on the two different substrates have a preferred orientation along the *c*-axis regardless of T_s. The crystallity of GZO/COP is lower than that of GZO /glass at any given T_s. The minimum resisitivity for GZO on glass and COP substrates was as low as 5.0μΩm and 5.8μΩm, respectively. The total light transmittance of all the GZO films on the two different substrates was more than 86% regardless of T_s. The optical absorption loss in the visible range decreased according in order of increasing Hall mobility with increasing T_s. All the GZO films were found to be compressively stressed. Analysis of calculated residual stresses in GZO films based on the biaxial stress model shows that the residual stresses in GZO films on glass substrates are a decreasing function of T_s, whereas the residual stresses are an increasing function of T_s for GZO films on COP substrates. This finding indicates that for the GZO films on COP substrates deposited at higher temperature, thermal stress is dominant.

10:40am **C2-1-11 Optical and Electrical Properties of Transparent Conductive Ga-Doped ZnO Thin Films**, ***H. Makino*** *(makino.hisao@kochi-tech.ac.jp), T. Yamada, N. Yamamoto, T. Yamamoto*, Kochi University of Technology, Japan

Ga-doped ZnO (GZO) is one of promising candidate as transparent electrodes in optoelectronic applications, such as flat panel displays and solar cells. It has been well known that electrical properties of GZO films strongly depend on its deposition parameters and conditions of post-deposition thermal annealing. In this paper, we studied optical absorption (OA) and photoluminescence (PL) of GZO films in order to explore mechanisms of change in electrical properties of GZO films. 150 nm thick GZO films were deposited on alkali-free glass substrates by an ion-plating with DC-arc discharge at a substrate temperature of 110 °C. During the deposition, high purity oxygen gas was introduced into the deposition chamber, and the oxygen flow rate was varied from 8 to 15 sccm. The minimum resistivity of 2.8 μΩm was obtained at the oxygen flow rate of 11 sccm. Carrier concentration monotonously decreased with increasing the oxygen flow rate. The OA spectra showed a fundamental optical gap in ultra violet region and a free-carrier absorption in the mid-infrared region. In addition, an absorption band in visible wavelength region was clearly observed for the GZO films deposited under the oxygen flow rate of 8 sccm . The absorption band decreased with increasing the oxygen flow rate. The absorption band is most probably due to intrinsic defects, like as interstitial Zn, oxygen vacancy or others in the GZO film caused by lacking of oxygen during the deposition. Post-deposition thermal annealing also decreased the absorption band. The intensity of the absorption band decreased with increasing thermal annealing temperature. We found that the evolution of absorption band showed some correlation with the decrease of carrier concentration. In PL spectra, we observed a broad emission band, which can be assigned as near band edge (NBE) emission. By the thermal annealing, the PL intensity decreased with increasing the annealing temperature. In addition, a deep level emission band was appeared in lower energy side of the NBE emission band after the annealing in air. It was suggested that several mechanisms to kill carrier in GZO films simultaneously contribute to the change of carrier concentration. It is crucial to control intrinsic defects in transparent conductive GZO films.

11:00am **C2-1-12 Effect of Organic-Buffer-Layer on Electrical Properties and Environmental Reliability of GZO Films Prepared by RF Plasma Assisted DC Magnetron Sputtering on Plastic Substrates**, ***T. Hinoki*** *(t-hinoki@oike-jp.com), C. Kyuhara, H. Agura, K. Yazawa,* Oike & Co., Ltd., Japan*, K. Kinoshita, K. Ohmi, S. Kishida*, Tottori University, Japan

ZnO thin films are expected as one of candidate transparent conductive oxide films alternative to indium tin oxide films. Considering an application for large size transparent electrode such as electronic display panels and solar panels, ZnO coated plastic sheets have an advantage of easily producing large area transparent electrodes by using a roll-to-roll mass production system. To prepare ZnO transparent conductive thin films on plastic sheets, a low temperature deposition at less than 100°C is required. Recently, we have reported on Ga-doped ZnO (GZO) thin films prepared by RF plasma assisted DC magnetron sputtering without intentionally heating substrate. In this study, we have attempted to deposit GZO thin films on polyethylene telephthalate (PET) sheets. Effects of organic-buffer-layer (OBL) formed between GZO films and PET substrates on electrical properties and environmental reliability of GZO films have been investigated.

GZO films were deposited by RF plasma assisted DC magnetron sputtering on OBL coated PET substrates, which ware not intentionally heated during the deposition. The reductive gas of Ar + H_2 (10%) was locally supplied just below the substrate. To generate RF plasma near a substrate, a 2.5-turns-coil was located between a target and a substrate. Several kinds of organic silicone were used as an OBL. The sheet resistance was measured by 4-prove method. To confirm an environmental reliability of GZO films, an accelerated aging test was performed under the storage condition at 60°C and relative humidity of 95% for 250 hours.

The resistivity of the GZO film prepared on the OBL-coated PET substrate is decreased to one half compared to that on the OBL-uncoated PET substrate. A moderate OBL thickness is 0.02 - 0.2 μm. The resistivity of the GZO film is decreased by providing the RF plasma, especially at the position facing the erosion area in the source target. A similar result has been obtained for GZO films on glass substrates. The total transmittance of the GZO film and the PET substrate is improved from 79% to 83% by installing the OBL. After the accelerated aging test, the sheet resistance maintains almost the same as the initial value for the GZO film on the OBL-coated PET substrate. Contrary, for the film prepared on the OBL-uncoated PET substrate, the sheet resistance increases by 10 times. The OBL is thought to play a roll of relaxing the stress between the GZO film and the PET substrate under high temperature and high humidity environment, and of suppressing the formation of crack in GZO films. One can be also thought that the OBL increases an adhesion strength between GZO films and PET substrates.

11:20am **C2-1-4 Synthesis and Characterization of 1-Phenyl-3-(4-phenyl-[1,2,3]triazol-1-yl)-4-Styryl-Azetidin-2-One Films for Light Emitting Applications**, ***A. Mahajan*** *(dramanmahajan@yahoo.co.in), V. Kumar, R.K. Bedi*, Guru Nanak Dev University, India

Triazole derivatives have attracted considerable interest in OLEDs because of their electron transporting as well as hole blocking and/or exciton confining properties. To improve the quantum efficiency and lower the operating voltage of OLEDs, a novel derivative of triazole namely 1-phenyl-3-(4-phenyl-[1,2,3]triazol-1-yl)-4-styryl-azetidin-2-one (TAZ) has been designed as an electron transporting material. This organic material has been synthesized by [2+2] ketene-imine cycloaddition reaction popularly known as Staudinger reaction of 1-azadiene with azidoketene to yield the desired compound, which is then subjected to Cu-catalyzed click chemistry with phenylacetylene in dichloromethane to yield the TAZ compound.

Thin films of TAZ have been prepared by vacuum evaporation technique onto glass substrate kept at different temperature under different experimental conditions. These films have been systematically studied for their structural, optical and electrical properties. X-ray diffraction and FESEM studies of these films show increase in crystallinity with increase in substrate temperature. The electrical resistance of these films are found to lie in 106-107 ohm at room temperature. Analysis of optical absorption measurements on these films indicate that the interband transition energies lies in 3.4-3.6 eV. These wide band gaps show that TAZ layers can work as hole blocking (HB) material in OLED.

11:40am **C2-1-8 Effect of Cationic Surfactant on the Sensing Behavior of Nanocrystallite CuO Films Deposited by Spray Pyrolysis**, ***R.K. Bedi***, Guru Nanak Dev University, India, *I. Singh (iqbalsgh@yahoo.com)*, Khalsa College, Amritsar, India

P-type nanocrystalline CuO thin films have been deposited by chemical spray pyrolysis from cupric nitrate trihydrate ($Cu(NO_3)_2.3H_2O$) solution in water with cetyltrimetylammonium bromide (CTAB) as cationic surfactant, at different substrate temperature of 300 and 400˚C. The films were studied by X-ray diffraction (XRD) to obtain the information about structural properties in detail, the grain size (D), strain and lattice parameter were calculated. In the X-ray diffraction profile of thin films, the more intense contribution is systematically the (002) peak in all the samples. The surface properties and elemental analysis were characterised using scanning electron microscopy and energy dispersive X-ray spectroscopy, respectively. The SEM micrographs showed different distribution of surface particles dependent on the substrate temperature and CTAB addition influences the shape, size with homogeneous distribution on the substrate. The sensitivity of the thin films was measured using two probe technique for ammonia vapors at room temperature. The presence of cationic surfactant resulting in an increase in the sensitivity of CuO thin film sensor for ammonia vapours at room temperature.

Carbon and Nitride Materials: Synthesis-Structure-Property Relationships
Room: Pacific Salon 3 - Session D2-1

Diamond and Diamond-Like Carbon Materials
Moderator: O. Shenderova, International Technology Center & Adámas Nanotechnology, Inc, R. Hauert, Empa

8:00am **D2-1-1 Synthesis, Properties, and Applications of Ultrananocrystalline Diamond (UNCD$^{®}$) Thin Films**, ***J.A. Carlisle*** *(carlisle@thindiamond.com)*, Advanced Diamond Technologies, Inc. **INVITED**

Like many other platform technologies, Ultrananocrystalline diamond has faced many hurdles on its way from the laboratory into products. In this talk I will highlight our efforts over the past several years to transfer the technology out of Argonne National Laboratory and into the real world. UNCD®, ADT's trademarked technology, spans a family of diamond materials that all share two attributes: THIN and SMOOTH. The critical value building exercise of developing and implementing a set of reproducible production processes to make UNCD films has resulted in ADT being able to launch three separate product lines (wafers, mechanical seals, and NaDiaProbes®) in the past 1-2 years into three very different markets. How ADT looks at wafer-scale production of UNCD-based MEMS devices going forward as well as our technology roadmap for UNCD-enabled products under development will be reviewed. Particular emphasis will be placed on the development of UNCD coatings and MEMS devices for bio-related applications.

8:40am **D2-1-3 HF-CVD of Diamond Coatings Onto Fluidized Bed Machined (FBM) CrN Interlayers**, *R. Polini, M. Barletta (barletta@ing.uniroma2.it),* Università di Roma Tor Vergata, Italy, *G. Cristofanilli,* Università di Roma Tor Vergata, Itlay, ***G. Rubino***, Università di Roma Tor Vergata, Italy

The deposition of diamond coatings onto Co-cemented tungsten carbide (WC-Co) substrates can be extremely troublesome as Co can catalyze the formation of graphitic carbon. CrN-based interlayers deposited by PVD-arc technique have been recently proposed to prevent the formation of graphitic carbon. CrN films act as physical (diffusion) barriers to the Co, interposing themselves between the underlying WC-Co and the growing diamond. Yet, the adhesion of diamond coatings onto CrN interlayers is still poorly investigated. In the present investigation, Fluidized Bed Machining (FBM) is applied to pre-treat CrN interlayers onto WC-Co substrates to promote the growth on them of highly adherent diamond coatings. During Fluidized Bed Machining (FBM), CrN interlayers are submitted to high speed impacts of loose abrasives. The action of their cutting edges is able to deeply change the starting morphology of the as-deposited PVD CrN interlayers, thus promoting the establishment of a highly corrugated surface on which to grow HF-CVD diamond coatings.

Growth, morphology, adhesion and wear resistance of the CVD deposited diamond coatings onto Fluidized Bed Machined (FBM) CrN interlayers were looked into and compared to diamond coated WC-Co substrates with untreated CrN interlayers or pre-treated with two-step chemical etching (Murakami's reagent and Caro's acid, MC-treatment). Fluidized Bed Machining proved to be an effective technique to tailor the surface morphology and roughness of CrN films deposited by PVD-arc technique, and was found to be very useful in improving the adhesion and wear resistance of CVD diamond onto CrN-interlayers.

9:00am **D2-1-4 Pretreatment of Cemented Carbides with Different Seeding Powders for Diamond Hot Filament CVD (HFCVD)**, ***C. Bareiss*** *(christian.bareiss@cemecon.de), W. Reichert, O. Lemmer*, CemeCon AG, Germany

Diamond deposition on cemented carbides is widely used to improve the lifetime of tools, blades and components for abrasive applications. These deposition processes are performed in CVD coating units. For better initial growth and a good adhesion of the deposited films to the cemented carbide, the substrate surfaces are seeded with diamond powders before deposition.

In this work 3 different diamond cluster sizes were used for the seeding pretreatment (0 – 4 nm, 0 – 250 nm, 0 – 500 nm). Diamond Hot Filament CVD (HFCVD) was carried out on polished tungsten plates to study the initial growth steps. Further on, cemented carbide substrates with different cobalt content (6 – 12 % Co) were coated to study the growth rate and adhesion of the deposited layers. For the 4 nm powder SEM pictures showed a closed diamond film on the polished tungsten plates after 12 min deposition time. With 250 nm pre-treatment the diamond film is not completely closed yet and with 500 nm powder only few diamond crystallites can be found on the surface.

The cemented carbides are chemically etched before deposition to remove the cobalt binder from the surface. After 12 min of diamond deposition we confirmed the initial growth results of the polished tungsten discs. The deposition rate and morphology in long time deposition processes is almost the same for all pre-treatment particle sizes. The adhesion of the diamond film in the blast wear test was the same for all powders on cemented carbides with low cobalt content (6 % Co). With higher cobalt content (10 % Co) the adhesion of the diamond film increase with the decrease of particle size in the seeding powder.

We attribute this to the faster covering of the surface with a closed diamond film at the beginning, which comes along with the following benefits:

- better interlocking of diamond with the cemented carbides due to a higher number of small diamond crystallites
- fast passivation of the cobalt phase in the cemented carbide, which means less interaction of cobalt with the gas phase in the deposition process

In this study we found, that the seeding cluster size before diamond deposition has enormous effect on the initial growth rate on polished and etched surfaces. Furthermore the adhesion of the deposited diamond film depends on the cluster size for high cobalt cemented carbides.

9:20am **D2-1-6 Applications of Nanodiamond and Onion-Like Carbon Particles in Composites**, ***G. McGuire*** *(gmcguire@itc-inc.org),* International Technology Center, *O. Shenderova,* International Technology Center & Adámas Nanotechnology, Inc, *S. Hens,* International Technology Center, *V. Kuznetsov,* Boreskov Institute of Catalysis, Russia, *M.G. Ivanov*, Ural State Technical University, Russia **INVITED**

Within the last few years world-wide interest in applications of nanodiamond particles has grown rapidly. Nanodiamond particles with the smallest monocrystalline size of about 4nm are produced by detonation of carbon-containing explosives, so called detonation nanodiamonds (DND). Numerous applications of DND are under development including high precision polishing; wear resistant additives to metal coatings; anti-friction additives to lubricants and oils; polymer nanocomposites and coatings with enhanced strength, impact resistance, and scratch resistance; nanocomposites with improved thermal stability and thermal conductivity; UV-protection coatings, sunscreens; seeding slurries for growth of CVD diamond films and many others applications. Also, DNDs serve as a source material for the production of onion-like carbon (OLC) by high temperature annealing of DND in an inert atmosphere. Recently it was demonstrated that OLCs are strong absorbers of electromagnetic (EM) radiation from the gigahertz, to terahertz, to visible spectral ranges, providing efficient EMI shielding. Several examples of applications under development at ITC and its collaborators using the modified/fractionalized DND will be discussed with major emphasis on applications of DND and OLC in composites. For example, it was demonstrated that nanodiamond particles in a polydimethilsiloxane matrix attain very pronounced photoluminescent when irradiated with a flux of MeV protons. This suggests application of the ND-polymer coatings as fluorescence-induced indicators of acquired proton dose, for example, by spacecraft. We will report on the fabrication of novel composites of carbon nanotubes incorporated into a nanodiamond matrix producing mixtures from nanocarbons that are complementary in chemical and mechanical strength and are expected to produce unique physical properties. Photonic structures made of DND as well as other applications will be also discussed. Results of tribological testing of stable colloidal dispersions of DND in polyalphaolefine (PAO) oil will be reported. DND-PAO colloids are transparent and have a specific amber color. The results of tribological tests from pure PAO oil and different formulations with DNDs demonstrated very significant improvements for all tribological characteristics for certain formulations. Effects of different parameters of the formulations on their tribological properties will be discussed.

10:00am **D2-1-8 Bi-Layer Diffusion Barrier Used to Optimized Diamond Deposit onto Cermets: A Proposal**, ***A. Poulon-Quintin*** *(a.poulon@icmcb-bordeaux.cnrs.fr), C. Faure, J.-P. Manaud*, CNRS, Université Bordeaux, ICMCB, Pessac, France

Thermo chemical computing validates the stability of different nitrides against Co, Mo, and methane up to 1150K, showing the highest chemical stability against carburization for ZrN and TaN under static conditions.

Single zirconium and tantalum nitrides layers have been sputtered onto WC-Co substrates as diffusion barriers and buffer layers under specific reactive sputtering conditions. To improve the nuclei density of diamond during CVD processing, a thin Mo extra layer has been added (<500 nm). Nano crystalline diamond has been grown under negative biased substrates.

After diamond deposition, a massive carburization of molybdenum and tantalum nitride is observable whereas zirconium nitride is not. Nevertheless, a small amount of cobalt has migrated through the ZrN layer. The better efficiency of the TaN layer to prevent diffusion of the Co element, leads to expect an increased adhesion of diamond on TaN-Mo bi-layer coating. A TEM study is done to better understand phenomena occurring at the interfaces during process.

10:20am **D2-1-9 Design of Interlayer Materials for Adhering Diamond Coating on Steel Substrates**, *Y. Li (yul088@mail.usask.ca),* ***Y. Tang***, University of Saskatchewan, Canada

Metallic and ceramic materials have been widely used as intermediate layers for diamond coating on various substrates to enhance diamond nucleation, growth and adhesion. Properties of diamond formed are strongly dependent upon the chemical nature, thickness, and complex reaction between the diamond-interlayer and interlayer-substrate interfaces. Steels are known as difficult-to-coat substrates for diamond, due to the low diamond nucleation density and low interfacial bonding strength. The interlayers in use are usually as thick as several micrometers. We will report on the successful application of ultrathin dual metal interlayers, to obtain continuous, dense and well adhering diamond coatings on stainless steels.

Applications, Manufacturing, and Equipment
Room: Pacific Salon 1 - Session G7

Advances in Industrial PVD & CVD Deposition Equipment

Moderator: R. Cremer, KCS Europe GmbH, K. Yamamoto, Kobe Steel Ltd.

8:00am **G7-1 Functional Nano Color Coatings: Basics, Preparation and Applications**, ***R.W. Domnick*** *(rdomnick@ara-coatings.de), M. Belzner*, Ara-Coatings GmbH & Co. KG, Germany **INVITED**

In the field of decorative coatings the technique of magnetron sputtering plays an important role: Since a couple of years a lot of different products like watches, jewelery, door latches and pens are color coated. For these coatings materials like ZrC_xN_y,TiAlCN or TiZrN were used.

Due to the fact that with these coatings the selection of different colors is limited, it is an interesting alternative to use interference based effects to generate a broad range of different, very strong colors. Interference based colors occur when thin layers of optically transparent materials are involved (e.g. oil drop on water, soap bubble,…).

With magnetron sputtering the controlled deposition of thin films with appropriate optical properties leads to brilliant colors. Nearly every color within the optical spectrum can be produced with this method.

Due to the fact that such Interference coatings consist of very thin layers their mechanical or chemical properties are very poor.

But for the most applications in the field of surface enhancement a good quality of the coatings is absolutely necessary. A solution for this could be the covering of the interference stack with a thick transparent protective topcoat. But with increasing thickness of the topcoat the brilliance of the interference color decrease.

In this work a new technology is presented – called "Aradierung$^{©}$" – which enables the production of brilliant Color Coatings with enhanced mechanical, chemical or thermal properties.

These brilliant color coatings consist of an adhesive layer, the color generating stack (2-4 thin layers) and the protective topcoat. The materials of the color coatings vary – depending on the desired color and the specific requirements. The topcoat can show good corrosion behaviour or wear resistance – or other features like an "Anti-Fingerprint" effect. This effect is based on the reduction of the contrast between the fingerprint and the surrounding area and make the fingerprint invisible.

The color coatings can be applied on metals, ceramics, glass and plastics. To reach the best results, the adaption and optimisation of the color coating stack on the given substrate is necessary.

In this paper different fields of applications are presented, examples are shown and their properties are discussed.

For the verification of optical properties Reflection Spectrometry and Ellipsometry is used; morphology and mechanical properties were analysed with SEM, XRD and Nanoindentation.

8:40am **G7-3 The New Platit Pi111 PVD Coating Unit**, ***B. Torp*** *(b.torp@platit.dk),* Platit Inc., USA, *T. Cselle, O. Coddet, A. Lümkemann, M. Morstein,* Platit AG, Switzerland, *P. Holubar, M. Jilek jr*, Pivot, Czech Republic

Flexible coating systems will only be integrated into proprietary production processes when they provide pre- and post-treatment of cutting edges and surfaces, stripping, cleaning, quality control systems and the system enables the deposition of conventional, e.g. TiN and AlTiN as well as high performance coatings, e.g. nanocomposites, oxides and DLC together with dedicated coatings for specific applications. We will give a short presentation of the turn-key Platit in-house coating systems.

We will introduce the new flexible PVD coating unit from Platit, the Pi111. It will be described in detail with emphasis on the upgradeability for DLC and Oxide/Oxynitride coatings and we will show our new coatings produced in this unit, the triple coatings, in particular DLC, oxynitride/oxide coatings and general triple coatings, a combination of nanocomposites and conventional hardcoatings in one.

As general triple coatings, we will focus on $nACRo^3$ and show results on drilling and reaming of cast iron and steels.

Finally we will talk about the new TiXCo coatings for hard milling and drilling including an example on dry hard finishing in steel 1.2080 with a hardness of 61HRC.

9:00am **G7-4 Characterization of Inductively Coupled Plasmas in a Commercial Etcher**, ***B. O'Shaughnessy****, S.H. Lee (shlee@utdallas.edu),* University of Texas at Dallas, *K.J. Park,* DMS, Korea, *C.W. Chung,* Hanyang University, Korea, *M.J. Kim, G.S. Lee*, University of Texas at Dallas

Plasmas of CHF_3/Ar, SF_6, and O_2 are characterized with the floating harmonic method, using a Wise probe system, under a variety of etching conditions in a commercial etcher made by Plasma-Therm. The floating harmonic method is a novel measurement technique for electron temperature and ion flux. The current of a 50 kHz sinusoidal voltage applied to the probe is measured continuously. These data then undergo a spectral analysis, and the ratio of first and second harmonics is calculated. From this ratio the plasma parameters can be calculated. Since the measurement technique relies only on high frequency currents, it is insensitive to contamination of the probe tip, providing a major advantage over the conventional Langmuir probe.

Characterization was performed under bias powers of 10-100 W and source powers of 200-900 W. Measurements were conducted at two different distances of samples to plasma source: 4 cm and 14 cm. Real time measurements of electron temperature and ion flux were recorded with dummy wafers and under actual etching of $SiO_{,2}$, Si_xN_y, and photoresist. Plasma parameters in the inductively coupled plasmas are largely independent of bias power, as would be expected. At very low source powers the plasma undergoes a transition to capacitive coupling. In the capacitively coupled plasma high electron temperatures combined with low ion fluxes are observed, and an increase in the effect of bias power can also be seen. Although more ions are generated in the bulk plasma at higher pressures, the ion flux to the substrate at higher pressure is reduced, due to the shorter mean free path of ions, which causes slower diffusion.

The effect of the distance of samples to the plasma source was investigated at distances of 4 cm and 14 cm. Ion fluxes at longer distance were much lower, due to longer diffusion distance to the sample surface. The transition from ICP to CCP also occurred at higher powers than at shorter distance. This results in many of the plasma conditions studied producing relatively unstable plasmas with large fluctuations in electron temperature.

When etching through SiO_2 and Si_xN_y films, the electron temperature and ion flux showed measurable changes dependent on the substrate material. This opens the possibility of using the Wise probe system for endpoint detection in certain etching processes. An increase in electron temperature over the course of oxygen cleaning can also be observed, which may also prove useful for the purpose of maintaining chamber conditions more efficiently.

9:20am **G7-5 Tungsten Carbide Coatings on New Coating Machine RS50**, ***A. Mueller*** *(arnd.mueller@oerlikon.com), M. Esselbach, H. Rudigier*, OC Oerlikon Balzers AG, Liechtenstein

Thin film tungsten carbide coatings are widely used in different applications to reduce wear and friction of components in sliding or rolling contact. In many cases these films are deposited by a PVD sputter process of tungsten carbide targets in a carbon gas containing atmosphere.

In this presentation the results of a statistical design of experiments for the performance optimization of a tungsten carbide layer will be presented. The influence of gas composition, target power and bias voltage on layer hardness, wear behavior, and coefficient of friction was examined. The measurement methods used are micro indentation, calo grinding and pin on disc test. In addition, the coatings have been analyzed by XRD and EDX measurements.

The experiments were carried out on the new coating machine RS50. The vacuum chamber of the RS50 allows a carousel diameter of 950mm and a loading height of 650mm. Its new flange concept gives a high flexibility and easily allows the implementation of new technologies. The RS50 coating machine will be presented also.

9:40am **G7-6 Deposition of Low-Stress Thick Coating by Modified Cathodic Arc Source**, ***K. Yamamoto*** *(yamamoto.kenji1@kobelco.com), S. Tanihuji, Y. Kurokawa, H. Fujii, S. Kujime*, Kobe Steel, Ltd., Japan

Cathodic arc evaporation process (AIP) is nowadays well established and widely adopted in many industries relating to thin film technology, mostly for triboligical applications such as cutting tools. As already well recognized, arc plasma is characterized by a high degree of ionization ratio up to 90 % which assures superior adhesion and densification of the deposited coating. However, due to the high ion ionization of evaporated species, relatively large residual stress is common for arc evaporated hard coatings. This often leads unwanted chipping of the coating at very sharp cutting edge and also prevents using of arc evaporated coating for the application that thick coating is requested.

Kobe steel has been a pioneer in realization of magnetically steered arc technology for industrial use and in this paper, a novel cathodic arc evaporation source and coating properties deposited by the new arc source is reported. A magnetically arc evaporation source based on a new magnetic field design was developed and deposition of various hard coating, such as TiN, (Ti,Al)N, (Al,Cr)N and (Ti,Cr,Al)N was conducted in an industrial coating system. (Ti,Al)N coating which is deposited by our conventional cathode, residual stress is up to a few GPa, whereas far less than 1 GPa is realized by using the new cathode. A very thick (Ti,Al)N coating up to 20 µm can be grown on very sharp edge of a cutting tool without any spontaneous failure of the coating. Surface roughness can also be decreased by using new cathode. Cutting test showed a significant enhancement in the tool life compared to a standard (Ti,Al)N coating with a few microns of thickness. Application of the new source to other coating systems will be reported.

10:00am **G7-7 Mechanical Properties and Structure Determination of High Al Containing $Al_{1-x}Ti_xN$ Coatings by High Ionization Plasma for Advanced Coatings**, ***J. Alami*** *(jones.alami@sulzer.com), G. Erkens, J. Mueller, P. Zaruba*, Sulzer Metaplas GmbH, Germany

High ionization plasma for advanced coatings (HIPAC) is a new adaptation of the high power pulsed magnetron sputtering technique, especially fitted for industrial applications. HIPAC is characterized by its highly ionized plasma including that of the sputtering gas. It is known that by using ions for bombardment of the substrate during the deposition process, coating properties such as density, surface smoothness, phase composition and structure can be altered even at low bias voltages. The use of a highly ionized sputter gas can, in addition, further decrease the substrate bias voltage, and minimize in such a way, the risk for arcing on the substrate. In the present work, high aluminum containing AlTiN coatings are deposited on steel substrates at a bias voltage of ~ 20 V. The mechanical properties and the structure of the coatings are investigated showing that the AlTiN coatings exhibit a high hardness and a low elastic modulus. Furthermore, the crystalline structure of the coatings is examined showing that for the same average power and depending on the target peak current, a number of crystalline structures and morphologies are possible. It is concluded that the HIPAC deposition technique can provide a new means to better control these properties and help, in such a manner, to design coatings for well-specified cutting and milling applications.

New Horizons in Coatings and Thin Films
Room: Royal Palm 4-6 - Session H2-2

High Power Impulse Magnetron Sputtering

Moderator: R. Bandorf, Fraunhofer IST, J.-E. Klemberg-Sapieha, Ecole Polytechnique de Montreal

8:00am **H2-2-1 Reactive HiPIMS Processes for Optical Coatings**, ***M. Vergöhl*** *(michael.vergoehl@ist.fraunhofer.de), S. Bruns, O. Werner, R. Bandorf, V. Sittinger, G. Bräuer*, Fraunhofer Institute for Surface Engineering and Thin Films, Germany **INVITED**

Reactive magnetron sputtering processes have gained considerable attraction for the production of optical coatings. Pulsed sputtering techniques allows the deposition of high quality optical materials at high deposition rates.

In recent years highly ionised pulse plasma processes (HIPP processes), especially high power impulse magnetron sputtering (HiPIMS) processes are under intensive investigation. Due to the high content of ions of the growing material available in the plasma significant modifications of the resulting film properties are expected and new and improved film properties may be realized.

Especially in reactive HiPIMS processes which is required for high rates and/or for deposition on larger scales, an active process control is required. Lambda-probes can be used as controlled parameters, but new parameters have to be found for the control values since standard power control may lead to different ionization values. In addition, it turned out that the control of the oxygen partial pressure is much more important to get high quality films than in standard pulsed magnetron sputter processes.

The deposition of isolating materials as Al_2O_3 or SiO_2, standard HiPIMS processes suffer from low process stability and arcing due to the low frequencies. We report about the development of a modified HiPIMS process wherewith mid-frequency pulses are superimposed to the low-frequency HiPIMS pulses. This yield a higher stability in the case of highly isolating oxides compared to the superposition of a DC signal.

In the present paper, the process modifications made up to now are presented and the properties of Al_2O_3, TiO_2 and ZrO_2 obtained with reactive HiPIMS sputtering will be shown.

8:40am **H2-2-3 Measuring the Negative Oxygen Ion Density in a Reactive Pulsed DC Magnetron**, *J.W. Bradley (j.w.bradley@liv.ac.uk),* ***R. Dodd****, S. You*, University of Liverpool, United Kingdom

Using laser photodetachment in conjunction with a Langmuir probe the absolute density of O- ions in the bulk plasma of a 100 kHz pulsed magnetron discharge have been determined at different times in the pulse. The average discharge power was 400 W and the total discharge pressure (90% argon + 10% oxygen) was 10 mTorr.

At a position 80mm from the target on the centreline of the discharge it was found that over the plasma on-time (5 microseconds duration) the negative ion density decreases from 10 to 8 x 10^{15} m^{-3}, while the electron density rises from 13 to 17 x 10^{15} m^{-3}, whereas during the plasma off-time the opposite is true, namely the negative ion density increases from 3.8 to 9.9 x 10^{15} m^{-3} as the electron density decreases from 23 to 15 x 10^{15} m^{-3}.

Negative O^- ion densities were also obtained at different positions on the centre line, during the on and off phases, with the negative densities increasing from 3 to 11 x 10^{15} m^{-3} as the distance from the magnetic null away from the target increases. The laser photodetachment measurements showed clearly that the O^- ions dominate over the O_2^- ions.

The maximum ratio of the negative ion to electron density, α was found to be 0.7, i.e. the plasma is weakly electronegative (α <1). These new results show that significant concentrations of negative ions are present in the bulk magnetron plasma when operated in argon-oxygen gas mixtures during pulsed DC sputtering. The possible effects of these ions on the growth of oxide thin films is discussed.

9:00am **H2-2-4 Process Control and Hysteresis in HIPIMS Reactive Deposition of Oxide Coatings**, ***G.T. West*** *(g.west@mmu.ac.uk), P. Kelly*, Manchester Metropolitan University, United Kingdom

High Power Impulse Magnetron Sputtering (HiPIMS) has shown important advantages over conventional DC and mid-frequency pulsed-DC magnetron sputtering, such as high ionisation fractions of the target material, low thermal energy flux delivered to the substrate and the formation of high quality coating structures. However, these benefits have been offset by some disadvantages - in particular low deposition rates, and problems with process control during reactive sputtering - which have inhibited the rate of commercial uptake of the technique.

Transparent conductive oxide (TCO) coatings are increasingly important to industry due to their incorporation into a range of commercial products such as display screen applications, microelectronics and photovoltaics. These coatings are commonly deposited via reactive magnetron sputtering and the inherent complications due to the hysteresis effect experienced when using conventional sputtering techniques are well reported. Recent studies suggest that when using HiPIMS, some TCO materials exhibit little or no hysteresis effect. This is highly significant to the control of the reactive sputtering process, but as yet the reasons for this modified behaviour have not been fully explained.

The deposition of TiO_2 and aluminium-doped zinc oxide films via a reactive HiPIMS process has been investigated in order to study hysteresis and its effect on process control. Various process control techniques including partial pressure control, plasma emissions and target voltage monitoring have been evaluated and compared for these systems. TCO coatings grown via these techniques have been analysed in terms of a number of properties for comparison.

9:20am **H2-2-5 Control of Reactive High Power Impulse Magnetron Sputtering Processes**, *M. Audronis (martyn@gencoa.com)*, Gencoa Ltd., *V. Bellido-Gonzalez, B. Daniel,* ***S. Williams***, Gencoa Ltd

High Power Impulse Magnetron Sputtering (HIPIMS) is a technologically important PVD process that is able to provide a highly ionised flux of sputtered species. It is thought to be particularly important for applications where there is a need to coat 3D features (e.g. vias and trenches in semiconductor industry). HIPIMS may have other added benefits, as compared to DC or medium frequency AC/pulse-DC magnetron sputtering, related to better coating structure-property relationship control through self-species plasma/ion assistance.

Many of the technologically important thin films (e.g. transparent conductive oxides, permeation barrier coatings, etc.) are sputtered from metal targets in a reactive gas atmosphere, usually argon + oxygen/nitrogen, i.e. using reactive magnetron sputtering to ensure industrially relevant coating deposition rates. Enhanced structure-property relationship control of these thin film materials is highly desirable; hence, it also is desirable to use HIPIMS in a reactive deposition mode. Preliminary trials of reactive HIPIMS however have indicated that the control of this process using conventional means is difficult. Thus, the application of reactive HIPIMS is rather limited and the potential benefits are not realised, especially in the areas where precise process control in a reactive environment is required.

The objective of this paper was to investigate reactive HIPIMS process and evaluate various control options. It was also an objective of this paper to present a recently invented PEM based sputtering control method developed specifically for reactive HIPIMS. Ti was chosen as a material for reactive HIPIMS in oxygen atmosphere. Performance of the new technique is compared to that of the conventional PEM, Penning-PEM and Lambda sensor based methods. Examples of controlled deposition processes are presented. It is shown that the new PEM process control technology allows operation of a stable reactive HIPIMS discharge anywhere within the hysteresis.

9:40am **H2-2-6 Modulated Pulse Power Sputter Deposition of Thick Tantalum Coatings**, ***W.D. Sproul*** *(bsproul@cox.net), J. Lin, J.J. Moore,* Colorado School of Mines, *S. Lee,* US Army ARDEC-Benet Labs, *J. Wang,* HeFei University of Technology, *B. Mishra*, Colorado School of Mines

Thick tantalum coatings up to 150 µm in thickness have been sputter deposited using Modulated Pulse Power (MPP) onto steel substrates. At an average target power of 4.5 kW, the average deposition rate was 13-14 µm/hr. Both the alpha and beta phases of Ta were deposited depending on the deposition conditions. The substrate bias has a pronounced effect on the crystalline structure of the coating. As the bias voltage was increased negatively from 0 to -70 volts, the crystalline phase changed from an all beta phase when the bias voltage was 0 volts, to a mixed alpha and beta phase when the bias voltage was in the range of -12 to -40 volts, and finally to an all alpha phase when the negative bias voltage was -50 volts or greater. With the substrates at floating potential, the working pressure determined the phase of the deposited coating. When the working pressure was increased from 2.3 to 4 mTorr, the crystalline phase of the coatings changed from pure alpha to a mixed alpha and beta phase, whereas at 5 mTorr and above the crystalline structure was the beta phase. The working pressure also affects the hardness of the deposited coatings. With the substrate bias set at floating potential, the hardness of alpha-Ta films deposited at pressures between 2-4 mTorr was 9-11 GPa, but for beta-Ta films deposited between 5-10 mTorr the hardness was in the range of 19-17 GPa.

10:00am **H2-2-7 A Comparative Study of Conventional Magnetron Sputtering, Plasma Enhanced Magnetron Sputtering (PEMS) and HIPIMS**, ***R. Wei*** *(ronghua.wei@swri.org)*, Southwest Research Institute, *S. Lee,* US Army ARDEC-Benet Labs, *W.D. Sproul*, Colorado School of Mines

In this paper, we present the results of a comparative study in which conventional magnetron sputtering, plasma enhanced magnetron sputtering (PEMS) and high power impulse Magnetron sputtering (HIPIMS) are used for depositing Cr filmes on carbon steel and stainless steel. DC magnetron sputter deposition has been studied for many years and it is also used in many commercial coaters. PEMS deposition using hot filaments-generated global plasma, in addition to the magnetron plasma, has shown advantages over conventional magnetron sputtering. HIPIMS has recently become a hot topic and also shown superior properties of the deposited films. In this study, these three techniques are compared using a planar geometry with a Cr target of 170 mm in diameter. The average power for the three sputtering techniques was set at 2 kW and the deposition was conducted in Ar and the deposition time was one hour. During the deposition using the HIPIMS, three tests were conducted. In the first test, no substrate bias was used. In the second tests, the substrate was biased with -40V, while in the third test not only was the substrate biased with -40V, but also a filament generate-plasma was used to further enhance the plasma production as in the PEMS process. After the depositions, SEM, XRD, AFM, microhardness, Rc indentation, and scratch test were performed to understand the coating properties and the differences. It has been observed that the deposition rates for the DC magnetron and the PEMS process are comparable, and are much higher than that from the HIPIMS, as observed by many other studies. The adhesion of the DC magnetron sputtered film is not as strong as those of the PEMS and HIPIMS deposited films. The surface roughness of the HIPIMS deposited films is lower than all other one prepared by DC or PEMS. The stress, however, of the HIPIMS deposited films are much higher than that from all others. Other properties are also studied and will be presented in the paper.

10:20am **H2-2-8 Effect of Substrate Bias Voltage on the Structure and Properties of ZrN Coating Deposited by HIPIMS Technology**, ***Y.P. Purandare*** *(y.purandare@shu.ac.uk), A.P. Ehiasarian, P.Eh. Hovsepian*, Sheffield Hallam University, United Kingdom

Monolayer ZrN coatings were deposited solely by the novel High Power Impulse Magnetron Sputtering (HIPIMS) technology in an industrial scale PVD machine (HTC-1000-4 target system). Coatings were deposited on 1 micron polished M2 High speed steel (HSS), 304 L Stainless steel (SS) specimens and on Si (100) specimens. Prior to deposition, HIPIMS plasma sustained on a Zirconium (Zr) target was utilised to pretreat the specimens.

Coatings were deposited at 400°C in a mixed N_2 and Ar atmosphere using 2 magnetrons in HIPIMS mode, at three different bias voltages keeping all other process parameters constant. The thicknesses of the coatings measured by the ball cratering technique were in the range of 1.84 µm, 1.96 µm to 2.13 µm at bias voltages of -95 V, -75 V and -65 volts respectively where the difference in thickness can be attributed to the re-sputtering effect. X-ray diffraction experiments on SS specimens revealed a dominating 111 texture for all three coatings irrespective of the bias voltage. Cross-sectional scanning electron microscopy revealed extremely dense coating structures at all bias voltages, similar to the transition zone structure (Zone T) reported by Thornton. The coatings appeared extremely smooth on the top and with no dome shaped structures often associated with low ion bombardment during deposition. HIPIMS pretreatment lead to high adhesion (LC) of the coatings to the substrate. A continuous ductile perforation of the coating was observed at progressive loads greater than 65 N however no spallation of the coating was observed up to loads of 100 N. High values of hardness (40.4 Gpa), Young's Modulus (424 Gpa) and compressive stress (11 Gpa) were recorded for coatings deposited at -95 bias voltage. The hardness and internal stress of the coating was found increasing with more negative bias voltages. All the coatings exhibited high dry sliding wear resistance (KC) in the range of 6 x 10-15 m3N-1m-1. Cross-sectional Transmission Electron Microscopy (TEM) and Atomic Force Microscopy (AFM) analysis has been used to study the effect of ion bombardment obtained from HIPIMS on the structure of the coatings.

10:40am **H2-2-9 Effect of Substrate Bias Voltage on the CrN Film Depositions Using Modulated Pulse Power Magnetron Sputtering**, *J. Lin, J.J. Moore (jjmoore@mines.edu), W.D. Sproul, B. Mishra,* Colorado School of Mines, ***S. Myers***, Colorodo School of Mines

Stoichiometric CrN coatings have been deposited by Modulated Pulse Power (MPP) magnetron sputtering in a closed field unbalanced magnetron sputtering system at different bias voltages from 0 to -150 V. During the depositions, the peak and mean substrate ion current densities (I_{sub}) increased rapidly from 67 to 250 mA/cm^2 and from 10 to 48 mA/cm^2 respectively as the substrate bias was increased from -20 to -50 V. A saturation of both the peak and mean I_{sub} was observed as the substrate bias was higher than -50 V. The applied substrate bias during the MPP CrN depositions also exhibited an effect on the number of arcs generated on the target surface. An increase in the number of arcs was observed as the substrate bias was increased from 0 to -50 V and above. The structure and properties of MPP CrN coatings deposited at different substrate bias voltages were characterized using x-ray diffraction, scanning electron microscopy, nanoindentation, microscratch and ball on disk wear tests. The effects of the substrate bias voltage on the deposition rate, residual stress, microstructure and mechanical and tribological properties of MPP CrN coatings will be presented.

11:00am **H2-2-10 Advances in HIPIMS$^+$ Deposited Hard Coatings for Tooling Applications**, *F. Papa (fpapa@hauzer.nl), R. Tietema, T. Krug,* ***I. Kolev***, Hauzer Techno Coating BV, Netherlands

The deposition of smooth, well adhered hard coatings such as Aluminum Titanium Nitride (AlTiN) and Chromium Nitride (Cr_xN) remains a challenge for industrial scale production. High Power Impulse Magnetron Sputtering (HIPIMS) technologies offer the ability to deposit such coatings but typically suffer from low deposition rates and problems with industrial reliability at high average powers. High Power Impulse Magnetron Sputtering Plus (HIPIMS$^+$) is a technology by which dense, defect free coatings can be deposited with high deposition rates. The superior performance of HIPIMS$^+$ deposited AlTiN coatings for several applications will be discussed. It will also be shown that there is potentially a significant increase in productivity for low temperature deposition (< 250°C) of Cr_2N and CrN.

11:20am **H2-2-11 High Rate Deposition of Thick Cr_2N and CrN Coatings using Modulated Pulse Power (MPP) Magnetron Sputtering**, ***J. Lin***, *J.J. Moore (jjmoore@mines.edu), W.D. Sproul (bsproul@cox.net), B. Mishra,* Colorado School of Mines, *S. Lee,* US Army ARDEC-Benet Labs, *J. Wang*, HeFei University of Technology

Modulated pulse power (MPP) is a variation of high power pulsed magnetron sputtering (HPPMS) that utilizes pulsed high peak target power density for a short period of time on the target to achieve the enhanced ionization of the sputtered material. By using relatively long pulses on the order of 1-3 ms and controlling the peak power/current of the pulse, it can achieve a high deposition rate while at the same time achieving a high degree of ionization of the sputtered material. Thick Cr_2N and CrN coatings with the thickness in the range of 10- 55 micrometer have been successfully deposited using MPP on various substrates (including AISI 304 stainless steel, 440C tool steel, Cement carbide, Cu, and Al-Si compound) in a closed field unbalanced magnetron sputtering system. High deposition rates of 15 and 10 μm per hour have been obtained for the Cr_2N and CrN depositions respectively using a 3 kW average target power, a 50 cm substrate to target distance and an Ar/N2 gas ratio of 3:1 and 1:1 respectively. The coatings exhibited excellent adhesion on various substrates in the scratch test. The thick Cr_2N and CrN coatings exhibited fully dense microstructure. The residual stress of the coatings was measured using XRD stress analyzer. Typical hardness values of the Cr_2N and CrN coatings deposited by MPP were 27.5 Gpa and 25.5 Gpa respectively. These thick coatings also exhibited good wear resistance and corrosion resistance.

11:40am **H2-2-12 Reactive High Power Impulse Magnetron Sputtering of Titanium Carbide Thin Films**, ***M. Samuelsson*** *(matsa757@ifm.liu.se),* Linköping University, Sweden, *H. Högberg, H. Ljungkrantz,* Impact Coatings AB, Sweden, *U. Helmersson*, Linköping University, Sweden

High Power Impulse Magnetron Sputtering (HiPIMS) is a technique known to ionize a substantial fraction of the sputtered species. This gives ideal condition for ion bombardment of the growing film and allows for favourable film properties even at low substrate temperatures or deposition conditions restricted by low temperature and low ion bombardment. Such characteristics allow for a wider range of choice of substrate materials as well as the possibility to obtain film properties normally requiring more demanding deposition conditions. The process has also proven suitable for reactive depositions of nitrides as well as for oxides, where for the latter; a diminished hysteresis effect is reported along with reduction in substrate temperature for α-alumina growth.

In the present work, we have investigated the reactive growth of TiC utilizing the HiPIMS and DC Magnetron Sputtering (DCMS) techniques in an ambience of argon and acetylene. All depositions were carried out in a high vacuum, commercial deposition system, InlineCoater™ at ambient temperature. To overcome the doubtfulness in comparing film properties for films grown by the two techniques all films were deposited using matched deposition rates of 35 nm/min for the metallic films. The bias voltage was -150 V, and C_2H_2 flows of 0 to 10 sccm resulted in films of varying film carbon content. XPS analysis reveals an increase in C content with C_2H_2 flow for DCMS, and a frequency dependent self limiting behaviour in the HiPIMS process, where for certain conditions the carbon content would not exceed that of titanium. Additionally, the tendency to form free carbon in the HiPIMS films was low, and found to occur at a significantly higher overall C content than found for DCMS. Contamination levels were found to be low (~2%) in the HiPIMS films but noteworthy higher for DCMS. As a possible consequence of the low presence of free carbon, XRD analysis indicated no reduction in grain size for the HiPIMS films, and a smooth densified morphology was observed by SEM. The aforesaid was in distinct contrast to the DCMS films, where the opposite behaviour was found. The resistivity for DCMS films was found to exceed 100 μΩm, being more than 50 times that of HiPIMS. The hardness values as determined by nanoindentation were found to be 6 and 23 GPa for DCMS and HiPIMS films respectively.

The pure Ti films grown by DCMS showed a typical low temperature 001 growth, while the HiPIMS Ti films displayed a transition from random to X-Ray amorphous growth with increased average power.

Coatings for Use at High Temperature
Room: Sunrise - Session A3-2

Thermal Barrier Coatings
Moderator: A. Bolcavage, Rolls-Royce Corporation, R.G. Wellman, Cranfield University, B.T. Hazel, General Electric

1:30pm **A3-2-1 Novel Thermal Barrier Coatings that are Resistant to Molten-Deposits Attack**, ***P. Padture*** *(padture.1@osu.edu)*, The Ohio State University **INVITED**

Although the use of thermal barrier coatings (TBCs) has allowed for higher gas-turbine engine operating temperatures, it is engendering new materials issues. Specifically, fine sand particles ingested by aero engines deposit on the hotter TBC surfaces as molten calcium-magnesium-aluminosilicate (CMAS) glass, which penetrates the TBCs resulting in loss of strain tolerance and premature failure of the TBCs. In the case of industrial engines, impurities such as fly ash from alternative fuels, accumulate as molten deposits on the hotter TBCs, degrading them. In this context, a generic approach for mitigating molten-deposits attack on TBCs is being developed. In this approach, the compositions of metastable TBCs are tailored such that the TBCs serve as chemical-species reservoirs. These then interact with the molten deposits rendering the deposits more benign. Examples of such novel TBCs are presented, together with strategies for testing the TBCs under molten-deposits attack and thermomechanical modeling of TBCs failure.

2:10pm **A3-2-3 Lifetime Approximation Based on Quantitative Microstructural Analysis for Air Plasma Sprayed Thermal Barrier Coatings**, ***C Bargraser***, *P. Mohan,* University of Central Florida, *K Lee,* Andong National University, Korea, *B.I. Yang, J.I. Suk, S.J. Choe,* Doosan Heavy Industries & Construction Co, Ltd., Korea, *Y. Sohn (ysohn@mail.ucf.edu)*, University of Central Florida

Air plasma sprayed (APS) thermal barrier coatings (TBCs) are widely used in gas turbine engines for thermal protection. In this study, we first examine the microstructural degradation of ZrO_2-8wt.%Y_2O_3 APS TBCs with a low-pressure plasma sprayed (LPPS) CoNiCrAlY bond coat coated on IN 738LC superalloy substrate. Furnace thermal cyclic tests were carried out at 1100°C in air with 1, 10, and 50-hr dwell period with 10-minute heat-up and 10-minute forced-air-quench. Extensive and quantitative microstructural analyses were carried out to document the population and growth of micro-cracks near the YSZ/bond coat interface, growth of thermally grown oxide (TGO), and depletion of Al-rich β-NiAl phase in the bond coat. Evolution in these microstructural features was correlated with furnace thermal cyclic lifetime of TBCs. Based on the results of microstructural analyses, a lifetime approximation model was developed based on the population and propagation of micro-cracks near the YSZ/bond coat interface. The lifetime approximation method was devised by modifying the Paris' Law that models the steady-state crack growth. Constants in the modified Paris' Law were determined based on quantified microstructure, and related to the parameters of furnace thermal cyclic test and specific characteristics of TBC degradation.

2:30pm **A3-2-4 Delamination-Indicating Thermal Barrier Coatings Incorporating Luminescent Sublayers Produced by Continuous Versus Interrupted Deposition**, ***J.I. Eldridge*** *(jeffrey.i.eldridge@nasa.gov),* NASA Glenn Research Center, *D.E. Wolfe*, Pennsylvania State University

Previous work has demonstrated that thermal barrier coating (TBC) delamination can be monitored by using near-infrared (NIR) and upconversion luminescence imaging of TBCs composed of yttria-stabilized zirconia (YSZ) incorporating a thin base layer co-doped with erbium and ytterbium (YSZ:Er,Yb). The co-doped base layer produces both NIR luminescence emission at 1550 nm and upconversion luminescence emission at 562 nm using 980-nm laser excitation. The progression of TBC delamination can be successfully monitored by the increase in luminescence intensity that accompanies the occurrence and propagation of buried delamination cracks during the course of thermal cycling. In the present work, a comparison is made between delamination-indicating TBCs that have been produced by electron-beam physical vapor deposition (EB-PVD) where the transition between the co-doped base layer and the thicker undoped overlayer was produced by either continuous or interrupted deposition. While both approaches produce sharp boundaries in dopant concentration, interrupted deposition produces a disruption of the TBC columnar growth while continuous deposition does not. Both the delamination-indicating performance and the cyclic life of the delamination-indicating TBCs prepared by these approaches are compared. In addition, the performance of hybrid delamination-indicating TBCs with a co-doped EB-PVD base layer and a plasma-sprayed undoped overlayer is investigated.

2:50pm **A3-2-5 Insight into the Phase Evolution of Thermal Barrier Coatings Upon Aging**, ***J.A. Krogstad*** *(jkoschmeder@engineering.ucsb.edu), R.M. Leckie, S. Kraemer,* University of California, Santa Barbara, *Y. Gao, D.M. Lipkin,* GE Global Research Center*, C. Levi*, Univrsity of California, Santa Barbara

The maximum operating temperature of conventional thermal barrier coatings is ultimately limited by the rate of evolution of the "non-transformable" t'-phase into a depleted tetragonal form susceptible to the monoclinic transformation upon cooling. Recent work has shown that the t'-phase decomposes rather rapidly into a modulated microstructure comprising a coherent array of yttria-rich and yttria-lean lamellae. These lamellae have compositions close to those expected from equilibrium considerations for the cubic and tetragonal phases, and hence the latter should be in principle transformable to monoclinic but constrained from doing so by the interleaving cubic phase. The onset of transformability requires coarsening of the microstructure and apparently loss of coherency. Hence, it is the rate of coarsening and not the initial decomposition that determines the durability of the coating in thermal cyclic environments. Understanding the formation and coarsening mechanisms of such a microstructure would provide valuable insight for increasing the durability of future thermal barrier coatings.

3:10pm **A3-2-6 A UK Study of Failure Mechanisms in EBPVD Thermal Barrier Coatings**, ***A. Atkinson*** *(alan.atkinson@imperial.ac.uk), D. Balint,* Imperial College, United Kingdom, *J.R. Nicholls*, Cranfield University, United Kingdom **INVITED**

This contribution describes a UK collaborative project aimed at improving understanding of the thermal cycling failure mechanisms of EBPVD YSZ TBCs on CMSX4 superalloys.

The project involved the production of TBCs with different bond coats and with controlled surface morphologies, measurement of residual stress in the alumina thermally grown oxide (TGO) using luminescence, and measurement of YSZ mechanical properties and inter-layer adhesion by indentation. Generation of stress in the coating on thermal cycling, and its relief by plastic deformation and fracture, was studied by finite element modelling (FEM). The bond coats studied include two beta-structured Pt-Al types and a gamma-gamma prime structure produced by Pt diffusion without aluminising.

Luminescence piezo-spectroscopy has been shown to be capable of high spatial resolution stress mapping through the YSZ and detecting imminent coating failure. The differences in failure mechanisms between the different bond coat types have been clarified and shown to be determined by the high temperature plasticity of the bond coat which leads to rumpling in the beta BCs. but not in the gamma-gamma prime BCs. The different failure modes lead to different optimum substrate surface finishes for the different BC systems. The YSZ top coat provides a large contribution to the driving force for spallation in all cases and its mechanical properties are shown to be sensitive to its complicated microstructure and changes with thermal cycling. Finally an indentation test has been developed that reveals qualitatively how the practical adhesion of the coatings degrade with cycling.

3:50pm **A3-2-8 The Evolution of Y_2SiO_5 EBCs Under Combined CMAS and Water-Vapor Exposure**, ***K. Grant*** *(kendra@engineering.ucsb.edu), S. Kraemer, G. Seward, C. Levi*, University of California, Santa Barbara

The volatilization of Si-based ceramic matrix composites CMCs in moisture-laden combustion environments is alleviated by the application of an enviromental barrier coating (EBC). In principle all current (e.g. BSAS) and prospective (e.g. Y_2SiO_5) EBC materials are susceptible to thermochemical degradation by Calcium-Magnesium Alumino-Silicate (CMAS) deposits. The mechanism involves dissolution of the parent EBC into the CMAS melt and re-precipitation as silicate reaction products. The primary reaction product for Y_2SiO_5 EBCs is $Ca_2Y_8(SiO_4)_6$O2 oxy-apatite in all cases, but the secondary products and morphological characteristics of the reaction zone depend on time, temperature and whether the environment is stagnant laboratory air or flowing H_2O/O_2. Mechanisms and their implications to the durability of EBCs in potential gas turbine applications are discussed in light of experiments exploring the effect of these variables (Work sponsored by the Office of Naval Research).

4:10pm **A3-2-9 Durability Assessment of Electrophoretically Deposited Environmental Barrier Overlay for Air Plasma Sprayed Thermal Barrier Coating**, ***P. Mohan*** *(pmohan@mail.ucf.edu), T. Patterson, Y. Sohn*, University of Central Florida

TBCs can degrade by a variety of mechanisms including by corrosive molten deposits that could arise from fuel impurities (sulfates and vanadates) and air-ingested CMAS (calcium magnesium alumino-silicate) sand deposits. Electrophoretic deposition (EPD), a versatile, cost-effective, scale-up ready technique, has shown promising ability to fabricate environmental barrier overlay of desired thickness, porosity and chemistry to protect TBCs from these degradation modes. In this study, two different overlay coatings, pure Al_2O_3 and Al_2O_3-MgO composite, were processed by EPD on air plasma sprayed (APS) Yttria Stabilized Zirconia (YSZ) TBCs. Optimizing the EPD process parameters such as DC voltage, deposition time and densification conditions (sintering temperature and time) has yielded a dense, continuous, and crack-free overlay of desired thickness. Dense Al_2O_3 and Al_2O_3-MgO composite overlay coatings processed by EPD on free-standing APS YSZ showed promising results in arresting molten deposit attack by V_2O_5 and CMAS at temperature ranging from 800°C and 1300°C. When exposed to V_2O_5 melt, TBCs protected by Al_2O_3-MgO composite overlay formed magnesium vanadates with high melting point ($Mg_3V_2O_8$ and $Mg_2V_2O_7$). Crystallization of CMAS melt due to enrichment of Al/Mg content was observed to arrest of melt ingression. In order to demonstrate the durability of protective EPD overlay for TBC applications, commercial APS TBCs (APS YSZ/LPPS MCrAlY/IN738 Superalloy) were coated with pure Al_2O_3 and Al_2O_3-MgO composite overlay coatings. The EPD-modified TBCs were subjected to 1-h thermal cyclic tests at 1100°C that consisted of 10 min heat up, 60 min hold at 1100°C and 10 min forced air quench. Adhesion and structural integrity of the EPD overlay were examined along with TBC failure by cross-sectional microstructural analysis. Results demonstrating the promising durability and the attributing mechanisms for superior resistance against molten deposit attack will be presented in detail.

4:30pm **A3-2-11 Simultaneous Synthesis of Thermal Barrier Coating Top Coat and Bond Coat by Spark Plasma Sintering**, ***J. Song***, Wuhan University of Technology, China, *K. Ma, J.M. Schoenung (jmschoenung@ucdavis.edu)*, University of California - Davis

As-fabricated thermal barrier coating (TBC) systems generally consist of a superalloy substrate, a MCrAlY bond coat (M=Ni, Co, Fe), and a ceramic (usually partially stabilized zirconia) top coat. The conventional methods for fabricating the two coating layers generally derive from thermal spray and physical vapor deposition techniques. The present work demonstrates the feasibility of using an innovative method for synthesizing both the top coat and bond coat simultaneously. The selected fabrication technique, Spark Plasma Sintering (SPS), provides not only the opportunity to synthesize both coatings at once, but the process is quite rapid and can produce dense layers. This paper describes the results for the application of this method to a ZrO_2 top coat with a NiCrAlY bond coat on a Ni base Hastelloy X substrate. Select variations in densification parameters are considered. The resulting multi-layer system is characterized with optical microscopy, scanning electron microscopy (SEM), Energy-Dispersive X-ray analysis (EDAX) and X-ray Diffraction (XRD).

Hard Coatings and Vapor Deposition Technology
Room: Town & Country - Session B5-2

Properties and Characterization of Hard Coatings and Surfaces

Moderator: M. Fenker, FEM Research Institute, Y.W. Chung, Northwestern University, G. Abadias, University of Poitiers

1:30pm **B5-2-1 Transition Metal Nitride-Based Complex Coatings: Kinetic and Thermodynamic Effects Resulting to Ternary Films or Nanocomposites**, ***P.A. Patsalas*** *(ppats@cc.uoi.gr)*, University of Ioannina, Greece, *G. Abadias*, University of Poitiers, France, *G. Matenoglou, L.E. Koutsokeras*, University of Ioannina, Greece **INVITED**

Nitrides of the group IVb-VIb transition metals have been well known for their unique combination of exceptional mechanical and electrical properties sharing high hardness values and electrical conductivity. Ternary transition metal nitrides (TMN) have lately gained special attention (with $Ti_xZr_{1-x}N$ being the most widely studied) in an effort to improve further these properties. Another pathway in tailoring the structure and properties of TMNs is by alloying with noble metals (Cu, Ag), which do form bonds with the transition metal but not with N. In this case nanocomposite films are produced.

In this work we present a comparative study of a very wide range of ternary transition metal nitrides of the form: $Ti_xMe_{1-x}N$ (Me=Zr,Hf,Nb,Ta,Mo,W) and $Ta_xMe_{1-x}N$ (Me=Zr,Hf,Nb,Mo,W) over the whole x range (0<x<1) grown by Pulsed Laser Deposition (PLD), Dual-Cathode Confocal Magnetron Sputtering (MS) and Dual Ion Beam Sputtering (DIBS). The density, chemical composition and structure are investigated using X-Ray Diffraction and Reflectivity (XRD/XRR), *in-situ* Auger Electron Spectroscopy (AES) and Electron Energy Loss Spectroscopy (EELS). We study the stability of the rocksalt structure in all these films using and map the lattice constant determined from XRD and *ab-initio* calculations. We consider the electron hybridizations and the bond nature of the ternary nitrides based on the *ab-initio* calculation results. Despite the possible different valence electron configuration of the constituent elements, (e.g. Ta-d^3s^2 and Ti-d^2s^2), we show that TMNs are completely soluble to each other due to the hybridization of the *d* and *sp* electrons of the metals and N, respectively. Optical absorption bands are manifested due to the N-*p*→Me-*d* interband transition and the t_{2g}→e_g transition due to splitting of the metals' *d* band, proving the partial ionic character of the bonds in TMNs. The texture development mechanisms are considered and a critical comparison of ternary films grown by different techniques is presented. The key thermodynamic and kinetic factors that determine the structure of such films are investigated.

Finally, we consider the growth of Ti-Cu-N nanocomposites by PLD and MS. We investigate the kinetic and energetic effects that determine the microstructure and the atomic configurations in the films; we identify the conditions for forming intermetallic phases within the nanocomposite and study the bonding and coordination number of the atoms at the interfaces.

2:10pm **B5-2-3 Thermal Stability of Arc-Evaporated $Nb_{1-x}Al_xN$ Hard Coatings**, ***R. Franz*** *(robert.franz@unileoben.ac.at)*, Montanuniversität Leoben, Austria, *M. Lechthaler*, OC Oerlikon Balzers AG, Germany, *C. Polzer*, Plansee Composite Materials GmbH, Germany, *C. Mitterer*, Montanuniversität Leoben, Austria

Ternary MeAlN hard coatings, especially TiAlN and CrAlN, have been intensively studied during the past 20 years. Due to the incorporation of Al into the face-centered cubic crystal lattice, superior mechanical properties and improved oxidation resistance were obtained. Recently $Nb_{1-x}Al_xN$ hard coatings were successfully synthesised by cathodic arc-evaporation and analysed as to their crystal structure, mechanical properties and oxidation resistance. Coatings with the face-centered cubic structure of δ-NbN generally present a higher hardness, whereas the onset temperature for oxidation rises with increasing Al content regardless of changes in crystal structure. However, these coatings are metastable and decomposition occurring at elevated temperatures might limit the applicability or, on the other hand, could be beneficial if hardness enhancing effects take place. The aim of the present work was, therefore, to investigate the thermal stability of $Nb_{1-x}Al_xN$ hard coatings and its influence on the mechanical properties. All coatings were deposited in an Oerlikon Balzers arc-evaporation system using powder-metallurgically prepared NbAl targets with different Al to Nb ratios. X-ray diffraction measurements of vacuum annealed samples revealed first changes in the crystal structure of coatings with high Al contents, i.e. with the wurtzite structure of AlN, at 1000°C. The face-centered cubic configuration is stable at temperatures exceeding 1000°C and no significant change in hardness could be observed in nanoindentation measurements with values in the range of 30-32 GPa. The change in crystal structure for the high Al containing coatings is associated with a reduction in hardness from ~25 GPa at room temperature to ~20 GPa at 1000°C.

2:30pm **B5-2-5 Influence of Zr on Structure, Mechanical and Thermal Properties of Ti-Al-N Thin Films**, ***P.H. Mayrhofer*** *(paul.mayrhofer@unileoben.ac.at), L. Chen, D. Holec*, Montanuniversität Leoben, Austria, *Y. Du*, Central South University

Ti-Al-N thin films are widely used for various applications where hard, wear and oxidation resistant materials are needed. To meet the ever growing industrial demand of increased performance, quaternary or multinary Ti-Al-N based thin films are developed. Here, we discuss the structure, mechanical and thermal properties of stoichiometric $Ti_{1-x-z}Al_xZr_zN$ coatings as a function of the ZrN mole fraction z up to 0.17 and the AlN mole fraction x up to 0.6. These coatings, deposited by unbalanced dc magnetron sputtering exhibit a single phase cubic structure (NaCl-type). This is in agreement to *ab intio* calculations suggesting a transition from cubic to wurtzite structure $Ti_{1-x-z}Al_xZr_zN$ at x ~0.62 for a ZrN mole fraction z of ~0.15. With increasing z from 0 to 0.05 to 0.17 while keeping x at ~0.5, the hardness increases from 32.7 to 38.1 GPa and then slightly decreases to 36.7 GPa, and the lattice parameter *a* increases from 4.18 to 4.22 to 4.24 Å, respectively. The latter are comparable to *ab initio* obtained *a*-values of 4.18, 4.21, and 4.21 Å for cubic $Ti_{1-x-z}Al_xZr_zN$ with x = 0.5 and z = 0, 0.055, and 0.11, respectively. Differential scanning calorimetry and thermo gravimetric analyses in inert and ambient atmosphere indicate an increase in thermal stability of Ti-Al-N coatings by alloying with ZrN. Consequently, also the formation of stable wurtzite AlN during annealing of cubic $Ti_{1-x-z}Al_xZr_zN$ is shifted to higher temperatures from ~1100 to 1300°C when increasing the ZrN mole fraction z from 0 to 0.17 while keeping x at ~0.5.

2:50pm **B5-2-6 Incorporation Effects of Si in TiC_x Thin Films**, ***O. Tengstrand*** *(olote@ifm.liu.se),* Linköping University, Sweden, *N. Nedfors,* Uppsala University, Sweden, *A Flink,* Impact Coatings AB, Sweden, *A. Andersson,* ABB AB, Corporate Research, Sweden, *H. Högberg, H. Ljungkrantz,* Impact Coatings AB, Sweden, *U. Jansson,* Uppsala University, Sweden, *P. Eklund, L. Hultman*, Linköping University, Sweden

TiC coatings are technologically important materials given their high hardness and good wear resistance. Addition of Si has been seen as a promising way to further improve the properties of TiC_x. For example Ti-Si-C nanocomposites have been demonstrated as suitable coatings in electrical contacts [1-2]. However, to develop multifunctional Ti-Si-C coatings requires increased understanding on how Si is incorporated in the NaCl-structure TiC_x phase as well as how Si segregates to form a composite material at low temperatures. In this study we investigate these phenomena by growth of Ti-Si-C thin films using low temperature deposition by dc magnetron sputtering. The effect on microstructure, mechanical and electrical properties was studied by incorporating different quantities of Si in crystalline TiC_x thin films. The Ti-Si-C films were deposited onto Al_2O_3 (0001) and Si (100) substrates kept at 350°C. During the process three elemental targets were used in an Ar discharge with an Ar pressure of 4 mTorr. XRD results show that the growth of pure TiC_x onto Al_2O_3 was epitaxial. By increasing the Si content from 5 to 20 at.%, the structure of the films becomes nanocrystalline. SEM reveals a segregation of Si on the surface. Initial TEM results shows that the epitaxial growth is retained up to approximately 50 nm in films containing 5 at.% Si, while thicker films exhibit nanocolumnar grains.

[1] Eklund,P., Surface Engineering, 2007, 23, 406

[2] Eklund,P., et al. J. Vac Sci Technol B, 2005, 23, 2486

3:10pm **B5-2-7 Texture Effect on the Hardness Enhancement of Nanocomposite Ti-Si-N Thin Films Using Reactive Magnetron Co-sputtering**, *C.-K. Chung (ckchung@mail.ncku.edu.tw),* ***S.-C. Chang****, J.J. Jhu, T.-S. Chen, B.-H. Wu*, National Cheng Kung University, Taiwan

The nanocomposite Ti-Si-N thin films were prepared by reactive magnetron co-sputtering system. The texture effect on the hardness enhancement of Ti-Si-N films at different N_2 flow rates ($FN_2\% = FN_2$ / ($Far+FN_2$)) of 3-20 % and titanium (Ti) power of 75-200 W were investigated. The thickness, microstructure, morphology, chemical composition and mechanical properties of films were characterized by alpha-stepper profiler, grazing incidence X-ray diffraction (GIXRD), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and nanoindenter, respectively. GIXRD patterns revealed that nanocomposite Ti-Si-N thin films at constant 100 W Ti and 100 W Si have a broad diffraction peak for the quasi-amorphous microstructure with nanocrystalline grains embedded in an amorphous matrix at 3 FN_2%, then high crystallization with multiple diffraction peak at 5 FN_2%, but the reduced peak intensity at 7 FN_2% and even to form amorphization of Ti-Si-N films without peak at high 10-20 FN_2%. The hardness of Ti-Si-N films was concerned with crystallization behavior. They are 18.10, 21.52, 20.42, 17.84 and 15.72 Gpa for Ti-Si-N films at 3, 5, 7, 10 and 20 FN_2%, respectively. Based on the high-hardness Ti-Si-N at constant 5 FN_2%, increasing Ti power from 75 W to 200 W could enhance the hardness from 18.95 Gpa to 31.97 Gpa. GIXRD patterns also show the highest hardness Ti-Si-N film has the strongest diffraction peak intensity. The main diffraction peaks were from crystalline TiN(111), (200) and (220) planes. The preferred orientation in TiN crystallites was along (200) normal with highest intensity. The degree of preferential orientation could be quantitatively represented through a coefficient of texture T_{hkl}, defined as

$$T_{hkl} = [I_m(hkl)/I_0(hkl)]/\{ 1/n * \text{sum } [I_m(hkl)/I_0(hkl)]_{1..n}\}$$

where $I_m(hkl)$ is the measured relative intensity of the reflection from the (hkl) plane, $I_0(hkl)$ is that from the same plane in a standard reference sample. In this study, n=3 for (111), (200) and (220) diffraction planes. In case of extremely preferential orientation, $T_{hkl} = 3$ while that for the random one, $T_{hkl} = 1$. From calculated results, the hardness over 21GPa had T_{200} larger than than 1.5. The highest hardness of 31.97 Gpa at Ti 200 W, Si 100 W and 5 FN_2% was corresponding to T_{200} of 1.954. The amount of grains grown along the textured orientations play a significant role on the hardness enhancement of Ti-Si-N films.

3:30pm **B5-2-8 Raman Spectroscopy Investigations of CVD Hard Coatings in the Ti-B-C-N System**, ***I. Dreiling*** *(ines.dreiling@uni-tuebingen.de),* University of Tuebingen, Germany, *D. Stiens,* Walter AG, Germany, *T. Chassé*, University of Tuebingen, Germany

Hard coatings in the Ti-B-C-N system possess very interesting properties for cutting applications. They combine the advantages of TiCN with the potential of improved wear resistance due to increased coating hardness.

A series of $TiB_xC_yN_z$ (x+y+z=1) coatings deposited on cemented carbide by chemical vapor deposition (CVD) has been investigated. The choice of precursors (CH_4/CH_3CN) and deposition temperature (850-1000°C) influenced the microstructure, crystallinity, microhardness and chemical composition. The B:C:N ratio could easily be changed by varying the gas precursor flow rates in the CVD process.

Laser Raman Spectroscopy was used to study the coatings since it has been shown to be a very sensitive technique regarding composition changes. Even small changes in the B:C:N ratio resulted in systematical shifts of the Raman peaks.

Low-boron containing coatings are known to possess improved thermal stability. Therefore, Raman spectroscopy was further used to investigate the oxidation resistance of Ti-B-C-N coatings in comparison with TiCN. Depending on the annealing temperature, different oxidation products like anatase and rutile could easily be distinguished.

3:50pm **B5-2-9 High Oxidation Resistance and Phase Stability of Cr-Si-O-N Coatings**, ***L. Castaldi*** *(lorenzo.castaldi@empa.ch),* Empa, Switzerland, *D. Kurapov, A. Reiter,* OC Oerlikon Balzers AG, Liechtenstein, *V. Shklover,* ETH, Switzerland, *P.S. Schwaller, J. Patscheider*, Empa, Switzerland

Cr-Si-O- N hard coatings 5 micrometer thick, with excellent oxidation resistance, phase and nanocrystalline stability were deposited by reactive arc evaporation on onto cemented carbide substrates . The systematic variation of the O_2/N_2 flow ratios resulted in a oxygen atomic concentration $C_{O2} = O/(N + O)$ between 0 and 100 at. %. For $C_{O2} < 80$ % the films exhibit a cubic fcc crystallographic structure, while at higher oxygen content the structure of the samples is rhombohedral. The crystallite size of about 20 nm remains approximately constant for the cubic Cr-Si-O-N phase in the 0 – 80 % C_{O2} range. An enhancement of a (002) preferred orientation is observed for samples with the fcc structure with increasing the oxygen concentration. The progressive decrease of the stress-free lattice parameter of the films with the cubic structure with increasing oxygen content suggests the formation of a $Cr_{0.92}Si_{0.08}O_xN_{1-x}$ solid solution. The microstructure of the samples, studied by scanning electron microscopy (SEM), is dense with smooth fracture faces for all samples. The hardness H of the coatings increases with increasing oxygen content up to a value of 27 GPa for $C_{O2} = 44$ %. Higher oxygen contents result in a reduced hardness of the coatings. Conversely, the elastic modulus E decreases with increasing C_{O2}. As a consequence, the coatings exhibit a resistance to plastic deformation H^3/E^2 up to 0.19 for $C_{O2} = 44$ %. X-ray powder diffraction (XRD) studies were performed in situ at high temperatures up to 1000°C, in high-vacuum (HV) and in air. In general, the crystallite growth, occurring at elevated temperatures both in HV and in air, is hindered considerably by the presence of oxygen and silicon. The grain growth is hardly observable up to 1000°C. The Cr-Si-O-N coatings with the cubic structure, annealed both in HV and in air, provide an exceptional thermal stability and oxidation resistance, with no evidence of oxidation or the formation of the Cr_2N phase up to 1000°C.

4:10pm **B5-2-10 A Spectroscopic Scanning of Magnetron Sputtered FeSiN Thin Films: Variations of the Nanostructure Induced by the Deposition Parameters**, ***A. Mège-Revil****, J.F. Pierson (Jean-Francois.Pierson@mines.inpl-nancy.fr), J.Ph. Bauer*, Ecole des Mines de Nancy, France

The recent discovery of the metastable γ’’’-FeN phase has opened a new field of investigation for the thin films community. Indeed, this phase crystallizes with the same cfc structure as TiN and CrN. However, the literature also reports the existence of another cubic phase with a ZnS-like structure: γ’’-FeN. Recently, we succeeded in the magnetron sputtering deposition of γ’’’-FeN free from its cubic-centred twin. By introducing silicon, the formation of a nanocomposite structure can be expected.

This study is focused on the evolution of the structure of γ’’’-FeN thin films as a function of the amount of silicon introduced. Within this objective, thin coatings were deposited on glass, mirror-polished silicon and steel substrates by magnetron co-sputtering of distinct iron and silicon targets. The films were then analysed by means of various spectroscopic measurements. A large range of wavelengths was used in order to register information on every aspect of the structure, from infra-red to gamma rays.

FTIR spectroscopy gave information on the linking bonds inside the material, showing proofs of Si-N bondings. Shifting in UV-visible spectra traduced the disturbances in the grains induced by the introduction of silicon. X-ray diffractograms showed only peaks of γ'''-FeN whatever the Si content. EDS measurements indicated that the silicon content was proportional to the current applied on the Si target and was ranging between 0 and 13 at. %.

Finally, the structure was assessed by Mossbaüer spectroscopy in order to evaluate the chemical environment of iron atoms, and thus the main locations of the Si atoms in the complex FeSiN nanostructure.

4:30pm **B5-2-11 Characteristics of Pulsed DC Reactive Magnetron Sputtered Nanocomposite Cr-Zr-N and Cr-Zr-Si-N Thin Films**, *S.-T. Chang,* Tungnan University, Taiwan, *J.-W. Lee (jefflee@mail.mcut.edu.tw),* Mingchi University of Technology, Taiwan, *C.-H. Chien, J.-J. Chen, S.-S. Ting,* Tungnan University, Taiwan, *L.-C. Chang,* Mingchi University of Technology, Taiwan, *C.-J. Wang,* ***S.-T. Chang***, National Taiwan University of Science and Technology, Taiwan

The nanocomposite Cr-Zr-N and Cr-Zr-Si-N thin films with various Zr contents have been deposited by a bipolar asymmetric pulsed DC reactive magnetron sputtering system. The Cr-Zr-N and Cr-Zr-Si-N thin films with Zr contents ranging from 1.5 to 15 at.% were achieved. The structures of coatings were characterized by XRD. The surface and cross sectional morphologies of thin films were examined by scanning electron microscopy (SEM) and transmission electron microscopy (TEM), respectively. The surface roughness of thin films was explored by atomic force microscopy (AFM). The hardness, elastic modulus and fracture toughness were evaluated by a nanoindenter and microhardness tester, respectively. The electrochemical test in 3.5 wt.% NaCl aqueous solution was also conducted to evaluate the corrosion performance of each coating. The microstructures of coatings were influenced by the Zr content. In general, the corrosion resistance of coatings was improved by the addition of Si and increased with increasing Zr content.

4:50pm **B5-2-12 Structure and Property of Nanocrystalline ZrN$_x$O$_y$ Thin Film: Effect of Oxygen Content and Film Thickness**, ***K.-C. Lan*** *(loocmit@gmail.com), J.-H. Huang, G.-P. Yu*, National Tsing Hua University, Taiwan

The main purpose of this research was to investigate the effect of oxygen content and film thickness of zirconium oxynitride (ZrN$_x$O$_y$) on the structure and properties. By introducing the oxygen flow during coating, ZrN$_x$O$_y$ thin films shows good mechanical properties, chemical inertness, and have various colors. ZrN$_x$O$_y$ thin films were deposited on P-type Si(100) wafer using hollow cathode discharged ion-plating (HCD-IP) by changing O$_2$ flow rate from 0 to 8 sccm and deposition time from 14 to 56 min. Effect of thickness and other composition, structure, and properties of ZrN$_x$O$_y$ thin films were characterized. The thickness of ZrN$_x$O$_y$ films, measured by scanning electron microscopy, increased with increase of deposition time, and increased with increase of oxygen flow rate. Phase separation of ZrN$_x$O$_y$ to ZrN and monoclinic ZrO$_2$ was identified by X-ray diffraction pattern when the oxygen content was higher than 11 at.%. Hardness of ZrN$_x$O$_y$ thin films increased with increasing thickness and packing density of film and with crystallinity of ZrN as 0 and 5 sccm O$_2$ flow rate. No significant change of the overall and ZrN residual stress with thin thickness was found while they were decreased with the decrease of oxygen content. The resistivity of ZrN$_x$O$_y$ thin films increased with decreasing thickness.

Fundamentals and Technology of Multifunctional Thin Films: Towards Optoelectronic Device Applications
Room: Royal Palm 1-3 - Session C2-2

Thin Films for Active Devices and Microstystems

Moderator: T. Miyata, Kanazawa Institute of Technology, N. Drolet, Konarka

1:30pm **C2-2-1 Investigation on Post-Deposition Annealing of Amorphous Indium-Zinc-Oxide Thin-Film-Transistors**, ***W.-F. Chung***, National Chiao-Tung University, Taiwan, *T.-C. Chang (tcchang@mail.phys.nsysu.edu.tw),* National Sun Yat-Sen University, Taiwan, *H.-W. Li,* National Chiao-Tung University, Taiwan, *Y.-C. Chen,* National Sun Yat-Sen University, Taiwan, *T.-Y. Tseng, Y.-H. Tai*, National Chiao Tung University, Taiwan

In this paper, the influence of post-deposition annealing conditions on sputtered amorphous indium zinc oxide thin film transistors (a-IZO TFTs) are investigated. From literature, the portion of oxygen vacancies (V$_o$) in amorphous phase and the Zn-O bonding in crystalline phase directly affect the electrical characteristics of ZnO-based device. Also, the threshold voltage and the mobility were examined at increased annealing duration. In addition, X-ray Photon-emission Spectra (XPS) analysis was used to distinguish the Zn-O bonds and V$_o$ after prolonging annealing time.

1:50pm **C2-2-3 Leakage Current and Dielectric Constant Dependencies on Single and Double Layer of Oxides in MOS Structure**, *I. Banerjee (indranibanerjee@bitmesra.ac.in), P. Laha, A. Bihari Panda,* Birla Institute of Technology, India, *B. Saha, Chakraborty,* Saha Institute of Nuclear Physics, India, *P.K. Barhai,* ***Mahapatra***, Birla Institute of Technology, India

Metal/Oxide layers of Al/Al$_2$O$_3$, Al/TiO$_2$ and Al/Al$_2$O$_3$/TiO$_2$ were deposited on silicon substrate to make Metal/Oxide/Semiconductor (MOS) structures using RF Magnetron Sputtering system. The thickness (40 ± 5 nm) of the oxide layer was kept constant. Performance of MOS structure depends on leakage current & dielectric constant of the oxide layer. The leakage current of these Metal/Oxide/Semiconductor (MOS) structure was investigated using I-V characteristic. It was observed that the leakage current density was maximum for Al/TiO$_2$/Si (~ 7.4 X 10^{-8} amp/cm^2) and minimum for Al/Al$_2$O$_3$/Si (~ 1.02 X 10^{-8} amp/cm^2), whereas for Al/Al$_2$O$_3$/TiO$_2$/Si compensated to ~1.12 X 10^{-8} amp/cm^2 at 1 Volt. The dielectric constant of the multilayers was measured by C-V analyzer. The dielectric constant increased from 10 for Al/TiO$_2$/Si and 4 for Al/Al$_2$O$_3$/Si to 40 for Al/Al$_2$O$_3$/TiO$_2$/Si at 1 Volt bias voltage. Variations of the leakage current density were due to band gap variation of the deposited layers and pinning of the Fermi level of the multilayer. The interdiffusion of the two layers at the interface (heterojunction) was responsible for this pinning of Fermi level. Secondary Ion Mass Spectrometry (SIMS) was employed to probe in-depth elemental distributions in the individual layers and intermixing of the layers across the interfaces. The interface broadening in SIMS depth profiles gave a measure of the intermixed layer thickness. The chemical composition and band gap of the deposited oxide layers were characterized by X-ray photoelectron spectroscopy (XPS) and UV-Visible spectroscopy, respectively. It was observed that Al/Al$_2$O$_3$/TiO$_2$/Si is a promising grown hetero-structure with high dielectric constant and less leakage current for fabrication of MOS devices.

2:10pm **C2-2-4 Dielectric Properties of Sc$_x$Al$_{1-x}$N Thin Films Deposited by Dual Reactive DC Magnetron Sputtering**, ***A. Zukauskaite*** *(agne@ifm.liu.se), G. Wingqvist, F. Tasnádi, J. Birch, L. Hultman*, Linköping University, Sweden

Wurtzite-structure (w) AlN is commonly used in the fabrication of high-frequency electro-acoustic devices. Its main advantages are high acoustic velocity and low acoustic and dielectric losses. Recently, an increased piezoelectric effect in w-Sc$_x$Al$_{1-x}$N with increased Sc content ($0<x<0.5$) was reported [1] and for $x>0.5$, a non-piezoelectric cubic phase was found favorable [2]. To reveal the true potential of this material, the dielectric and elastic properties as well as the piezoelectric properties of high quality crystalline material need to be investigated. In this work we present an experimental, as well as theoretical investigation of the dielectric constants of w-Sc$_x$Al$_{1-x}$N(0001). Thin films with $0<x<0.5$ have been grown as single crystal epitaxial layers onto TiN(111)/Al$_2$O$_3$(0001) substrates by dual reactive magnetron sputtering epitaxy using Sc and Al targets in an N$_2$/Ar discharge. XRD and HRTEM confirmed the epitaxial nature of the layers and were used to quantify the lattice parameter ratio c/a of the as-deposited layers. RBS and ERDA measurements have confirmed Sc$_x$Al$_{1-x}$N film growth with negligible oxygen content or other contaminants. A strong non-linear increase of the dielectric constant e_{33} was observed with increased x, as determined by electrical measurements of the (Au/Cr)/Sc$_x$Al$_{1-x}$N/TiN capacitor structures in the microwave frequency range. For $x=0$, $e_{33}= 10$ and dielectric losses <0.02 were measured, corresponding well to published values of pure AlN. Preliminary analyses show a ten-fold increase of e_{33} for Sc$_{0.2}$Al$_{0.8}$N. However, the dielectric losses also increased with Sc content which ultimately could limit the electromechanical coupling of the material. First-principles calculations showed a monotonous, non-linear enhancement of the piezoelectric constant e_{33} with increasing x. For $x=0.5$, e_{33} approaches 3.02 C/m^2, a value twice as large as for pure w-AlN (1.55 C/m^2). Furthermore, the stiffness constant C_{33} shows a monotonous linear decrease with Sc content, from 367 GPa down to 131 GPa. In conclusion, the observed increased piezoelectric constant and decreased elastic constant of w-Sc$_x$Al$_{1-x}$N epitaxial layers work in favor of an improved electromechanical coupling, but an associated observed increase in the dielectric constant, may limit the effect.

[1] M. Akiyama, T. Kamohara, K. Kano, A. Teshigahara, Y. Takeuchi, N. Kawahara, Adv. Mater. 21 (2009), 593.

[2] C. Höglund, J. Bareño, J. Birch, B. Alling, Zs. Czigany and L. Hultman, J. Appl. Phys. 105, (2009) 113517.

2:30pm **C2-2-5 Resistance Switching Mechanisms of Partial Doped SiO_2 With Fe Irons in a MIM Structure**, ***L.-W. Feng***, *C.-Y. Chang (cyc@mail.nctu.edu.tw),* National Chiao Tung University, Taiwan, *T.-C. Chang*, National Sun Yat-Sen University, Taiwan

In this study, large and stable resistive switching characteristics were observed on a novel structure of Ti/TiN/SiO_2/PtFe . This structure would form a thin Fe-O constituent examined by X-ray photoelectron spectroscopy between SiO_2 and bottom PtFe electrode . The metal-insulator-metal structure with alloy PtFe bottom electrode was also studied and current transport characteristics after forming process. In addition, a physical mechanism was proposed to explain the role of oxygen vacancies in the resistive witching process.

2:50pm **C2-2-6 Broad Visible Photoluminescence from Two-Layer Si/C Film Deposited on Si (100) Substrate Under Rapid Thermal Annealing**, *C.-K. Chung (ckchung@mail.ncku.edu.tw),* ***C.-W. Lai***, National Cheng Kung University, Taiwan

In order to investigate the effect of annealing temperature on the photoluminescence property of two layer Si/C film for potential optoelectronic devices, the Si/C film was deposited on the crystalline Si(100) substrate by using ultra high vacuum ion beam sputtering (UHV IBS) at room temperature and annealed at 750°C and 900°C for 2 min . Raman spectra, Fourier transform infrared spectroscopy (FTIR), high resolution scanning electron microscopy (HRSEM), atomic force microscopy (AFM) and photoluminescence (PL) spectrometry were used to characterize the evolution of bonding, optoelectronic behavior and microstructure of two-layer C/Si films, respectively .

From the experimental results, Raman spectra revealed that more disordered state as well as higher I_D/I_G ratio was obtained at higher annealing temperature. In addition, AFM and HRSEM image showed the bigger nanocluster appeared at 900°C. More Si-C bonding formation with increasing annealing temperature was identified by means of FTIR. Under 325 nm excitation, an asymmetric broad PL peak around 400~700 nm was observed in the PL spectrum. The broad visible PL spectrum can be deconvoluted by auto curve-fitting of Gaussian function into three bands of blue (~500 nm), green (~560 nm) and yellow (~600 nm yellow band ()) emission, corresponding to the formation of crystalline SiC, sp^2 carbon cluster and oxygen vacancy, respectively. PL intensity of three bands distinctly enhanced at 900 °C due to the increased amount of crystalline SiC, sp^2 carbon cluster and oxygen vacancy. The center of yellow band from oxygen vacancy almost fixed at same position during the thermal treatment. Redshift behavior of blue and green PL bands can be attributed to quantum confinement of nanoscale size effect .

3:10pm **C2-2-7 Low-Temperature Fabrication of Superconducting FeSe Thin Films by Pulsed Laser Deposition**, ***T.K. Chen*** *(tkchen@phys.sinica.edu.tw), J.-Y. Luo, C.-T. Ke,* Academia Sinica, Taiwan, *H.-H. Chang,* National Tsing Hua University, Taiwan, *T.-W. Huang, K.-W. Yeh, P.-C. Hsu, C.-C. Chang, M.-J. Wang, M.-K. Wu*, Academia Sinica, Taiwan

Superconducting FeSe thin films were prepared at a substrate temperature of 320°C by pulsed laser deposition. X-ray diffraction and transmission electron microscopy showed that highly orientated and high quality films could be grown at various substrate materials, including STO, LAO, MgO, Si, a-SiO_x, and SiN, at such low temperature. A film thickness of at least 400 nm is required to overcome the substrate-to-film strain for a low temperature (~ –173°C) structural distortion, which is indispensible for the occurrence of superconductivity. The superconducting transition temperature (T_c) varied slightly with substrate materials. The low deposition temperature and insignificant to substrate materials make them more compatible for real applications in electronic devices.

Carbon and Nitride Materials: Synthesis-Structure-Property Relationships
Room: Pacific Salon 3 - Session D2-2

Diamond and Diamond-Like Carbon Materials
Moderator: O. Shenderova, International Technology Center & Adámas Nanotechnology, Inc, R. Hauert, Empa

1:30pm **D2-2-1 Comparison of DLC Deposited by Different Techniques**, ***I. Gorokhovsky*** *(vgorokhovsky@swri.org), K. Coulter, M.A. Miller, R. Wei, C.A. Ellis*, Southwest Research Institute

Diamond like carbon (DLC) samples were prepared by different techniques: filtered cathodic arc deposition, vacuum arc source with hot evaporating cathode (VAHEC), plasma assisted low pressure chemical vapor deposition (PACVD) and ion beam assisted deposition (IBAD). The VAHEC source utilized a graphite cathode heated by an electron beam. The influence of characteristic processing parameters, reactive gas environment (H_2, CO_2, O_2) and substrate temperature on the properties of DLC films were investigated. The structure and morphology of the coatings was studied by optical and scanning electron microscopy, Raman spectroscopy, and X-ray and electron diffraction methods. The mechanical properties of DLC coatings on different substrates (diamond, cemented carbide, steel, copper and aluminum) were investigated by indentation and acoustic emission methods. The correlation between the interlayer thickness and the adhesion of the DLC films deposited by different techniques vs. substrate bias was studied. In addition, the resistance of DLC to etching by low energy ion beams (Ar^+, H^+, or O^+) in comparison to other carbon materials was studied. Results of Raman scattering show that the DLC films are amorphous, with a mixed sp^2 and sp^3 bonding. The ratio of sp^3 to sp^2 bonds varied from some units up to 20-30% and, in some cases, to more than 50% depending on the bias potential and concentration of hydrogen atoms in the plasma. It was found that most DLC films exhibit an elastic response to low loads. When the load met certain critical values, catastrophic delamination of the films occurred. The critical load depends on the substrate material, bias and deposition technique. Films with a high concentration of sp^3 bonds and high ion etching resistance typically also exhibit good mechanical properties.

1:50pm **D2-2-2 Surface and Structural Properties of DLC Coatings and their Influence on Protein Adsorption**, ***W. Waldhauser*** *(wolfgang.waldhauser@joanneum.at), M. Kahn, B. Pointner,* Joanneum Research Forschungsgesellschaft GmbH, Austria, *R. Kargl,* Karl-Franzens University Graz, Austria, *M. Reischl, S. Köstler, V. Ribitsch, E. Brandstätter*, Joanneum Research Forschungsgesellschaft GmbH, Austria

Diamond-like carbon (DLC), also known as amorphous hydrogenated or non-hydrogenated carbon (a-C:H, a-C), is a class of coating materials with excellent mechanical, tribological and biological properties. Depending on the deposition conditions and by the addition of other elements into the DLC these properties can be varied within a certain range. In the present work DLC coatings were deposited by employing DC magnetron sputtering of graphite targets, rf magnetron sputtering of titanium and silicon targets, respectively, in an argon/acetylene atmosphere and by the use of a special ion gun (anode layer source (ALS)) working with acetylene as carbon precursor. The structure and the topography of the coatings deposited onto silicon, glass and PET substrates were investigated by Raman spectroscopy and atomic force microscopy. The surface energy and the contact angle of the different coatings were determined by the sessile drop technique. Protein adsorption was investigated by fluorescence spectroscopy, fluorescence microscopy and a quartz crystal micro-balance method (QCM) using a bovine serum albumin.

For a-C:H coatings deposited by the ALS the discharge voltage varied from 1 kV to 3 kV was found to be the critical parameter to control the bonding structure and sp^3 content in the coatings. The metal content of the doped DLC coatings was adjusted by varying the sputtering power density and the C_2H_2/Ar ratio.

The bonding structure in the a-C:H coatings showed a slight influence on the surface properties and on the protein adsorption. For metal doped DLC a higher protein adsorption was found whereas a-C:H:Si coatings showed the highest values very closed to the glass reference substrate.

2:10pm **D2-2-3 Industrial Filtered Laser-Arc Film Deposition, New Quality of ta-C Films**, *J. Acosta,* ITESM-CEM, Mexico, *H.-J. Scheibe (hans-joachim.scheibe@iws.fraunhofer.de),* Fraunhofer Institute for Materialsand Beam Technology IWS, Germany, *C.-F. Meyer, M. Leonhardt,* ***A. Leson***, *V. Weihnacht*, Fraunhofer Institute for Material and Beam Technology, IWS, Germany **INVITED**

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 for tool applications. An efficient deposition of ta-C coatings within a series production is only possible by vacuum-arc technologies, e.g. arc ion plating or pulsed arc deposition. Especially the laser controlled pulsed arc deposition (Laser-Arc) was successfully implemented as a module source (Laser-Arc-Module / LAM) on industrial batch coaters, due to its excellent long-term stability of the pulsed graphite cathode erosion process. A disadvantage of all these processes for ta-C deposition is the high surface roughness resulting from the particle emission during the plasma creation from the solid graphite cathode. Therefore, most of the coated components and tools have to be surface smoothened in order to reach an optimized sliding behavior with very low-wear loss in a tribological system. For the deposition of smooth films by arc technologies, magnetic filter equipment has been successfully applied. However, for the industrial usage of such techniques for the deposition of thicker films they are not productive enough due to their high loss in deposition rate.

A newly developed filter module will be presented which was successfully developed from the laboratory state into an industrially usable LAM source. The principle of this filter for the separation of the charged plasma from macro- and micro-particles will be demonstrated. The advantages of this kind of filtering are the unlimited linear extension of the deposition area, a simple construction as well as the high efficiency. The transparency of the filter has been measured to be more than 60% in the case of super hard carbon (ta-C) film deposition. It is shown that the starting surface quality of components will be hardly changed by coating with ta-C up to a film thickness of more than 2 µm.

2:50pm **D2-2-5 Tetrahedral Amorphous Carbon (t-aC) Deposited by Filtered Cathodic Vacuum Arc (FCVA) Bombarded by Argon Ions**, ***C. Marques*** *(marques@ifi.unicamp.br), H. Oliveira, F. Motta*, Universidade Estadual de Campinas, Brazil

Structural properties of tetrahedral amorphous carbon (t-aC) deposited by the filtered cathodic vacuum arc (FCVA) technique is investigated. The films were prepared with 5 ms current pulses of 180 A and frequency of 3 Hz. The deposition substrate was polarized in a range of 0 to - 500 V bias voltage. Argon gas was incorporated in a series of films using an ion gun source to simultaneously bombard the films with a beam of argon ions with energy in the 0-180 eV range. Argon concentration in the films was determined by RBS measurements. A study of argon effusion, realized in the range from room temperature up to about 1000°C, shows that the structure of the films depends on the argon ion bombardment energy. 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 films are extremely stressed (up to about 10 Gpa) as determined using the bending beam technique, which limited the deposition of films to about 50-70 nm. It was observed that the stress reduces significantly as a function of annealing temperature. Nanohardness measurements show that the hardness of the films prepared in the 100-200 V bias voltage is about 30 Gpa. This value is underestimated since the films are very thin. Raman measurements were used to investigate the structure of the films as a function of the bias voltage and annealing temperature.

3:10pm **D2-2-6 Multı-Pass Scratch Test of DLC Coatings Deposited by CFUBMS on Anodized-CP-Ti at the Different Temperatures and Potentials**, ***C. Albayrak*** *(calbayrak@erzincan.edu.tr), O. Baran,* Erzincan University, Turkey*, A. Alsaran, I. Efeoglu, A. Celik*, Atatürk University, Turkey

Diamond-like carbon(DLC) coatings have a great deal properties such as high microhardness, high adhesion, high chemical stability and low friction coefficient. But ,the DLC films adhesion becomes poor if the hardness and the termal expansion difference between the substrate and the coating is considerable. Therefore, the DLC film seperates rapidly under loading. In this work, with a anodizing process was formed oxide layer on the Ti specimen surface at the varios temperatures and potentials to increase adhesion between DLC film and substrate. After anodizing treatment on CP-Ti substrates were deposited DLC films at the 2 µm thickness by Closed-Field Unbalanced Magnetron Sputtering. Structural and mechanical properties of this films are analyzed by XRD, SEM and microhardness tester. To determination adhesion properties of this coatings have been multi-pass scratched in the same track at different fractions of critical load. Consequently, anodization process effected morphology of DLC films and this process improved adhesion and wear properties.

3:30pm **D2-2-7 In Situ Real-Time Ellipsometry Study of Diamond-Like Carbon Films on Metal Substrates**, *D. Escaich, M. Azzi, O. Zabeida, J.-E. Klemberg-Sapieha,* ***L. Martinu*** *(ludvik.martinu@polymtl.ca)*, Ecole Polytechnique de Montreal, Canada

Hydrogenated amorphous carbon (a-C:H, or diamond-like carbon, DLC) films containing significant amounts of sp^3 bonding are of great interest in different areas, especially in the biomedical field. Widespread applications are, however, frequently hampered by insufficient adhesion of DLC to metal substrates such as stainless steel or titanium alloys in medical instrumentation, implants and others. In the present work, we investigate the kinetics of DLC film growth on 316L stainless steel, Ti-6Al-4V titanium and c-Si substrates using UV-VIS-NIR *in situ* real-time spectroscopic ellipsometry (SE). In particular, we focus on the substrate/film interface at the early stage of growth, and on the effect of substrate characteristics on the growth mechanisms. DLC films were prepared in radio-frequency powered plasma-enhanced chemical vapor deposition (RF-PECVD) system. In addition to SE measurements, complementary polarization modulated infrared spectroscopy (PM-IRRAS), Raman spectroscopy, atomic force microscopy (AFM), and scanning electron microscopy (SEM) analyses have been performed. We found that the early stages of deposition on c-Si exhibit an island growth mode, followed by a layer-by-layer mode, while on metal substrates, the DLC films directly grow in the layer-by-layer mode since the very beginning. Optical properties (refractive index, n, and the extinction coefficient, k) of the growing films were constantly evolving at the first moments of the deposition, but they stabilized after 4 minutes (140 nm thick films) and 2.5 minutes (85 nm thick films) on c-Si and metal substrates, respectively. The difference during the initial steps of growth was found to affect the properties of the final (300 nm) DLC deposits. While on both metals the films are quite similar, their counterparts on c-Si possess lower roughness, lower amount of sp^3 bonds, reduced index of refraction, and higher extinction coefficient. The growth mechanisms are discussed with respect to the substrate surface characteristics including roughness, surface energy, temperature, and ion bombardment energy.

3:50pm **D2-2-8 Anisotropic Texturing of Diamond-Like Carbon Films by Colloidal Lithography with Sub-Micron Spheres**, ***C. Corbella*** *(corbella@ub.edu), S. Portal, M. Rubio-Roy, M.A. Vallvé, J. Ignés-Mullol, E. Bertran, J.-L. Andújar*, University of Barcelona, Spain

Diamond-like amorphous carbon (DLC) surfaces have been patterned by a combination of colloidal lithography and pulsed-DC plasma-enhanced chemical vapour deposition. A self-assembled monolayer of silica sub-micron particles (~ 300 nm) was deposited on monocrystalline silicon (~5 cm^2) by Langmuir-Blodgett, in order to act as sacrificial template for hole-mask lithography. A sub-micrometric pattern was generated on the substrate via ion beam etching (argon) of the colloid samples (550 eV), which was held at different incidence angles. As a result, in-plane anisotropy in the sub-micron range was generated. The fabrication was completed by plasma deposition of DLC thin film on the textured substrates. The samples were morphologically characterized by SEM and AFM. The surface properties evidenced the formed anisotropy, as shown by the directional dependences of friction coefficient (nanotribometer) and wettability (water contact angle). This fabrication technique finds applications in the industry of micromechanical devices, anisotropic tribological coatings, nanoimprint lithography, microfluidics, photonic crystals, and patterned surfaces for biomedicine.

4:10pm **D2-2-9 High Temperature Tribological Behaviour of Carbon Based (B_4C and WC-DLC) Coatings Against Aluminum**, ***A. Abougharam*** *(abougha@uwindsor.ca),* University of Windsor, Canada*, M.L. Lukitsch,* GM Research & Development Center*, A.T. Alpas*, University of Windsor, Canada

Carbon based coatings, particularly diamond like carbon (DLC) surface films are known to mitigate aluminum adhesion and reduce friction at room temperature. This attractive tribological behaviour is useful for applications such as tool coatings for aluminum forming and machining. However, for those operations that are performed at elevated temperatures (e.g., hot forming) or generate frictional heat during the contact (e.g., dry machining) coatings are expected to maintain their tribological properties at high temperatures. The candidates for these demanding applications include boron carbide (B_4C) and DLC coatings reinforced with nanoparticles. An understanding of the micromechanisms of friction, wear and adhesion of carbon based coatings against aluminum alloys at high temperatures will help designing coatings with improved high temperature tribological properties. With this goal in mind, this study was focused on B_4C and DLC reinforced with WC nanoparticles coatings sliding against a 319 grade cast aluminum alloy by performing pin-on-disk experiments at temperatures up to 400°C. Experimental results have shown that the 319 Al/B_4C tribosystem generated coefficient of friction (COF) values ranging between 0.51 and 0.65, independent of the testing temperature However, increased amounts of aluminum adhesion was detected inside the B_4C coating's wear tracks at elevated temperatures. Focussed ion beam (FIB) milled cross-sections of the wear tracks revealed that the coating failed due to shearing along the columnar grains. The 319 Al/WC-DLC tribosystem generated much lower COFs; in fact, the room temperature COF of 0.15 decreased to 0.06 at 200°C, in contrast WC-DLC wear increased slightly with the temperature. The wear and adhesion mechanisms of these coatings were further assessed using FIB, HRTEM and FTIR analyses and will be discussed in the meeting.

4:30pm **D2-2-10 Synthesis of Ultra-Smooth and Ultra-Low Friction DLC Based Nanocomposite Films on Rough Substrates**, ***K.P. Shaha*** *(k.p.shaha@rug.nl), T. Pei, C. Chen, J.T.M. De Hosson*, University of Groningen, The Netherlands

Surface roughness and dynamic growth behavior of TiC/a-C nanocomposite films, deposited by non-reactive pulsed-DC (p-DC) sputtering of graphite-targets, were studied using atomic force microscopy, cross-sectional scanning and transmission electron microscopy. Upon increasing the intensity of concurrent ion impingement by raising the frequency of p-DC sputtering, a transition from dynamic roughening to dynamic smoothing was revealed. Rough TiC/a-C films were intentionally grown on smooth surface at low pulse frequency (100 kHz) to simulate a rough finishing of industrial substrates and then rapid smoothening of such initial rough films at higher pulse frequency (350 kHz) was observed. From detailed analyses of surface morphology and growth conditions it was concluded that a transition in dominating growth mechanism from geometric shadowing at p-DC 100 kHz to surface diffusion driven by impact-induced atomistic downhill flow process due to enhanced impingement of Ar+ ions at 350 kHz occurs. It was shown that rapid smoothing of initially rough surfaces with RMS roughness ~ 6 nm to < 1 nm can be effectively achieved with p-DC sputtering at 350 kHz pulse frequency, leading to a transition from a strong columnar to a columnar-free microstructure. The observed dynamic smoothing phenomenon was applied to obtain ultra-smooth (RMS roughness ~ 0.19 nm) and ultra-low friction (μ~0.05) TiC/a-C:H nanocomposite films on rough steel substrates by p-DC sputtering of Ti-targets in an argon/acetylene atmosphere.

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

Friction and Wear of Coatings: Lubrication, Surface Effects and Modeling
Moderator: E. Broitman, Carnegie Mellon University, J.C. Sanchez-Lopez, Instituto de Ciencia de Materiales de Sevilla (CSIC-US), O.L. Eryilmaz, Argonne National Laboratory

1:30pm **E1-1-1 Identification of Hard Turning Signature of Coated Tools on Cut Surface**, *A. Zawada-Tomkiewicz (annazt@wp.pl),* Koszalin University of Technology, Poland, *M. El Mansori*, Arts et Métiers ParisTech, France

This paper reports on the use of wavelets to identify the machining signature of coated tools. Both coated and uncoated CBN tools were experienced in hard turning (CBN tools).The idea is to assess the correlation between the changes in tool geometry (i.e. the quality of coating) and the induced surface integrity by hard turning.

Indeed, the cut surface in hard turning process is different from conventional machining because of high strength of hardened steel and brittleness of CBN tools. The machined surface was then modeled as a set of non-stationary signals generated by uneven material removal process. The digital wavelet transform was hence developed to extract the features of the quality of tool coating. Different qualities of tool coatings (tool wear, tool chipping, tool breakage) were identified which exhibit different characteristics in signal components of the machined surface. The surface roughness increased indeed gradually with the increase of tool wear. The results show, in general, that the surface modification in term of integrity was reflected in both the static component (approximation component) and the dynamic one. The surface roughness changed suddenly when tool chipping or breakage was observed. Different form and size of tool coating change was exhibited in different dynamic components and created specific signature of the coating on the machined surface.

1:50pm **E1-1-2 On the Early Stages of Friction of Tetrahedral Amorphous Carbon Thin Films Deposited by Femtosecond Laser Ablation**, *P. Paolino,* Ecole Centrale de Lyon, France, *A. Sikora,* Université Jean Monnet, France, *C. Guerret-Piécourt,* ***J. Fontaine*** *(julien.fontaine@ec-lyon.fr),* Ecole Centrale de Lyon, France, *F. Garrélie, C. Donnet, A.-S. Loir,* Université Jean Monnet, France, *M. Belin*, Ecole Centrale de Lyon, France

Tetrahedral amorphous carbon (ta-C) coatings are known for providing high hardness and good wear resistance, together with low friction coefficients in ambient air. Such paradox – high hardness, meaning difficult to shear, and low friction, meaning easy to shear – can be explained by the growth of a "tribofilm" or "third-body" on the sliding counterface. However, the role of surface layers on these interfacial materials is still unclear, especially the influence of sp^2-rich top layer reported in the literature for some ta-C films.

In this study, we are considering ta-C coatings deposited on 52100 bearing steel coupons by femtosecond laser ablation of a graphite target. Their tribological behaviour has been investigated with a reciprocating pin-on-flat tribometer, not only measuring friction coefficient but also electrical contact resistance. The ta-C surface, both inside and outside wear tracks, has been then characterized by electrically conductive Atomic Force Microscopy. Additionnal analysis of the wear tracks have been carried out by Scanning Electron Microscopy with Energy Dispersive X-Ray spectrometry, abd by X-Ray Photoelectron Spectroscopy.

During friction experiments, a "running-in" period is systematically observed for few tens of cycles, with concomittant decrease of friction coefficient and increase of electrical contact resistance. The relatively low initial electrical contact resistance is explained by the presence of tiny "droplets" that appears to be more conductive on AFM electrical images than the smooth surrounding surface of the films. However, even a single sliding cycle affects these spots, making them much more resistive.

In light of these results, the surface modification phenomena involved in such early stages of friction will be discussed, in order to account for the observed tribological behaviour, and for the growth of interfacial materials.

2:10pm **E1-1-3 Recent Developments on DLC Films and Tribomechanical Characterizations**, ***V.J. Trava-Airoldi*** *(vladimir@las.inpe.br), P.A. Radi, F.R. Marciano, L.V. Santos, D.A. Lima-Oliveira, E.J. Corat*, Instituto Nacional de Pesquisas Espaciais, Brazil **INVITED**

The ressearch on diamond-like carbon (DLC) films are growing and developing and is a completelly opened area to development of news composites with new properties. The challenge is to obtain films with very high hardness and adhrence and with high resistance to corrosion and wear. We developed in our ressearch group, at the first time, DLC films with extremally high hardness and very resistant to corrosion by incoporating nanocrystalline diamond (NCD) particles during the deposition process.

Another ressearch challenge is on the characterization of these films, the usual experimental approach on tribomechanical characterization is to vary one parameter at time while keeping the others constant, thus measuring the influence of each variable. This approach requires more experimentation, ignores the interactions between the parameters and can lead to wrong conclusions. We develop, also at the fist time, a methodology that combine statistical and tribomechanical analysis in order to improve the film characterization.

This paper presents the experimental/statistical tribomechanical studies on NCD-DLC composites. The factorial design was used to describe the overall effect on the friction and wear of the NCD particle size and test conditions such as 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 the tribologic maps. Nano hardness was also measured as a part of the whole characterization.

2:50pm **E1-1-5 Fretting Contact Study of Ti-6Al-4V/Carbon Couples in a Dry Shaft/Bearing Contact with Trust: Influence of a Plasma Nitridation of the Titanium Alloy**, ***M. Sylvestre*** *(manuel.sylvestre@lms.univ-poitiers.fr), H. Zaidi, J.-P. Rivière, D. Eyidi,* Université de Poitiers, France, *F. Doyen*, Carbone Lorraine Composant, France

Fretting wear or wear by small displacements is defined when two contacting surfaces ("first-bodies") are subjected to reciprocating motion of small amplitude in micron order. This phenomenon is observed in many mechanical assemblies and that can significantly reduce the life of the mechanisms

This paper reports on the influence of a nitridation treatment of the titanium alloy on the fretting tribological behaviour of carbon/ Ti-6Al-4V couples in a dry shaft/bearing contact with trust. Two contact geometries are investigated: cylinder-in-cylinder and plan/plan. Both of them are subjected to low-amplitude oscillatory movements, with temperature reaching 270°C .

The treatment of nitridation for the Ti-6Al-4V is a N_2-H_2 plasma nitridation at low temperature (700°C), during 12 hours. In these conditions, the top surface hardness was improved by a factor three.

In this study, the mechanism of transfer and wear of carbon against Ti-6Al-4V nitrided or not, have been studied with the scanning electronic microscope, the optical microscope and the interferential microscope.

The morphological and profile analyses performed on rubbing surfaces showed various aspects of wear: prints, craters, transfer… This permits each degradation to be linked its location, development and origin.

The friction couples recorded during the test have showed differences between the tests with the shafts with or without nitridation and especially at rise temperature.

We discuss the experimental results and we suggest many possibilities in order to understand some specific tribological behaviours: impact of the third body, of the abrasion, etc.

3:10pm **E1-1-7 Nanoscale Deformation Mechanism in the Sliding Contact of TMD-C Nanocomposite Coatings**, ***T. Polcar*** *(polcar@fel.cvut.cz),* Czech Technical University in Prague and University of Coimbra, Portugal, *A. Cavaleiro*, University of Coimbra, Portugal **INVITED**

The reduction of friction continues to be a hot-topic in mechanical engineering. Lower friction between mechanical parts in contact diminishes the energy consumption, vibrations, noise, contact temperature, and wear.

Among many ways to fight the friction, solid lubricants in the form of thin films deposited by physical vapor deposition methods are widely used in industrial applications. Transition metal dichalcogenides (TMD) are suitable as solid lubricants due to their anisotropic layered structure, where the adjacent lamellae with strong covalent bonding interact through relatively weak van der Waals forces. Pure sputtered TMD films are almost friction-less at ultra-high vacuum sliding conditions; however, the films are sensitive to environmental attack, particularly in the presence of oxygen and water, which limits their mechanical properties and wear resistance. Alloying of TMD with other element has improved their properties, such as adhesion, hardness and load bearing capacity. Nevertheless, the high sensitivity to environmental attacks still remains the main restriction for full the industrial use of TMD-based coatings as self-lubricants.

In this talk, we will show the tribological behavior of different TMD coatings alloyed with carbon (WSC, WSeC, MoSC and MoSeC systems) deposited by magnetron sputtering. Three TMD microstructures have been prepared: i) randomly oriented platelets in amorphous carbon matrix, ii) nanograins of TMD in amorphous carbon matrix and iii) mixture of carbide and TMD nanograins embedded into the carbon matrix. Special attention has been paid to the analysis of the frictional and wear mechanisms under different operating conditions, such as contact pressure, air humidity or temperature. Nanoscale analysis of the wear track revealed the formation of a thin tribolayer exclusively consisting of TMD platelets oriented to exhibit the lowest friction. In some cases, the depth reorientation of the originally randomly oriented TMD platelets as a reaction to the sliding process has been observed. Such self-adaptation explains the extremely low friction coefficient together with a high load-bearing capacity; moreover, the films are much less sensitive to environmental conditions compared to pure TMD.

3:50pm **E1-1-9 Growth, Structure and Tribological Properties of Atomic Layer Deposited Lubricious Oxide Nanolaminates**, ***B.A. Mensah***, *H. Mohseni, T.W. Scharf (scharf@unt.edu)*, University of North Texas

Oxides have been studied lately as good potential candidates for solid lubricants because they are thermodynamically stable and environmentally robust. Oxide surfaces are generally inert and typically do not form strong adhesive bonds like metals in tribological contacts. To this end, nanolaminate $ZnO/Al_2O_3/ZrO_2$ films were grown via atomic layer deposition (ALD) on high temperature M50 bearing steels. The lubricious, nanocrystalline ZnO layer was structurally-engineered to achieve low surface energy {0002}-orientated grains, which provided low sliding friction coefficients (0.2 to 0.3) and wear factors (1-3 x 10^{-7} mm^3/Nm). The amorphous Al_2O_3 layer played an important role in achieving this preferred orientation, while {101}-orientated tetragonal ZrO_2 acted as a high toughness/load bearing layer. It was determined that the ZnO defective structure (oxygen sub-stoichiometric with growth stacking faults) aided in shear accommodation by reorientating the nanocrystalline grains where they realigned to create new friction-reducing surfaces. Specifically, high resolution transmission electron microscopy (HRTEM) inside the wear tracks revealed the presence of basal stacking faults and partial dislocations which aided the shear accommodation during the interfacial sliding between the film and the ball counterface. This velocity accommodation mode was intrafilm shear where this friction-induced subsurface aided in shear accommodation and prevented brittle fracture. The solid lubrication mechanisms of these reorientated, plastically sheared ZnO grains will be discussed along with how ex situ annealing to 400°C affects structure-tribological property relationships. Environmentally-robust, l ubricious ALD $ZnO/Al_2O_3/ZrO_2$ nanolaminates are good candidates for providing low friction interfaces in moving mechanical assembles, such as fully assembled bearings, that require thin (~10-200 nm), uniform and conformal films.

4:10pm **E1-1-10 Sophisticated New Analyzing and Simulation Tools for Scratch, Impact, and Wear Tests**, ***M.C. Fuchs*** *(m.fuchs@siomec.de), N. Bierwisch*, Saxonian Institute of Surface Mechanics, Germany

In the work it will be presented how the extended Hertzian theory and the Oliver&Pharr method extended for layered materials[1] can be applied to scratch tests, indentation measurements, and impact experiments in order to extract more physical information from them. The methods also work perfectly for multilayer and gradient coatings and in principle allow the extraction of the mechanical parameters of any of the constituents of even very complex coating structures. By taking into account, that with lateral forces additional boundary effects like indenter tilting and mixed loads of sticking-sliding areas are coming into play, a much more profound simulation and modelling of even the classical scratch test is possible. But it will be shown, that one can particularly benefit from such a more comprehensive and sophisticated analysis when using a new multi-path scratch method combined with additional classical nanoindentation measurements[2] as it can extract a lot more mechanical properties from such experiments. It will be shown how the true initial failure can be detected and clearly defined critical stress values can be assigned to corresponding constituents of the coating.

Additionally, it will be shown how wear simulations based on an extended Archad's law and by means of both methods mentioned above can be used not only to predict the wear progress for contact situations of complex material structures, but also to extract wear parameters of any surface material. The method can also be used to quickly simulate wear behavior. Hence, on the one hand it enables one to determine the lifetime of the sample according to its supposed application and, on the other hand, to find out which modifications of the coating structure are necessary to enhance the surface and, therefore, its lifetime.

These new methods will be demonstrated on a variety of examples in combination with new analyzing modules woven into the software package FilmDoctor[3].

[1] N. Schwarzer: "The extended Hertzian theory and its uses in analysing indentation experiments", Phil. Mag. 86(33-35) 21 Nov - 11 Dec 2006 5153 – 5767

[2] N. Schwarzer: "Advanced scan procedures – Poly-Scan Scratches", www.siomec.de/docs/2008/001

[3] FilmDoctor: Special version for "next generation surface tester analysis", www.siomec.de/FilmDoctor

4:30pm **E1-1-12 Tribological Properties of Water Confined by Self-Assembled Monolayers**, ***M. Chandross*** *(mechand@sandia.gov),* Sandia National Laboratories*, C.D. Lorenz,* King's College London, United Kingdom*, J.M.D. Lane, G.S. Grest*, Sandia National Laboratories

We report the results of large-scale Molecular Dynamics (MD) simulations of water confined to sub-nanometer thicknesses between both hydrophobic and hydrophilic self-assembled monolayers (SAMS). We vary the amount of water and the applied pressure to examine the effects on the structure and dynamics of the confined water. Calculations of two dimensional diffusion constants indicate that the water remains liquid-like in all cases. The water confined between the hydrophilic SAMS is subjected to shear to measure the viscosity and microscopic friction. We find that while the viscosity increases by as much as a factor of 60 for low coverage and high loads, there is still no evidence of ice-like layers being formed. Friction coefficients can only be calculated at high shear velocities due to the low viscosity of the water and are found to decrease with increasing amounts of water, similar to experimental results.

4:50pm **E1-1-11 Multi-Scale Contact Modelling of Textured Surfaces Under Dry Sliding Conditions**, *O. Rashwan,* ***M. Stoilov*** *(vstoilov@uwindsor.ca)*, University of Windsor, Canada

Contact between rough surfaces has been drawing a lot of researchers' attention since 1960's since many engineering applications involving normal and siding contact, especially in the automotive components and metal forming dies. The effect of the different surface textures and surface topography on the friction and adhesion involved in the normal and sliding contact is the main concern. In this paper a multiscale model of textured rough surfaces was developed using a modulated two-variable Weierstrass-Mandelbrot function with fractal parameters determined from real surface images. A finite element model was used to analyze the contact between the textured surfaces of specified geometries, such as square and sine wave patterns with the surface roughness imposed on the top using the fractal geometry. The model yields insight into the evolution of elastic, elastic-plastic, and fully plastic deformation at the contact interface in terms of the maximum local surface interference. The obtained results showed strong dependence of the macro static friction coefficient on the minimum fractal length, emphasizing the intrinsic multiscale nature of the friction phenomena. In addition, it has been shown a significant effect of the modulated surface topology on the macro level adhesion and friction. Thus this approach provides a viable tool for exploring the macro-micro scale dynamics of adhesion and friction and the possibly for their control through surface patterning.

New Horizons in Coatings and Thin Films
Room: Royal Palm 4-6 - Session H4/C4

Thin Films for Photovoltaics: Synthesis and Characterization
Moderator: S.V. Khare, University of Toledo

1:30pm **H4/C4-1 The Characteristics of Zinc Oxide, Cadium Oxide and SnO$_2$ Prepared by RF Magnetron Sputtering**, ***Y. Zhou*** *(zhouyanwen@yahoo.com), F. Wu, C. Zheng*, University of Science & Technology Liaoning, China

Pure ZnO, CdO and SnO$_2$ films were prepared under closed-field unbalanced magnetron from powder target, by varying RF power and deposition time. The thicknesses of the films were measured by Alpha-Step IQ surface profile and therefore deposition rates of the three materials were calculated. The CdO has much higher deposition rate than SnO$_2$ and ZnO. The SEM and XRD graphs show that the films have the dense columnar structures, and the preferred orientations ZnO, SnO$_2$ and CdO films are (0002), (200), (200), respectively. Vacuum or controlled atmosphere annealing help the intensities of the diffraction peaks grow and FWHM narrow according to XRD results, therefore the mobility of the free charged carriers are increased, showed agreement with Hall Effect measurement. Also, the resistivities of the films decreased, from too higher to be measured to 10^{-4} Ωcm, and the concentrations of the free charged carriers increased, from 10^{19} to 10^{21}, after vacuum annealing, but the contrary results after controlled atmosphere annealing. The optical transmittances of these three films are: ZnO, 90%; SnO$_2$, 88%; and CdO, 85%, within the visible wavelength. Annealing treatment did not affect the transmittances of the films, but showed the blue shift and red shift after vacuum and controlled atmosphere annealing, respectively.

1:50pm **H4/C4-2 Three-Terminal Microcrystalline Silicon Solar Cell**, ***C.-H. Tai***, *C.-H. Lin (chlin0109@mail.ndhu.edu.tw)*, National Dong Hwa University, Taiwan

Like amorphous silicon, the microcrystalline silicon (μc-Si) can be demonstrated by plasma enhanced chemical vapor deposition. Hence, fabrication of μc-Si solar cells could be based on equipment for amorphous silicon (a-Si) solar cells. In addition, μc-Si has other advantages over a-Si. For example, the absorption coefficient of μc-Si is higher than a-Si in red light and infrared wavelengths, and the carriers mobility in μc-Si is also larger than a-Si. But for μc-Si, there are still a lot of defects inside it. These defects will lead to recombination of photo-generated carriers and the efficiency of μc-Si solar cells is limited. We have designed a new structure – the three-terminal μc-Si solar cell, a back-to-back pin-nip solar cell by the simulation tool, ISE. As compared with the typical μc-Si pin solar cells, the three-terminal μc-Si solar cell can increase the average electric field in the device. The electric field can help separation of photo-generated electron-hole-pairs and decrease the recombination velocity efficaciously. The comparison between the typical cell and the three-terminal μc-Si cell will be shown in this conference. The efficiency of the three-terminal μc-Si solar cell larger than 10 % can be expected.

2:10pm **H4/C4-6 Intergranular Microstructure and Residual Stress Investigation by EBSD on Laser-Crystallized Polycrystalline Si Thin Films on Glass Substrates for Photovoltaic Applications**, ***X Maeder*** *(xavier.maeder@empa.ch), C. Niederberger,* Empa, Sweden, *S. Christiansen,* Max-Planck-Institute of Microstructure Physics, Germany, *A. Bochmann, G. Andrä, A. Gawlik, F. Falk,* Institute for Photonic Technology, Germany, *J. Michler*, Empa, Switzerland

The combined process of diode laser crystallization of an amorphous Si seed layer and solid phase epitaxy (SPE) are used to produce polycrystalline silicon thin films on glass substrates for solar cells. The laser crystallization process is capable of producing large grains of several 100 µm in size while heating the temperature-sensitive substrate only for a very short duration. Grain size, orientation distribution, grain boundary population and lattice defects of polycrystalline silicon thin films are investigated by electron backscatter diffraction analyses (EBSD). The laser crystallization process caused a systematic and strong intergranular lattice twisting in the larger grains, with rotation axes parallel to the growth direction. This progressive lattice rotation is generally between 10 and 25° from one side of the grain to the other and can be up to 50° in the strongest cases. An intergranular misorientation rate higher than 0.2° per micron, constant for several hundred microns, has been observed. The intergranular misorientation is associated both with geometrically necessary dislocations and low angle boundaries which can serve as recombination centre for electron-hole pairs. The dislocation arrays associated with the lattice twisting can be observed by EBIC measurements. Since the lateral grain size is up to two orders of magnitude larger than the film thickness, these dislocations and low angle grain boundaries are an important factor in the degradation of the solar cell performance. An EBSD cross correlation technique has also been used to assess the residual stress in the grains that can influence the mechanical integrity of the device. The calculations show residual stresses values on the order of several GPa inside the grains with strong intergranular misorientation. The main component of stress is perpendicular to the grain growth direction.

2:30pm **H4/C4-7 Addition of Na into CuInS$_2$ Thin Film via Co-Evaporation**, ***W.-Z. Tsai****, C.-H. Tsai, C.-H. Chang, J.-M. Ting (jting@mail.ncku.edu.tw)*, National Cheng Kung University, Taiwan

The performance of CuInS$_2$ (CIS) thin film solar cells can be enhanced through the addition of Na into the CIS layer. In almost all of the cases, Na originates from substrate glass or a separate NaF layer that is deposited before, during, or after the growth of CIS, followed by thermal annealing. In the study, we have used an alternative approach by which NaF is incorporated into the CIS layer through co-evaporation. Cu, In, and NaF were first co-evaporated at desired ratios to allow the formation of precursor films having various nominal concentrations of Na. The composition of the precursor films was determined using inductively coupled plasma-mass spectrometer. The precursor films were then sulfurized to form CIS absorber layers in the same evaporation chamber. During the sulfurization, samples were removed at different temperatures for analysis in order to determine the desired sulfurization schedules. The morphology of Na-doped CIS layers was characterized using scanning electron microscopy and the crystalline structure was investigated using grazing incident X-ray diffraction. Secondary ion mass spectrometry was used to determine the concentration profiles along the film thickness. The optical and electrical properties of the absorber layers were investigated using UV-Visible spectroscopy and Hall measurement system, respectively. Effects of Na concentration on the absorber layer characteristics are addressed and discussed.

2:50pm **H4/C4-8 Fabrication of Densely Distributed Silver Indium Selenide Nanorods by Ag$^+$ Ion Irradiation**, ***D. Pathak*** *(dineshpathak80@gmail.com), R. Kumar,* Guru Nanak Dev University, India, *D. Kaur,* IIT Roorkee, India, *R. Kumar*, Inter University Accelerator Centre, India

We prepared polycrystalline AgInSe$_2$ thin films by vacuum evaporation on Si(100) substrate at a high temperature using the stochiometric powder. The thin films were characterized by X-ray diffraction and Uv-vis-NIR spectroscopy .For the fabrication of densely distributed one dimensional nanostructures of Silver Indium selenide on Si substrates, the thermally evaporated films of AIS on Si (1 0 0) substrate were irradiated by incident 200MeV Ag$^+$ ions at a fluence of 5 X 10^{11} Ion/cm^2. At elevated substrate temperatures AIS were featured by the nanorods -like structure. The optical and structural properties of the irradiated films were studied using UV–visible absorption spectroscopy , atomic force microscopy (AFM) , Field emission scanning electron microscopy (FESEM) and XRD .The controlled fabrication of such densely distributed one dimensional nanorods on Si substrate using ion beam technique, we believe, would open up a variety of applications such as nanoelectronics and optoelectronics devices.

3:10pm **H4/C4-10 Impregnation of Nano-Particles in Glancing-Angle Deposited Titania Films for Efficiency Enhancement in Dye-Sensatized Solar Cells**, ***C.-L. Chen***, *C.H. Huang, M.-S. Wong (mswong@mail.ndhu.edu.tw)*, National Dong Hwa University, Taiwan

Sculptured porous nano-columnar titanium oxide films used as photoanode in dye-sensitized solar cell (DSSC) were prepared on ITO glasses by glancing-angle deposition (GLAD) method using an electron-beam evaporation system. The as-deposited TiO$_2$ films are comprised of helical nano-columns and assembled in an orderly manner with open pores in between. The films were then partially impregnated with titania nanoparticles by spin coating method to increase their internal surface area for dye absorption. The modified porous nanostructured titania films provide a synergetic effect of high surface area, effective route for electron transfer, tight interfaces, and enhanced light trapping, which are all beneficial for higher cell efficiency. The DSSCs incorporated with the nanoparticles-impregnated GLAD films of 4 µm thick exhibited an increase of ~20% in light conversion efficiency over those with the as-deposited films.

3:30pm **H4/C4-11 Nano-Structured TiO_2 Films by Plasma Electrolytic Oxidation of Ti Combined with Chemical and Thermal Post-Treatments for Dye-sensitized Solar Cell Applications***, **P.-J. Chu**,* University of Sheffield, United Kingdom*, S.-Y. Wu, K.-C. Chen, J.-L. He,* Feng Chia University, Taiwan*, A. Aleksey (A.Yerokhin@sheffield.ac.uk), A. Matthews*, University of Sheffield, United Kingdom

Porous TiO_2 layers are known to be produced on titanium by the plasma electrolytic oxidation (PEO) process. Such coatings can be considered as potential candidates to use as surface electrode materials in photovoltaic devices, e.g. dye-sensitized solar cells (DSSCs), where the specific surface area of the TiO_2 electrode is required to be as large as possible for efficient dye absorption. However as shown in the literature and our previous work [1], the as-formed PEO layer does not provide a large enough specific area and thus the photovoltaic efficiency of the assembled device is low. The aim of this study is therefore to develop a nano-structured TiO_2 surface layer based on PEO treated titanium by using alkaline and thermal annealing post-treatment procedures. The specific surface area is expected to be increased due to re-formation of the original PEO layer in NaOH solution and the anatase content to be enhanced due to crystallisation during subsequent annealing. Microstructure of the post-treated TiO_2 and the photovoltaic efficiency of the assembled device are examined as a function of alkali concentration, bath temperature, and soaking time.

Experimental results show that, after the alkaline post-treatment, a 'nano-flaky' morphology was developed over the oxide surface. Higher alkali concentration, bath temperature and soaking time enhanced the roughening of the PEO treated surface and at the same time a thicker reformed layer can be obtained. However, a possibility of crack development in the oxide layer increases, compromising the photovoltaic efficiency. Following the alkaline post-treatment in 1.25 M NaOH solution at 40^{o}C for 12 h, the assembled device had an ultimate photovoltaic efficiency of 0.329% in contrast to that of 0.061% presented by the as-formed PEO TiO_2. Further annealing at temperatures above 300^{o}C significantly enhanced the formation of the anatase phase in the oxide layer and a maximum photovoltaic efficiency of 2.194% can be achieved when annealed at 400^{o}C.

[1] P-J Chu, A Yerokhin, A Leyland, A Matthews, J-L He, Through-thickness Microstructural Characterization of the Plasma Electrolytic Oxidized Titanium Oxide Fabricated on Metal Titanium, Abstracts of ICMCTF 2009, paper GP-6, p 99.

3:50pm **H4/C4-12 Depth Profile Analysis of Thin Layers on Conductive or Nonconductive Substrates by Rf GD-OES (Semiconductor, Photovoltaic and PVD/CVD Applications)***, **P. Hunault** (philippe.hunault@horiba.com),* HORIBA Jobin Yvon Inc., USA*, C. Tauziède, P. Chapon, A. Tempez,* HORIBA Jobin Yvon, France*, M. Ganciu,* NILPRP, Romania*, P. Guillot,* University JF Champollion, France*, P. Belenguer*, Laplace CNRS, France

Radio Frequency Glow Discharge-Optical Emission Spectrometry (RF GD-OES) is an established technique capable of Ultra Fast Elemental Depth Profiling of thin films down to < 1 nanometer.

The application of the technique to the characterization of thin layers on conductive substrates or non-conductive substrates such as glasses and ceramics is investigated. Issues related to heat and thermal damage as well as coupling efficiency are shown and solutions to overcome these issues are presented resulting from theoretical and experimental characterizations of the RF GD plasma and its interaction with the material's surface.

The new RF coupler allows sputtering of up to 5mm thick glasses or ceramics. It provides more than adequate performance for useful analysis as examples from solar cells and coated ceramics will illustrate. Other Semiconductor, Photovoltaic and PVD/CVD applications will be presented.

Coatings for Use at High Temperature
Room: Golden Ballroom - Session AP

Symposium A Poster Session

AP-1 Thermal Cycling Behavior and Interfacial Stability in Thick Thermal Barrier Coatings, *Y.-G. Jung (jungyg@changwon.ac.kr),* Changwon National University, Korea*,* ***P.-H. Lee****, S.-Y. Lee,* Changwon National Unviersity, Korea*, J.Y. Kwon, S.-W. Myoung,* Changwon National University, Korea*, U.G. Paik*, Hanyang University, Korea

The thermal cycling behavior of thermal barrier coatings (TBCs) with a thickness of 2000 µm, which were prepared by two different air-plasma spray (APS) systems using 9MB and TriplexPro-200 guns, has been investigated to understand the effects of the microstructure in the thick TBCs on the interfacial stability and its fracture behavior. The thermal exposure tests were performed at a surface temperature of 1100°C with temperature difference of 150°C between the surface and bottom of sample, with a dwell time of 1 h for 800 cycles, in a specially designed apparatus: one side of the sample was exposed and the other side air cooled. The defects on the section were characterized with an image analyzer before and after thermal cyclic tests, including defect percentage, species, and size. The mechanical properties, such as hardness, toughness, and adhesive strength of the developed TBCs were evaluated. The nominal porosities of the top coats is not much dependent on the APS system, showing a similar porosity of about 13%, which decreases slightly with the thermal cyclic tests. However, defects in the TBC by 9MB contain a large fraction of pores, whereas those in the TBC by TriplexPro-200 contain a large fraction of horizontal and vertical cracks due to the relatively higher flame velocity. After the thermal cyclic tests, defects such as interlamellar cracks, vertical cracks, and intrasplat cracks are newly produced in both TBCs. However, cracking or partial delamination at the interface are more severely propagated in the case of TBCs by 9MB, showing a relatively thicker thermally grown oxide layer. The hardness values are slightly increased after the thermal cyclic tests, whereas the toughness values show a reverse tendency in both TBCs. In the adhesive strength, the TBCs by TriplexPro-200 gun show the higher value of about 10 MPa, compared to the 9MB of about 8 MPa. Consequently, the newly developed TBCs using the specialized coating system could be promising for use in TBC application, resulting in improving the reliability and lifetime performance of components with APS-TBCs in gas turbines.

AP-2 Original Refractory Metallic Coatings on Fibers: Morphology and Behavior at High Temperature*, A.-S. Andréani,* ***A. Poulon-Quintin*** *(a.poulon@icmcb-bordeaux.cnrs.fr), F. Rebillat*, Université de Bordeaux, France

A method for testing high refractory metallic coatings at high temperature (up to 2000°C) in controlled atmosphere (inert or oxidizing), at low pressure (around 100mbar) and with an exposure time of 30 seconds maximum is developed here. Micronics metallic coatings on carbon fibers are deposited using different PVD (physical vapor deposition) process. The sample is then heated by Joule effect without control of cooling. So, the material undergoes quenching and keeps the microstructure and chemical composition produced at very high temperature under controlled atmosphere. PVD coatings on carbon fibers are sufficiently continuous and thick to be used as protective coatings during the oxidation tests at high temperature. This test allows studying the diffusion of carbon at the fiber/coating interface and of oxygen to the external environment/coating interface at high temperatures. The aim of this study is to highlight the effect of a modification of microstructure and composition of metallic coatings on the carburation and oxidation kinetic laws.

AP-3 Pulsed Magnetron Sputtering of Hard Amorphous Si-B-C-N Coatings with High Thermal Stability and Oxidation Resistance*,* ***P. Steidl*** *(steidl@kfy.zcu.cz), P. Calta, J. Vlcek, P. Zeman*, University of West Bohemia, Czech Republic

Quaternary Si-B-C-N materials are becoming increasingly attractive due to their possible high-temperature and harsh-environment applications. In this work, hard (22 - 24 GPa) amorphous Si-B-C-N coatings were deposited on various substrates (Si, SiC, steel, WC and WC with 250 nm TiN or CrN interlayers) by pulsed dc magnetron sputtering using a single B_4C-Si target in a 50% Ar + 50% N_2 gas mixture. A fixed 75% Si fraction in the target erosion area, an rf induced negative substrate bias voltage of -100 V, a substrate temperature of 350 °C and a total pressure of 0.5 Pa were held constant during depositions. A planar rectangular (127 x 254 mm^2) unbalanced magnetron was driven by a pulsed dc power supply operating at the repetition frequency of 10 kHz with a fixed 50% duty cycle and the average target power over a period of 470 W, being close to that used by us during a continuous dc magnetron sputtering of Si-B-C-N coatings [1-3]. Here, the aim was to avoid any discharge instabilities leading to possible defects in the coatings and thus, to improve quality of their surface. The high-temperature behavior of the coatings, including their oxidation resistance in air and thermal stability in inert gases up to 1700°C, was characterized by means of high-resolution thermogravimetry, differential scanning calorimetry, X-ray diffraction, Rutherford backscattering spectrometry and elastic recoil detection analysis. Pulsed magnetron sputtering of the B_4C-Si target in Ar atmosphere was performed prior to deposition at the duty cycle of 20%, the substrate temperature ranging from 350°C to 480°C and the substrate bias voltage of -1400 V for up to 30 min to enhance adhesion of the deposited Si-B-C-N coatings to various substrates.

[1] J. Vlcek, S. Hreben, J. Kalas, J. Capek, P. Zeman, R. Cerstvy, V. Perina, Y. Setsuhara, J. Vac. Sci. Technol. A 26, 1101 (2008).

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AP-4 Why Measurement at Higher Temperature is of Great Importance and How the Results Should be Used*,* ***N. Bierwisch*** *(n.bierwisch@siomec.de), L. Geidel, N. Schwarzer*, Saxonian Institute of Surface Mechanics, Germany

It is widely known, that many coating materials show very significant temperature dependence with respect to their mechanical properties, especially with respect to Young's modulus and Yield strength or Hardness.

In the work is 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 it is very important to measure mechanical properties at high temperature.

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. Meaning, the classical Oliver and Pharr method does not suffice. The authors will present the necessary extensions and how they have to be applied,

AP-5 Influence of APS Parameters on the Microstructural Properties of ZrO_2–10% Y_2O_3–18% TiO_2, ***S.L. Liscano*** *(lissug@gmail.com), L.G. Gil,* UNEXPO, Venezuela*, M.H. Staia,* Universidad Central de Venezuela*, M. Prato,* UCV, Venezuela*, A.S. Scagni*, Plasmatec Ingenieros CA, Venezuela

Experimental design is an effective method for conducting a reduced number of experiments in order to obtain the optimum spraying conditions and enhance the thermally sprayed coatings properties. In the present study, a 2^3 factorial design experiment was used to establish the effects of the variables on the coatings quality in relation to the coating microstructure (porosity and hardness). Response surface methodology (RSM) was employed to describe the empirical relationships among variables such as the arc current, the arc voltage and the powder feed rate. The maps obtained allowed the selection of the optimum operating conditions able to achieve the desired microstructural characteristics of these coatings deposited by APS. The analysis of the results indicates that the powder feed rate have the higher significant effect on both porosity and microhardness of these coatings.

AP-6 EBSD Study of Crystallographic Identification of Fe-Al-Si intermetallic Phases in Al-Si Coating on Cr-Mo Steel, ***W.-J. Cheng*** *(d9603505@mail.ntust.edu.tw), C.-J. Wang*, National Taiwan University of Science and Technology, Taiwan

5Cr-0.5Mo steel was coated by hot-dipping into a molten Al-10 wt.% Si bath at 700°C for 10, 60, 120 or 180 seconds. The identification of the phases in the Fe-Al-Si intermetallic phases formed in the aluminide layers during hot-dipping was carried out by using a combination of scanning electron microscope (SEM) with energy dispersive X-ray spectroscopy (EDS), X-ray diffraction (XRD) and electron backscatter diffraction (EBSD). The EDS results show a τ_5-Al_7Fe_2Si phase, which exhibited 2 distinct morphologies, small particles widely dispersed and a continuous layer. Also revealed by EDS were τ_6-Al_4FeSi and τ_4-Al_3FeSi_2 phases, which showed plate-shaped morphology, in an Al-Si topcoat. However, the XRD results show the intermetallic phases in the aluminide layer were composed of outer cubic τ5-$Al_7(Fe,Cr)_2Si$ and inner hexagonal τ_5-Al_7Fe_2Si. EBSPs and Mapping functions in EBSD helped to clarify the confused phase identifications yielded by EDS and XRD. In this way, the small intermetallic particles and the continuous intermetallic layer were identified as cubic τ_5-$Al_7(Fe,Cr)_2Si$ and hexagonal τ_5-Al_7Fe_2Si, respectively, and the plate-shaped intermetallic phase was identified as monoclinic τ_6-Al_4FeSi and tetragonal τ_4-Al_3FeSi_2 with the same metallographic morphology. EBSD proved to be a very effective technique for local phase identification of aluminide layers with complicated multiphase morphologies.

AP-7 CMAS Attack of Erbia Doped EB PVD TBCs, ***R.G. Wellman*** *(R.Wellman@cranfield.ac.uk)*, Cranfield University, United Kingdom

In recent years under certain operating conditions calcium, magnesium, alumino silicate (CMAS) attack of thermal barrier coatings (TBCs) has become a concern. CMAS attack is essentially a high temperature corrosion process which initiates at temperatures above 1240°C, the temperature at which CMAS, deposited on turbine blades during operation, melts and infiltrates the open columnar structure of the thermal barrier coating. The mechanism of attack, which involves the dissolution of the TBC and the re-precipitation on cooling, is fairly well understood.

This paper looks at the effects of CMAS attack on erbia doped electron beam (EB) physical vapour deposited (PVD) TBCs and correlates it to previous work on standard 8wt% yttria partially stabilised zirconia. The effects of time and temperature on the degradation of the coatings have been examined using a combination of scanning electron microscopy, Raman spectroscopy and XRD analysis. Temperatures of 1250°C to 1400°C for 1-12hrs have been studied for different initial CMAS deposit concentrations and the depth of penetration and the degree of phase transformation, as a result of both leaching and re-precipitation, have been studied. Finally the concept of a “safe” limit of CMAS deposition as a function of time and temperature is also discussed.

AP-8 Oxidation Resistance and Mechanical Properties of Quasi-Amorphous Ta-Si-N Sputtered Films, *C.-K. Chung (ckchung@mail.ncku.edu.tw), T.-S. Chen, N.-W. Chang, S.-C. Chang,* ***M.-W. Liao***, National Cheng Kung University, Taiwan

The quasi-amorphous Ta-Si-N thin films were generally applied to diffusion barriers for Cu interconnections due to the good diffusion barrier property and low resistivity. Also, the oxidation resistance and mechanical properties at high temperature are important issues for barrier development . In this paper, quasi-amorphous Ta-Si-N thin films were fabricated by using reactive magnetron co-sputtering at different Si/Ta power ratios and nitrogen (N_2) to total gas ($Ar+N_2$) flow ratios ($FN_2\%=FN_2/(FAr+FN_2)$ x 100%). Both levels of high vacuum furnace annealing (FA) and low vacuum rapid thermal annealing (RTA) at 600 -900 °C were performed to investigate the oxidation resistance and stability of films. The microstructure, surface morphology and mechanical property of the Ta-Si-N thin films were characterized by grazing incidence X-ray diffraction, scanning electron microscope and nanoindenattion, respectively. All Ta-Si-N thin films at 900 °C for 1 h under high-vacuum FA (6.5 x 10^{-3} Pa) only produce crystalline Ta-Si-N solid solution while the δ-TaO phase were produced under RTA at 750- 900 °C for 1 min at 2.6 Pa. Experimental results showed that the high silicon content was beneficial for the oxidation resistance of Ta-Si-N films. The islands or particles of oxide were formed on the surface morphology of films at high FN_2% after RTA. In brief, the oxidation resistance of Ta-Si-N films increased with increasing level of vacuum and silicon content. The harnesses of all Ta-Si-N films measured by nanoindentation were between 12.4 and 18.2 GPa. Correlation between the microstructure of films and oxidation resistance, mechanical properties of quasi-amorphous Ta-Si-N films was established and discussed.

AP-9 A Study of High Temperature Oxidation Behaviors of Zr-Si-N Nanocomposite Thin Films at 900^{o}C, ***J.-W. Lee*** *(jefflee@mail.mcut.edu.tw),* Mingchi University of Technology, Taiwan, *Y.-B. Lin,* Tungnan University, Taiwan, *L.-C. Chang,* Mingchi University of Technology, Taiwan, *F.-B. Wu*, National United University, Taiwan

The high temperature oxidation performance of nanocomposite coatings becomes an important issue recently. In this study, the ZrN and Zr-Si-N nanocomposite thin films have been prepared by a bipolar asymmetric pulsed DC magnetron sputtering system. The thin films with silicon content ranging from 2.2 to 10.4 at.% were prepared by adjusting the Si target power. An amorphous and featureless microstructure was observed on the coating with high silicon contents. A thermo gravity analyzer was adopted to study the oxidation resistance of thin films at 900^{o}C in static air. Surface and cross-sectional morphologies of coatings before and after oxidation tests were examined with a field emission scanning electron microscope, respectively. The crystalline phases of thin films were also analyzed with an X-ray diffractometer. It is observed that the high temperature oxidation resistance of Zr-Si-N thin films is better than that of pure ZrN coating. In general, the high temperature oxidation resistance of Cr-Si-N nanocomposite thin films increases with increasing Si content. The microstructure and phase evolutions were discussed in this work.

AP-11 Sol-Gel Thermal Barrier Coatings : Optimization of the Manufacturing Route and Durability Under Cyclic Oxidation, *J. Sniezewski, Y. LeMaoult, P. Lours (lours@enstimac.fr),* Université de Toulouse, ICA Mines-Albi, France, *V.M. Bekale, D. Monceau,* ***D. Oquab***, Université de Toulouse CIRIMAT-ENSIACET, France, *J. Fenech, F Ansart, J.-P. Bonino*, Université de Toulouse CIRIMAT-UPS, France

A new promising and versatile process based on the sol-gel transformation, i.e. the transition from a liquid phase, namely the sol, to a solid phase, namely the gel, by a series of hydrolysis and condensation reactions, has been developed to deposit yttria-stabilised thermal barrier coatings. The non-oriented microstructure with randomly structured pore network, resulting from the soft chemical process, is expected to show satisfactory thermomechanical behavior when the TBC is cyclically oxidized.

First stage of the research consists in optimizing the processing route to generate homogeneous microstructure and controlled surface roughness. The objective is to reduce as much as possible the size and depth of the surface cracks network inherent to the process. Indeed, the durability of the TBC when cyclically oxidized strongly depends on the sharpness of those cracks that concentrate thermomechanical stresses and generate detrimental propagation resulting in spallation.

Cyclic oxidation tests are performed using a newly developed equipment able to establish controlled thermal gradient through the thickness of the TBC and instrumented with CCD cameras to monitor in a real time basis the mechanism of crack propagation and spallation. The impact of various parameters, either directly related to the processing route, e.g. the intimate microstructure of the TBC and the TBC thickness, or to the thermal loading, e.g. the magnitude of the through thickness thermal gradient, the oxidation temperature and the cumulated hot time, on the durability of the TBC is investigated.

Hard Coatings and Vapor Deposition Technology
Room: Golden Ballroom - Session BP

Symposium B Poster Session

BP-1 Effects of Substrate Radial Positioning for TiAlN Films Deposited by an Inverted Cylindrical Magnetron Sputtering System, ***H. Abu-Safe*** *(habusaf@uark.edu),* Lebanese American University, Lebanon, *M. Gordon,* University of Arkansas, *K.N. Abushgair*, Albalqa Applied University, Jordan

In a previous study, the effects of substrate vertical positioning for TiAlN films deposited using an unbalanced inverted cylindrical magnetron sputtering system were analyzed. Results indicated that, due to the unbalanced magnetic fields, the substrates at the different axial locations in the deposition chamber were exposed to varying ion bombardment rates. This variation created a competition among re-sputtering, amorphitization, and atom surface diffusion, and the results of this competition affected the final film properties. Preliminary evidence also shows that the substrate’s radial location at a given axial position also affects the film’s composition. The TiAlN films for this study were deposited on glass and silicon substrates. The substrates were positioned on a vertical platform between the two targets at three different radial distances (0, 50, and 120 mm from the central axis of the targets). In addition, at each distance the substrates were positioned at three different angles (0, 45, and 60˚ measured from the vertical platform). Titanium and Aluminum cylindrical targets were used and the sputtering power during deposition was maintained at 2 kW for each target. The argon and nitrogen gas flow rates were kept at 75 and 40 sccm, respectively. No biasing voltage was applied during deposition. The films’ elemental compositions at the different radial distance were analyzed using energy dispersive X-ray spectroscopy. The X-ray diffraction measurements were used to determine the crystal structure of the films. Scanning electron microscope images were used to indicate the morphology for all samples.

BP-2 Pressure Dependent Stability of Cubic and Wurtzite Phases Within the TiN-AlN and CrN-AlN Systems, ***D. Holec*** *(david.holec@unileoben.ac.at), F. Rovere, P.H. Mayrhofer,* Montanuniversität Leoben, Austria, *P.B. Barna*, Hungarian Academy of Sciences, Hungary

Hard coatings based on $Ti_{1-x}Al_xN$ and $Cr_{1-x}Al_xN$ are well established and routinely used for various industrial applications due to their outstanding properties like high hardness, wear and corrosion resistance. While TiN and CrN crystallize in the cubic B1 structure, AlN is stable in the wurtzite B4 form. Consequently, there exist cubic (low AlN mole fraction) and wurtzite (high AlN mole fraction) stability ranges. It has been shown that the desired coating properties for machining and wear protective applications are obtained for their cubic allotrope. It is therefore of great interest to understand how various parameters affect the stability range of the cubic phase.

Ab initio calculations of the total energy for the cubic and wurtzite phases allow to estimate the maximum mole fraction, $x_{\max}$, of AlN while maintaining the desired cubic phase of the $Ti_{1-x}Al_xN$ and $Cr_{1-x}Al_xN$ systems. In this paper we investigate the influence of pressure on $x_{\max}$. Both systems exhibit a strong dependence of their cubic and hexagonal phase stability ranges on the applied pressure, or the inherent build-in stresses. Under a compression of 4 GPa an increase in $x_{\max}$ by 0.1 AlN mole fraction is obtained for both systems, $Ti_{1-x}Al_xN$ and $Cr_{1-x}Al_xN$. Consequently, stress-related effects cannot be neglected in the discussion of the wide spread of the experimental estimations of $x_{\max}$.

BP-3 Oxidation Resistance and Mechanical Properties of TiAlN/CrAlYN/TiAlN Three-Layer Film Deposited by Cathodic Arc Ion Plating Method, ***M. Takahashi*** *(hatti_porno@yahoo.co.jp), N. Fukumoto,* Keio University, Japan*, H. Hasegawa,* Okayama University, Japan*, T. Watanabe,* Kanagawa Academy of Science and Technology, Japan*, T. Suzuki*, Keio University, Japan

Researches on multilayer films to extend the life of cutting tools have been widely reported and have shown distinct results. In this research, TiAlN/CrAlYN/TiAlN three-layer films were deposited by conventional cathodic arc ion plating (AIP) method from two alloyed targets of TiAl and CrAlY. The designing of three-layer film was carried out based on the following factors; a) top-layer TiAlN for improvement in hardness and abrasion, b) middle-layer CrAlYN for improvement in oxidation resistance, c) base-layer TiAlN for improvement in adhesion strength to substrate. From past researches, the advantage of yttrium(Y) addition has been proposed [1] and similar results have been observed in our laboratory. However, the Y-added films show lower hardness compared to Ti-based nitrides because of the Cr-based nitrides. Therefore, if it is possible to increase the hardness of the Y-added film further possibility will arise for these films to be used in cutting tools. The effect of layering to hardness and oxidation resistance of the film was investigated by X-ray, electron microscope, and micro-hardness analysis. For comparison, monolayer TiAlN and CrAlYN films were deposited.

The three-layer film showed a high hardness of 28.4 GPa, even with insertion of softer CrAlYN with a hardness of 22.8 GPa. As a result, this would substantially reduce the abrasion for this three-layer film. The oxidation resistance was investigated by annealing the samples in air at 700,800,900 °C for one hour. X-ray results revealed that the three-layer films showed better oxidation resistance than TiAlN film. The three-layer film even annealed at 900 °C, showed strong peaks of nitride still existing . Hence, it was indicated that TiAlN/CrAlYN/TiAlN three-layer film was able to exploit the benefits of TiAlN monolayer film and CrAlYN monolayer film. Further oxidation experiment of the three-layer film is evaluated by cross-sectional observation and in-depth elemental distribution analysis by SEM and GDOES.

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BP-4 Mechanical Properties of Ti-Al-Si-N Thin Film Coatings Prepared by Filter Vacuum Arc and Sputtering Techniques, ***J.-K. Kim*** *(kjongk@kims.re.kr), S. Lee, J.-Y. Lee,* Korean Institute of Materials Science, Korea*, I. Svadkovski,* Belarussian State University of Informatics and Radioelectronics, Russia*, J.-D. Kwon, D.-G. Kim*, Korean Institute of Materials Science, Korea

Nano-composite deposition technology becomes an important issue in tribology industries due to excellent mechanical properties of nano-composite films. For nano-composite deposition, various co-deposition techniques are proposed because multi components coating is required to make nano-composite films. We have deposited Ti-Al-Si-N nano-composite films using filter vacuum arc and sputtering techniques to realize high hardness as well as thermal stability. Arc and sputter cathodes are $Ti_{50}Al_{50}$ alloy and Si, respectively. Argon and nitrogen gas are injected into arc cathode and process chamber. Deposition rate is changed from 9 nm/min to 14 nm/min as the variation of Si sputter power. Sputter current density (from 0 mA/cm^2 to 2.5 mA/cm^2) are modified to control Si content in Ti-Al-Si-N films. The Si content of Ti-Al-Si-N films was measured by electron micro probe analyzer (EMPA), which showed the results from 0.2% to 4.7%. In order to investigate the structural dependance of the films, X-ray diffractometer (XRD) and scanning electron microscopy (SEM) were adapted. In addition, adhesion strength, friction coefficient and nano-indentation are also obtained to investigate the mechanical properties of the samples.

BP-5 High Temperature Tribological Characterisation of AlTiISiN Coatings Produced by CAE-PVD Techniques, ***F. Fuentes*** *(gfuentes@ain.es), E. Almandoz, R. Martinez, R.J. Rodriguez,* Asociación de la Industria Navarra, Spain*, J. Caro, M. Vilaseca,* CTM Centre Tecnologic, Spain*, J. Fernández*, Asociación de la Industria Navarra, Spain

This study reports on the tribological characterization of TiAlSiN quaternary films deposited by cathodic arc evaporation PVD techniques, and the effects of the testing temperature on the wear mechanisms. The coatings have been produced in a commercial METAPLAS PVD chamber equipped with 6 arc sources. The coatings were deposited on mirror polished DIN 1.2344 hot work steels. Ti and AlSi cathodes were simultaneously evaporated at different arc currents and N_2 total pressures, in order to obtain different film properties. The micro-structure of the coatings has been evaluated using electron microscopies and x-ray diffraction techniques. All the films exhibited dense fine grained cubic fcc poly-crystalline microstructures. It was observed that the films exhibited lesser intense diffraction features as the aluminum content increased.

The plastic hardness of the coatings depends on the film chemical composition. Thus values between 39 GPa and 27 GPa were measured. The tribological tests have been conducted in a ball on disc configuration at room temperature, 200ºC, 400ºC and 600ºC using alumina balls as counter surfaces. At room temperature, the TiAlSiN films show wear rates comparable to these characteristics of TiN or TiAlN coatings, tested under the same conditions. Conversely, the wear rates of the TiAlSiN coatings measured at 200 and 400ºC are lesser than this measured at RT. In fact, the alumina balls worn off significantly during the tests, whilst the wear tracks on the coated discs were barely measurable. At 600ºC, however, a significant wear rate was observed. These results may be consistent with the formation of an oxide surface on the contact area that enhanced the wear resistance of the films when tested at high temperatures.

Finally, TiAlSiN coated hard metal curved surfaces have been tested against stainless steel (AISI316) planar counter surfaces to evaluate both, the wear of the coatings, and the adhesion of Fe on the hard metal surfaces. The rate of wear and adhesion will be compared with previous coating materials such as CrN, or gradient CrCN studied under similar experimental conditions [1].

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BP-7 Study on Characterization of Superlattice CrN/AlN Coating in Aluminum Alloy Die Casting Die Application, *D.-Y. Wang (jackaljr@mdu.edu.tw),* ***H.-C. Lin****, W.-C. Chen*, MingDao University, Taiwan

In this study, the superlattice CrN/AlN coating was synthesized by using unbalanced magnetron sputtering technique, using Cr (99.95wt%) and Al (99.95wt%) elemental cathodes which is improve the limit of the electroplate CrN with the ultrahigh hardness and have excellent oxidation resistance. When applied to cast Al-alloy melt into molded parts, aluminum die casting was always faced harsh conditions, such as corrosion, erosion and surface damage problem. Many of aluminum die casting dies have to bear high temperature at 600°C. The CrN coating was replaced the hard chrome plating for the environmental. The application of the single layer was only allowed under 600°C, which can't effectively meet the conditions for the use of aluminum alloy die casting dies.

The microstructure and mechanical properties of the coatings were analyzed by using the transmission electron microscopy (TEM), X-ray diffraction(XRD), scanning electron microscopy (SEM) X-ray photoelectron spectroscopy (XPS), and molten Al alloy dipping test was also conducted to evaluate the performance of CrN/AlN coating by wear test.

BP-8 Mechanical Properties of Multilayered $Al_xCr_{1-x}N$/ZrN Coatings Synthesized by a Cathodic-Arc Deposition Process, *Y.-Y. Chang (yinyu@mail2000.com.tw),* ***C.-Y. Hsiao***, Mingdao University, Taiwan

ZrN, $Al_xCr_{1-x}N$ and multilayered $Al_xCr_{1-x}N$/ZrN coatings with superlattice structure were deposited on tungsten carbides (WC) materials by using cathodic-arc evaporation with plasma enhanced duct equipment. Zirconium and AlCr alloy (50/50 and 70/30 at. % ratio) cathodes were used for the deposition of $Al_xCr_{1-x}N$/ZrN coatings. During the coating process of multilayered $Al_xCr_{1-x}N$/ZrN, ZrN was deposited as an interlayer. The total cathode current of both Zr and AlCr targets was controlled at 150 A. With different cathode current ratios [AlCr/(Zr+AlCr)] of 0.4, 0.5, and 0.6, the deposited multilayered $Al_xCr_{1-x}N$/ZrN coatings possessed different chemical contents and periodic thicknesses. The effect of alloy content (Al, Ti, and Zr) and periodic thickness on the mechanical properties of $Al_xCr_{1-x}N$/ZrN coatings were investigated. In this study, chemical composition of deposited coatings was evaluated by a wavelength dispersive X-ray spectrometer (WDS). Field emission scanning electron microscope (FESEM) equipped with secondary electron imaging (SEI) and backscattered electron imaging (BEI) detectors, and X-ray diffraction (XRD) were used to characterize the crystal structure and the residual stress of the deposited films. High resolution transmission electron microscope (HRTEM) and scanning transmission electron microscope (STEM) were used for nanolayered structure analyses of the multilayered $Al_xCr_{1-x}N/ZrN$ coatings. Hardness, Young's modulus and fracture toughness of the deposited coatings were determined by nano-indentation and Vickers indentation methods.

BP-9 Growth of AlN-Based Nanocomposites Grown by Pulsed Laser Deposition and Sputtering, *H. Zoubos,* RWTH Aachen University, Germany, ***P.A. Patsalas*** *(ppats@cc.uoi.gr)*, University of Ioannina, Greece

AlN is a very well know very wide bandgap semiconductor which exhibits absorption in the far UV spectral range, while being purely transparrent in the visible spectal region. In addition, it has excellent mechanical properties and substantial chemical and metallurgical stability. The combination of its properties makes AlN a promising matrix material for multifunctional, self-monitored coatings and/or durable optical sensors based on metal nanoparticles embedded into AlN and exhibiting surface plasmon resonance (SPR).

In this work we deal with the growth of AlN nanocomposite films with Ag inclusions (AlN:Ag) on Si(100) and polycrystalline sapphire by Pulsed Laser Deposition (PLD) and dual-cathode confocal magnetron sputtering. The films' structural properties, such as nanoparticle size and distribution, were studied in relation to the growth method and the used parameters. High resolution transmission electron microscopy, x-ray diffraction, and optical reflection spectroscopy (ORS) were employed in order to determine the film composition, inclusions' crystal structure and the optical properties, respectively. *In-situ* Auger Electron Spectroscopy (AES) has been used for the chemical analysis of the grown films.

We investigate the thermodynamic and the kinetic factors that determine the phase separation and the formation of nanocomposites or the dilution of Ag into the AlN matrix. Especially in the case of sputter-deposited films we investigate two growth approaches: (a) co-deposition of Ag and AlN using two magnetron sources, and (b) multilayer sequential growth of AlN and ultra-thin Ag layers (as thin as to approach the island coalescence threshold) and post-growth annealing.

The employed Ag nanoclusters had average sizes ranging between 3-10 nm. The critical parameters determining the nanoparticle size and distribution and the decisive role of the latter on the optical performance of AlN:Ag nanocomposite films are established. Thus, ORS has revealed that strong SPR exist in films with well defined metal inclusions of narrow size distribution.

BP-10 Effect of Carbon on the Microstructure and Properties of Cr-C-N Coatings Deposited by Pulsed Closed Field Unbalanced Magnetron Sputtering, *Z.L. Wu,* Dalian University of Technology, China, ***J. Lin****, J.J. Moore,* Colorado School of Mines, *M.K. Lei (surfeng@dlut.edu.cn)*, Dalian University of Technology, China

Nanocrystalline Cr-C-N coatings were deposited using pulsed closed field unbalanced magnetron sputtering at a 20% nitrogen flow rate percentage (f_{N2}). T he chromium target was powered at 1000 W, whereas the power on the graphite target was varied from 600 to1400 W to achieve different carbon contents . The microstructure and crystal phase of the coatings were investigated using transmission electron microscopy, scanning electron microscopy and glancing incident angle x-ray diffraction. The typical Cr-C-N coating structure contains nanocrystalline Cr_7C_3, CrN_x compounds embedded in an amorphous carbon and CN matrix. The CrN_x phase changed from β-Cr_2N to a mixture of β-Cr_2N and c-CrN, and then to the c-CrN when the carbon content was increased in the Cr-C-N coatings. Mechanical and tribological properties of the coatings were determined by nanoindentation and ball-on-disk wear testing. It was found that the hardness and H/E ratio of Cr-C-N coatings increased as the carbon content was increased. The Cr-C-N coatings exhibited a coefficient of friction in the range of 0.35-0.50 by sliding against a WC-Co ball.

BP-11 Shielded Cathodic Arc Deposition of Nanocomposite a-C:Cr Coatings, *L. Yate (l.yate@ub.edu),* ***L. Martinez-de-Olcoz****, J. Esteve, A. Lousa*, Universitat de Barcelona, Spain

Chromium incorporated amorphous carbon (a-C:Cr) coatings were deposited onto silicon substrates by cathodic vacuum arc deposition using a Cr target in an Ar/C_2H_2 gas mixture atmosphere. A linear magnetic shield was employed to reduce the macroparticle density in the films. Various negative bias voltages ranging from 50 to 450 V were applied to the substrates. The effectiveness of the magnetic shield was studied by atomic force microscopy (AFM). X-ray diffraction (XRD) analysis showed that amorphous structures are formed in all cases. High resolution transmission electron microscopy (HRTEM) revealed a nanocomposite structure with chromium carbide particles embedded in a carbon matrix. X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy were used to determine the carbon bonding and to study the presence of different forms of free amorphous carbon. The Raman spectra were decomposed into four single Gaussians and the results are discussed in terms of the ratio of the areas of the two D bands to the areas of the two G bands, I(D)/I(G). The results showed that the I(D)/I(G) ratio is proportional to the negative bias voltage.

Acknowledgements

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BP-12 Thermal Stability and Corrosion Performance of Cr-B-N Coatings Deposited Using Reactive Arc-Evaporation, ***K. Polychronopoulou*** *(kyriakip@ucy.ac.cy), A. Hadjiafxenti, C.G. Rebholz,* University of Cyprus, *J. Neidhardt,* Montanuniversität Leoben, Germany, *K. Kanakis,* University of Sheffield, United Kingdom, *M. O'Sullivan,* PLANSEE Composite Materials GmbH, Germany, *A. Reiter,* OC Oerlikon Balzers AG, Liechtenstein, *A. Matthews,* The University of Sheffield, United Kingdom, *C. Mitterer*, Montanuniversität Leoben, Austria

Ceramic hard coatings are commonly applied as protective overcoats on tools and components to enhance their performance. Although most nitride coatings deposited by physical vapour deposition (PVD) are chemically inert, one of the main obstacles for wider application has been the sensitivity to crevice corrosion and higher costs compared with electrochemically deposited coatings. Regardless the various applications of CrN-based systems, their decomposition routes and oxidation behavior is still not well resolved in literature.

In the present study the thermal stability and corrosion performance of arc-evaporated nanocomposite Cr-B-N coatings deposited from $CrB_{0.2}$ compound targets at 500°C in a commercial Oerlikon Balzers RCS system are explored. During synthesis the total pressure ($Ar+N_2$) was kept constant at 2 Pa, while the N_2 fraction was varied between 0 and 1 (0, 0.15, 0.25, 0.5 and 1). Differential scanning calorimetry (DSC) studies in Ar up to 1500ºC using different heating rates give a deeper understanding of the decomposition kinetics for the materials under study as a function of nitrogen content. In the as-deposited state, coatings are nanocrystalline with Cr and Cr_2B phases without nitrogen addition, with a Cr(N) solid solution, Cr_2B and Cr_2N at 0.15 N_2, and finally with CrN and an amorphous BN phase at N_2 fractions above 0.5, respectively. Coatings deposited at low N_2, namely 0.15 N_2 and 0.25 N_2, revealed exothermic DSC peaks at 750ºC, corresponding to film recovery and recrystallization processes. The decomposition for coatings deposited at 0.5 and 1 N_2 starts at 1000ºC with a phase transformation of fcc-CrN to hcp-Cr_2N. These results corroborate with thermogravimetric analysis (TGA) mass losses observed. For studying the oxidation behaviour, DSC/TGA studies up to 1500ºC were conducted in an O_2/Ar atmosphere. The differences observed, attributable to different structure, morphology and composition among the coatings investigated, are discussed.

The corrosion resistance of CrB_xN_y coatings, studied using potentiodynamic corrosion tests in 3.5% NaCl aqueous solution, is higher than the uncoated steel substrate, with passive behaviour over a large voltage range (−200 to +700 mV). Nanocomposite CrB_xN_y coatings deposited at 0.5 N_2, and consisting of nc-CrN+a-BN phases show the lowest passive current density of 7×10−6 A cm^{-2} (8×10^{-5}A cm^{-2} for CrN).

BP-13 Corrosion Characteristics of CrN/NiP-Based Dual Layer Sputtering Coatings, *Y.-Y. Li,* ***H.-H. Huang****, F.-B. Wu (fbwu@nuu.edu.tw)*, National United University, Taiwan

The CrN top layer with NiP-based interlayer was deposited on AISI 420 stainless steel with magnetron sputtering system. The variation in microstructure of the CrN, NiP-based, and dual coatings were controlled by process and post-annealing temperatures. The corrosion behavior the CrN/NiP-based composite coating in 3.5M NaCl solution was investigated by electrochemical impedance spectroscopy (EIS). The results of Nyquist and Bodes curves showed that there was a correlation between the electrochemical properties and corrosion mechanism of CrN/NiP-based composite coatings. In particular, the amorphous and crystallized structure of the NiP interlayer was significantly different. The interfacal reactions between the solution and CrN top layer or the CrN top layer and NiP-based interlayer could be explained with the equivalent circuit models. The corrosion resistance of the dual CrN/NiP-based coating could be enhanced through microstructure control on the NiP-based interlayer.

BP-15 Thermal Stability of CrZrN/Si_3N_4 Multilayer Coatings Synthesized by Closed Field Unbalanced Magnetron Sputtering, *Y.S. Kim,* National Core Research Center for Hybrid Materials Solution, Korea, ***S.-Y. Lee*** *(sylee@kau.ac.kr),* Korea Aerospace University, Korea, *J.J. Lee,* School of Materials Science and Engineering, Korea, *W.Y. Jeung*, KIST, Korea

Cr-Zr-N coatings have been reported to have not only much improved mechanical properties, but also a very low surface roughness with increasing Zr content. However, above 500 ℃, the Zr content causes some problems because of the presence of the zirconium oxide on the surface of Cr-Zr-N coatings. In this study, for the high temperature applications, CrZrN/Si_3N_4 coatings with various period between CrZrN and Si_3N_4 coatings were synthesized by closed field unbalanced magnetron sputtering (CFUBMS) and their chemical composition, crystalline structure, morphology, mechanical properties, and thermal stability were characterized by glow discharge optical emission spectroscopy (GDOES), X-ray diffraction (XRD), scanning electron microscopy (SEM), atomic force microscopy (AFM), nanoindentation, and thermo gravimetric analysis (TGA). Also, the thermal stability of the CrZrN/Si_3N_4 coatings was evaluated by annealing the thin coating s at temperatures between 500℃ and 1200℃ for 30 min in air. The experimental results revealed that the CrZrN/Si_3N_4 coatings exhibit higher thermal stability compared to that of Cr-Zr-N coatings with increasing Si content. Detailed experimental results will be presented.

BP-16 Effect of (Ti,Zr) Interlayer on the Structure and Properties of (Ti,Zr)N Thin Films, *Y.-W. Lin,* Instrument Technology Research Center, Taiwan, *J.-H. Huang,* ***G.-P. Yu*** *(gpyu@mx.nthu.edu.tw)*, National Tsing Hua University, Taiwan

The purpose of this study was to investigate the effects of (Ti,Zr) interlayer on the structure and properties of overlaying (Ti,Zr)N thin films. Films were deposited by reactive magnetron sputtering on substrates with varying composition of (Ti,Zr) interlayer. The single layer of (Ti,Zr) thin film was coated on the AISI 304 stainless steel initially. The composition of (Ti,Zr) interlayer was analyzed by X-ray Photoelectron Spectroscopy (XPS) and Rutherford Backscattering Spectrometer (RBS). The (Ti,Zr)N thin films was coated on the substrate of (Ti,Zr)/ 304 stainless steel. The diffraction peak of (Ti,Zr)N was influenced with different composition of (Ti,Zr) interlayer. The hardness of the (Ti,Zr)N films, ranging from 31~37 GPa. The results of potentiodynamic scan in both 5% NaCl and 0.5 M H_2SO_4+ 0.05 M KSCN solutions indicated that packing factor was more effective than film composition on the corrosion resistance of the coatings. Furthermore, adding a (Ti,Zr) interlayer could effectively protect the substrate from the corrosive medium, if the packing factor was sufficiently high. Experimental results showed that the corrosion current density I_{corr} and passive current density I_p increased with increasing polarization scan rate for all specimens. Compared with the bare substrate, the I_{corr} and I_p for the coated specimens decreased at least 1 order of magnitude. The corrosion power Q, i.e. the integrated electric charge per unit area of the specimen during potentiodynamic polarization test, was an effective index to evaluate the corrosion resistance of the coated stainless steel substrate.

BP-17 Resistance to Harsh Environnements of Ti-Zr-N Coatings for Future Nuclear Reactor Applications, ***G. Abadias*** *(gregory.abadias@univ-poitiers.fr),* University of Poitiers, France, *A.V. Sevriuk, S.V. Zlotski, V.V. Uglov,* Belarussian State University, Belarus, *K.K. Kadyrzhanov, S.B. Kislitsin, M.V. Koloderdin M.V*, National Nuclear Center of Republic of Kazakhstan

In order to protect structural steels (SS) used in fast neutron high temperature reactors from radiation induced defects and improve their resistance to irradiation-induced embrittlement, ceramic-based protective coatings are investigated as potential candidates. Among other materials, transition metal nitride coatings exhibit large hardness (> 20 GPa), chemical inertness, structural and thermal stability and may therefore be envisaged as a material of choice to surround the fuel. Preliminary measurements have been performed on Ti-Zr-N coatings to study their resistance to Xe ion irradiation at relatively low energy (360 keV), as Xe is a main product of reaction fissions in nuclear reactors.

In this study we investigate the resistance of Ti-Zr-N and Ti-Cr-N coatings to harsh environnements, including exposure to corrosive media and ion irradiation. Ti-Zr-N films, with thickness of~ 1 µm, were deposited by either dc reactive magnetron sputtering or vacuum cathodic arc deposition on SS and stainless steel substrates. The composition and crystalline structure of the as-deposited coatings was analyzed by energy dispersive analysis of X-rays (EDX) and X-ray diffraction (XRD), respectively. Ion irradiation with He, Kr and Xe ions in the range 20 keV-200 MeV was performed at the Nuclear Center of Kazakhstan. The effect of the ion fluence on the resulting structure, surface morphology and mechanical properties is reported. Electrochemical potentiodynamic polarization method was used to test the corrosion resistance of these coatings in acidic and basic media.

BP-19 Evolution of the Crystallographic Preferred Orientation of NbN Films by Grazing Angle X-ray Diffraction, ***G. Ramirez*** *(enggiova@hotmail.com), S.E. Rodil, J.G. Gonzalez-Reyes, S. Muhl,* Universidad Nacional Autónoma de México, Mexico, *E. Camps, L. Escobar-Alarcon,* Instituto Nacional de Investigaciones Nucleares, Mexico, *J.L. Benitez*, Universidad Nacional Autónoma de México, Mexico

Crystallographic texture in thin films, i. e. the preferred orientation of particular crystal planes relative to the film substrate, is a common feature in thin films. Since many of the materials properties (dielectric constant, elastic modulus, etc) are typically anisotropic, the properties obtained for thin films depend on the preferred orientation (PO). For metal nitrides, such as niobium nitride (NbN), it has been shown that the preferred orientation results as a combination of different deposition parameters; thickness, plasma density and ion energy [1]. These parameters affect the overall free energy of the film, i. e,. the balance between surface and strain energy defining one PO and in consequence the film properties are modified. Most of the studies reporting the change in the PO of hard metal nitride thin films use cross-section transmission electron images to demonstrate that the PO changes from [100] to [111] as the thickness increases. In this work, we have deposited 2 µm NbN thin films by magnetron sputtering and by doing grazing angle X-ray diffraction (XRD) at different incidence angles (1 to 16°), it was possible to observe the variation in the preferred orientation. The spectrum at very low incidence angle shows that the 2 µm film has a mixture PO [111] plus [100] with a intensity ratio close to 1:1. As the incidence angle increased, the intensity of the [100] increased, while the [111] decreased, so the ratio was 10 to 1. This result suggest that for the deposition conditions used, 2 microns is close to the critical thickness where the PO changed from [100] to [111]. Similar studies were done for NbN films of different thickness to show that using grazing angle XRD as a function of the incidence angle, it is possible to study the evolution of the preferred orientation in thin films. The mechanical properties of the NbN films were also studied by nanoindentation and correlated to the XRD data.

[1] S.E. Rodil, J.J. Olaya, S. Muhl, B. Bhushan, G. Wei. Surface & Coatings Technology 201 (2007) 6117–6121

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BP-20 TiCN Thin Films Grown by the Simultaneous Laser Ablation of Two Targets, ***E. Camps*** *(enrique.camps@inin.gob.mx), L. Escobar-Alarcon, S. Romero,* Instituto Nacional de Investigaciones Nucleares, Mexico, *S. Muhl, I. Camps,* Universidad Nacional Autónoma de México, Mexico, *D.A. Solis-Casados*, CIQS-UAEM, Mexico

In this work we propose the simultaneous ablation of two different targets in a reactive atmosphere in order to prepare thin films of a ternary compound. Particularly, titanium carbonitride (TiCN) thin films were deposited combining two crossed plasmas, produced ablating titanium and graphite simultaneously, in an Ar/N_2 atmosphere. Films were deposited at room temperature onto Si (100) and AISI 4140 steel substrates. Individual and combined plasmas were characterized, in the substrate position, by the Optical Emission Spectroscopy and Langmuir probe techniques in order to determine the plasma parameters, that is to say, the excited species present in the plasmas, the mean kinetic ion energy and the plasma density. In these experiments, the parameters of the titanium plasma were kept constant, meanwhile the parameters of the carbon plasma were varied in order to study their influence, on the char acteristics of the deposited films . The structure and composition of the films have been analyzed by X-ray Diffraction, Raman Spectroscopy and Elastic Forward Analysis. Mechanical properties, such as nanohardness, and adhesion of the films were also measured. The experimental results showed that the TiCN films can be deposited in the form of a composite of small TiN crystallites inmersed in a amorphous CN matrix, or it can form the TiCN compound, depending on the plasma parameters used in the experiment. It was found that the hardness increases with the carbon ion energy and plasma density, reaching a maximum hardness of about 33 GPa.

BP-21 Structure and Mechanical Properties of Hafnium Carbide Coating on Cemented Carbide Cutting Tools, ***W. Liu*** *(LWPCSU@126.com), X. Chen, S. Wang*, Zhuzhou Cemented Carbide Cutting Tools Co., Ltd., China

HfC possess similar properties to TiC, but their thermal stability is better, and the thermal expansion coefficient is closer to the cemented carbide. Because of this, the HfC are expected to lead to an improvement of cutting performance of cutting tools. The present study has been carried out in order to research the deposition technology of HfC coating and its applition on cutting tools. The morphology and orientation of the HfC coating are characterized by SEM and XRD respectively, The adhesive strength And mechanical properties of the HfC based multilayer coated cemented carbide cutting tools are evaluated by scratching test, cutting experiment and impact test .Based on our results: lower gas partial pressure favors the formation of smaller pyramid crystals and (100) texture, higher gas partial pressure favors the formation of lager rectangle crystals and (220) texture. And with the increasing partial pressure of hafnium tetrachloride, the HfC /HfN based multilayer coated cemented carbide cutting tools' wear resistance is decreasing, the antistrip performance is increasing.

BP-22 Performance Improvement of Metal-Core PCB Cutters using Nanocomposite Coatings Deposited by Cathodic Arc Ion Plating Process, ***S.-H. Huang***, *T.-E. Hsieh (tehsieh@mail.nctu.edu.tw),* National Chiao Tung University, Taiwan, *J.-W. Chen*, Gigastorage Corporation, Taiwan

Due to the earth warming and energy saving issues, high-brightness light-emitting diodes (HB LEDs) with high energy conversion efficiency prevail over present solid-state lighting applications. Though HB LEDs have higher efficiencies than filament lamps, a relatively large amount of energy is in fact dissipated in a form of heat during device operation. Hence, thermal management becomes the key issue for HB LEDs and various high thermal conduction substrate technologies, e.g., metal-core printed circuit board (MCPCB), alumina ceramics, direct bond copper (Cu), etc. have been proposed for the assembly of HB LEDs. Among these, MCPCB is the mainstream of HB LEDs substrate type due to the advantages including low cost and high thermal conduction ability.

Various thermal managements of HB LEDs have been reported; however, the study in regard to the machinery tools for MCPCB is relatively less. This work prepares the tungsten carbide (WC) cement cutters coated with TiAlN, ZrCN, CrCN or their nanocomposite layers via the filtered cathodic arc ion plating (FCAIP) process and the cutters are subsequently applied to the machining of Al-core MCPCBs using a computer-programmable router. Physical properties and microstructures of cutters were also investigated by the pin-on-disc tribometer, grazing incidence x-ray diffraction (GIXRD), transmission electron microscopy (TEM), energy dispersive x-ray spectrometer (EDS) and nanoindentation so as to elucidate the performance of cutters. Poor results were observed in traditional TiAlN- and ZrCN-coated cutters that a built-up edge in the cutters occurred due to the high friction feature of Al core of MCPCB and coating layers. Though the CrCN coating with low friction coefficient benefited the cutter life, good cutting quality was hardly obtained due to its low hardness. As to the multilayer-coated cutter, up to 5-time improvement of tool life was achieved by the CrCN/ZrCN/CrCN-coated cutter in comparison with the coating-free cutter. This is ascribed to the low friction coefficient and high hardness features of the CrCN/ZrCN/CrCN nanocomposite layer which effectively improves the performance and tool life of cutter.

BP-23 Effect of CO_2 Reactive Gas on Abrasion Behavior of AISI 304 Stainless Steel Arc-Deposited Ti-C-O Composite Coatings, *C.-H. Hsu (chhsu@ttu.edu.tw), C.-Y. Lee, S.-H. Chen,* Tatung University, Taiwan, ***P.-L. Sun***, *C.-K. Lin*, Feng Chia University, Taiwan

Due to the consideration on carbon reduction to protect environment, in this study, CO_2 gas and titanium target were adopted to synthesize Ti-C-O composite coatings on AISI 304 stainless steel by a cathodic arc deposition system with various CO_2 gas pressures. Coating morphology and properties such as coating structure, adhesion strength, hardness/elastic modulus (H/E) ratio, and abrasion behaviors were analyzed to evaluate the effect of CO_2 pressure on the coating performances for the surface modification on AISI 304 stainless steel. The results showed that the composite coatings mainly consist of TiO and DLC mixed phases. Moreover, when the pressure of CO_2 was controlled at 5 mtorr, the coatings had a lower Ra value, higher adhesion strength (HF1), and higher H/E ratio. Sequentially, the optimum coated specimen produced with the CO_2 pressure of 5 mtorr showed an outstanding wear resistance as compared to the uncoated and the other coated ones.

BP-24 Control of Phase Formation During Synthesis of ZrO_2 Coatings by Magnetron Sputtering, ***C. Walter*** *(claudia.walter@unileoben.ac.at), C. Mitterer*, Montanuniversität Leoben, Austria

The outstanding properties of ZrO_2 as a 'tough' ceramics are based on its martensitic phase transformation from tetragonal to monoclinic. The ability to control phase formation during synthesis is therefore a prerequisite to exploit the full potential of this material. This has been investigated in detail for bulk synthesis of ZrO_2 and a similar attempt is made here for deposition of ZrO_2 coatings by reactive magnetron sputtering. Using metallic Zr targets in an argon/oxygen atmosphere and sapphire substrates, coatings showing the stable monoclinic ZrO_2 can be synthesized. Formation of the monoclinic phase occurs independent of substrate heating (up to 500°C) and/or application of a pulsed bias voltage at the substrate (up to -100 V at 250 kHz). To synthesize coatings of the high temperature tetragonal and cubic phases of ZrO_2 two different approaches have been investigated: doping with yttria and reactive sputtering in the presence of nitrogen.

For bulk synthesis doping with rare earth metal oxides is a well known method to produce fully stabilized ZrO_2 in its cubic modification and also partially stabilized ZrO_2, which contains a mixture of the cubic and tetragonal phase. Here, a series of coatings with varying yttria content are deposited by magnetron co-sputtering from two metallic targets and one yttria-stabilised ZrO_2 target in an argon/oxygen atmosphere. With this deposition setup the whole range of phase compositions from monoclinic to tetragonal/cubic coatings via phase mixtures can be synthesized and the necessary yttria content to partially or fully stabilise the sputtered ZrO_2 coatings is determined by elastic recoil detection analysis.

An alternative method for tailoring the structure formation in reactively sputtered ZrO_2 films is the use of nitrogen as an additional reactive gas. It is not the incorporation of nitrogen into the coatings, but the target surface coverage with nitrogen that affects the structure formation. This allows for deposition of mainly tetragonal/cubic ZrO_2 coatings without significant amounts of additional elements in the coatings. Reported for the first time by Severin et al. in 2008 this is a new and exciting way not only to control the structure formation but also to stabilise the reactive sputtering process. This is shown to work effectively and coatings produced via this route and via the classical dopant route are compared with respect to structure, chemical composition, intrinsic stresses and grain size.

BP-25 Effect of Phase Transition and Microstructure of ZrO_2(N) Coating on the Corrosion Resistance AISI 304 Stainless Steel Substrate, ***P.-H. Huang***, *J.-H. Huang (jhhuang@mx.nthu.edu.tw), G.-P. Yu*, National Tsing Hua University, Taiwan

ZrO_2 coatings are often used for thermal barrier coatings due to their high oxidation resistance and good thermal stability. Previous X-ray diffraction (XRD) analysis indicated that there are two major phases (monoclinic and tetragonal phase) in ZrO_2 coatings, and the compressive residual stress caused by ion-peening effect during deposition processes may control phase transition. Previous literatures reported that corrosion resistance is strongly related to microstructure, phase transition, thickness and packing density of the ZrO_2 coatings. By adjusting O/N ratio, the structure and phase transition of ZrO_2 thin films can be controlled. The goal of this research is to perform a systematic study of the microstructure, packing density and the phase transition of ZrO_2 film and correlate the structure of the coatings to the corrosion resistance. In this study, ZrO_2 thin films were deposited on AISI 304 stainless steel substrate by hollow cathode discharge ion plating (HCD-IP) method. The coatings showed high packing density, good adhesion and high corrosion resistance. The preferred orientation and phase fraction were measured by XRD. The microstructure and thickness were examined by scanning electron microscopy (SEM). The residual stress was determined by modified $\sin^2\psi$ X-ray diffraction method. The packing density was obtained from the data by Rutherford backscattering spectroscopy (RBS). The corrosion resistance was evaluated using potentiodynamic polarization scan and salt spray test. In addition, the results in this study were compared with ZrO_2 coatings deposited by unbalanced magnetron sputtering (UBMS).

BP-26 A Comparison of PVD Alumina Films Deposited Using AC and Pulsed DC Power Supplies, ***K. Gangluff*** *(kgangluf@uark.edu), M. Gordon, A. Barito*, University of Arkansas

In this study, the use of AC and pulsed DC power supplies are compared in the deposition of alumina films on silicon in an Isoflux ICM-10 dual target inverted cylindrical magnetron sputtering system at varying pressures (2-8 mTorr), substrate bias (DC and pulsed), and oxygen partial pressure (35-75%). The system was alternately powered by an Advanced Energy PEII AC power supply, operating at 40 kHz, and an Advanced Energy Pinnacle Plus pulsed DC power supply operating at pulse frequencies between 100 and 350 kHZ.

Consistent with previous work in the literature, preliminary results indicate that lower pulse frequencies produced higher deposition rates and more dense films. In addition, films produced with the DC power supply were more dense than those produced with the AC power supply. X-Ray Diffraction (XRD) results indicated the presence of alpha alumina in most films as a mixed phase, with little dependence on power supply or pulse frequency. Scanning Electron Microscope (SEM) results showed increasing surface roughness with increasing pulse frequency.

BP-27 Low-Temperature Deposition of Mixed-Phase Alpha Alumina by Physical Vapor Deposition without a Chrome Template Layer, ***A. Barito*** *(abarito@uark.edu), M. Gordon*, University of Arkansas

Alpha alumina has many chemical and mechanical properties that make it an ideal candidate for cutting tool coatings and bio-medical applications. In previous work, we have deposited low-temperature (480°C) alpha-alumina with a chrome template layer, and low-temperature (480°C) mixed-phase alumina coatings without a chrome template layer using an AC inverted cylindrical magnetron sputtering system.

In this work we report on the systematic deposition of alumina films as a function of power (4-6kW), pressure (2-8mTorr), substrate bias (DC and pulsed), and oxygen partial pressure (35-75%). 39 total runs were performed and several substrates were used (glass, silicon, stainless steel, and a titanium alloy). Analysis of each film included XRD, SEM and TEM. Results indicate strong presence of the alpha phase at 5-6kW, 50% oxygen partial pressure, pulsed bias, and 2mTorr. The presence of alpha alumina has been indicated by TEM and corroborated by XRD. Both characterization methods show mixed-phase films with substantial amounts of alpha alumina. In general, pure aluminum films are observed at lower oxygen partial pressures. At lower powers, little alpha alumina is observed as the energy at the substrate is too low. Indicating noticeable pressure dependence, films deposited at lower pressure (2mTorr) tend to exhibit phases fairly independent of power and oxygen partial pressure. Initial evidence suggests that the deposited films have a weak dependence on substrate bias.

BP-28 On the Phase Stability of Vapor Deposited γ-Al_2O_3 Films

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α alumina (Al_2O_3) possesses exceptional mechanical properties, chemical inertness and oxidation resistance, and therefore extensively serve as protective coating. Among the metastable Al_2O_3 polymorphs, γ-Al_2O_3 exhibits wear performance comparable to that of thermodynamically stable α-Al_2O_3 phase and therefore, it is often considered as an alternative to α-Al_2O_3, when low deposition temperatures are required. However, the metastable nature of γ-Al_2O_3 limits the applicability at high temperatures.

In order to design γ-Al_2O_3 films with improved stability, the identification of atomistic mechanisms that determine the phase stability is of importance. Here, we investigate the effects of composition and microstructure on the thermal stability of γ-Al_2O_3 films grown by filtered cathodic arc (FCA) and plasma assisted chemical vapor deposition (PACVD) on TiAlN coated WC cutting inserts.

The as deposited PACVD films have a porous microstructure. 2at.% Cl that originates from the incomplete disassociation of the $AlCl_3$ precursor used for the growth is detected. The FCA films exhibit a fully dense microstructure. Combining the Differential Scanning Calorimetry (DSC) and X-ray diffraction analysis, we have determined a direct γ to α Al_2O_3 transformation for FCA films at a temperature of 1074°C and for PACVD films at 1023°C. Thermogravimetric analysis and desorption measurements suggest that mobilization of Cl and further release of Cl_2 gas from the PACVD films happen at ~1020°C.

TEM analyses at the interface between PACVD γ alumina and TiAlN interlayer indicates that, after annealing in air, the Al_2O_3/TiAlN film architecture is maintained at the transformation temperature.

On the other hand, in FCA films, the decomposition and further oxidation of the TiAlN interlayer occurs prior to the γ to α transformation, Based on these results, we suggest that Cl desorption in PACVD films may enhance the bulk diffusivity and therefore facilitate the γ to α phase transformation. In the case of FCA films, the γ to α transformation is promoted by the decomposition of the TiAlN into the cubic TiN and hexagonal AlN phases

BP-29 Phase Analysis of Dual Magnetron Sputtered Thin Films in the Al-Cr-O System – a TEM Study

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Highly wear resistant alumina coatings are of significant interest for the application as a metal cutting tool. Motivation for depositing a film in the ternary system Al-Cr-O is to obtain the thermo dynamical most stable alpha phase by alloying with chromium.

For the film deposition a dual magnetron system is used to overcome the hiding anode effect and to increase the ionization and the deposition rate. Metallic aluminum and 30at% chromium alloyed aluminum targets are used to fabricate two samples with different stoichiometric compositions. A detailed phase analyses is essential for understanding the deformation of the film. Transmission electron microscopy analysis is the method of choice for the demanding analysis of the nanocrystalline microstructure.

The mechanical properties are probed by indentation experiments and FIB prepared cross section SEM images of an indent to represent the fracture behavior of the thin films. This demonstrates the advantage of the PVD thin film in comparison to coarse grained alumina film.

As a result the combination of TEM bright and dark field images highlight a microstructure with a grain size of 30-80nm being strongly disordered. The electron diffraction pattern of the alumina and chromium alloyed alumina thin films are characterized by the same typical background signal combined with broad reflections corresponding to the same d-value. Note that only d_{hkl}-spacings smaller than 0.2 nm appear and that for smaller scattering angles no reflections are observed rather an intensity distribution typical for amorphous structures is found.

TEM-EDX is done locally with a spot size of 25nm showing a solid mixture chromium and alumina $(AlCr)_2O_2$ of the argon containing thin film. To our knowledge the disorder of the microstructure has not been described until now. However, in the literature the solid mixture of $(AlCr)_2O_3$ in the corundum structure is well established even at a deposition temperature within the miscibility gap of the phase diagram.

BP-30 Characteristics of Thickness Dependence of Vanadium Dioxide Thin Films Deposited by Pulsed-Laser Deposition Technique

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Thickness dependence of metal-insulator transition (MIT) properties was studied on vanadium dioxide for revealing epitaxial growth mechanism and the relationship between the MIT and the crystal structure. Vanadium dioxide with the thickness of 30, 60, 100 and 230 nm, respectively, were deposited on c-plane sapphire substrate by pulsed laser deposition technique. For the structural analysis, x-ray, scanning electron microscope (SEM), Transmission electron microscopy (TEM) and resistance measurement were carried out. X-ray diffraction patterns and TEM images show that b-axis of vanadium dioxide is normal to the surface of the substrate. This indicates that vanadium dioxide grows epitaxially on the sapphire substrate, even though the grain structure is observed on SEM images. Moreover, Grain size and the transition width near 68°C increased with the thickness, and which were demonstrated that the thickness of vanadium dioxide thin films plays important role in their electrical characteristics. The film with the thickness of 230 nm has the transition width of ~ 9.3×10^4 near transition temperature.

BP-31 On the Formation of Off-Axis Texture in Nanostructured Thin Films

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We present our recent experimental results on the formation of "off-axis texture" and crystallographic tilting of crystallites that takes place in nanocomposite and nanostructured thin films of transition metal nitrides. This appears by the inclination of preferred orientation and the formation of texture along high indices lattice planes like (113) and (115) contrary to conventional monolithic thin films that develop a preferred orientation following to low indices close-packed planes like (111) and (200).

X-ray diffraction techniques were used to characterize the state of stress and development of texture in TiAlN-based single layer and multilayer films deposited on Si (100) substrate using pulsed DC magnetron sputtering. Depositions were carried out under both normal and oblique angle of incidence. The reciprocal space maps around (200) reflections revealed a subtle oscillatory behaviour of the lattice spacing versus curves, which seems to be dependent on the magnitude of the stresses in the films. Pole figure XRD measurements showed that the preferred orientation of the crystallites exhibits cylindrical symmetry but it is inclined with respect to the sample surface. Moreover, the inclination angle of the (002) diffracting planes increases with the increase of the residual stress in the coating.

The results are analysed with respect to the classical growth theories taking into account the role of atomic shadowing, biaxial alignment, and crystallographic defects in particular nanotwin faults that develop in the lattice of growing crystal and change the stacking sequences of atom layers. Lowering the scale of structural and compositional periodicities in PVD thin films activates nanoscale mechanisms such as spinodal modulation, pseudomorphic stabilisation, compositional intermixing, and elastic aniostropies that influence nucleation and growth mechanisms and thereby film properties as measured by nanoindentation.

BP-32 Oxidation Study of Ta-Ru Hard Coatings

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Refractory metal alloy coatings have been widely used as protective coatings on glass molding dies. The formation of intermetallic compounds in the coatings inhibits grain growth at high temperature environment in the mass production of optical components. In this study, Ta-Ru binary alloy coatings with Cr interlayer were deposited on silicon wafers and cemented tungsten carbide substrates by DC magnetron sputtering processes at 400°C. The as-deposited Ta-Ru coatings possessed a hardness of 11 Gpa and a surface roughness of 1.2-1.5nm. The oxidation resistances of the Ta-Ru coatings were evaluated by annealing in an oxygen containing atmosphere at 600°C. Preferential oxidation of Ta in the Ta-Ru coatings was verified by X-ray photoelectron spectroscopy and the formation of tantalum oxides on the surface was observed by transmission electron microscopy. After annealing treatment, the variations in crystalline structure, hardness, surface roughness and chemical composition profiles in depth were intensively investigated.

BP-34 Mechanical and Tribological Properties of Nanocomposite MoN-Cu Coatings at Elevated Temperature, ***H.N. Lee*** *(yanayana@naver.com), S.-Y. Lee,* Korea Aerospace University, Korea*, M.-H. Rhee*, Korea Automotive Technology Institute, Korea

In this work, the nanocomposite MoN-Cu coatings were synthesized with a segment $Mo_{0.84}Cu_{0.16}$ target and Mo target by a closed field unbalanced magnetron sputtering system (CFUBMS). Various Cu contents were controlled by power density of a segment target. The crystalline structure, chemical composition and cross-sectional morphologies of nanocomposite MoN-Cu coatings were investigated using X-ray diffraction (XRD), glow discharge optical emission spectroscopy (GDOES), and scanning electron microscopy (SEM), respectively. Mechanical and tribological properties were evaluated by nano-indentation and ball-on-disc tribometer in the range of 25-500^{o}C. It was observed that the mechanical and tribological properties of MoN-Cu coatings were influenced by Cu content. Based upon the result from the nano-indentation test, the maximum hardness was observed at Cu contents approximately 5.0%. It was also found that the friction coefficients of nanocomposite MoN-Cu coatings increased significantly with increasing Cu contents in the film. Our preliminary results, however indicated that the oxide layer of $CuMoO_4$ in the film with high Cu content at elevated temperatures seemed to act as a lubricating layer and to contribute to improve tribological properties of the film. Detailed experimental results will be presented.

BP-35 Diffusion in Multilayer Coatings on Cemented Carbide by Chemical Vapor Deposition, ***X. Chen*** *(zccccxm@sohu.com),* Zhuzhou Cemented Carbide Cutting Tools Co., Ltd., China*, D. Yi,* Central South University, China*, S. Wang*, Zhuzhou Cemented Carbide Cutting Tools Co., Ltd., China

A series of multilayer coated samples deposited by chemical vapor deposition was prepared and the substance diffusion in multilayer coating systems was studied by SEM, TEM, EDS, XRD, SIMS etc. It was indicated that there were multiform substance interdiffusion between TiN coating and cemented carbide substrate, which influenced the growth process and microstructure of coatings obviously. It obtained Ti(C,N) coating actually during TiN coating process. The growth of TiN coating on WC substrate was epitaxial, but the exist of cobalt on the surface of WC grain broken the epitaxial relationship . Therefore, TiN coating occurred re-nucleation and growth, as a result obtaining fine crystal grain. There was a little substance diffusion between TiCO transition layer and Al_2O_3 layer. The crystal grain of Al_2O_3 coating was prone to coarsening.

BP-36 Microstructure and Corrosion Behavior of Co-Sputtered Ni-Al-P Coatings, ***K.-C. Chang****, H.-H. Huang, F.-B. Wu (fbwu@nuu.edu.tw)*, National United University, Taiwan

The Ni-Al-P alloy coatings were fabricated with various microstructure features by magnetron co-sputtering technique. The alloy coatings exhibited amorphous, nanocrystalline, and fully crystalline microstructures, under deposition heat treatments from room temperature to 550°C . The amorphous and nanocrutalline alloy coatings showed a dense microstructure whereas the fully crystallized Ni-Al-P coatings possessed a rougher surface with overaged NiP and NiAl precipitation phases. Through corrosion analysis, superior I_{corr} and E_{corr} values were found for the amorphous and nanocrystalline alloy coatings due to their denser microstructure feature. With the increase in heat treatment temperature, the I_{corr} decreased and the E_{corr} rose toward positive region, indicating a promotion in corrosion resistance. The corrosion behavior of Ni-Al-P coatings was discussed through alternating current (AC) impedence analysis. Severe cracks in the crystallized coating after corrosion test were observed, while limited corrosion attack was found for the amorphous to nanocrystalline Ni-Al-P coatings. The lower calculated porosity rate down to 0.02 was also evident for the enhancement in corrosion resistance of Ni-Al-P coatings through microstructure control.

BP-37 Microstructure and Characterization of Magnetron Sputtered Stoichiometric Ni_3Al Coatings, *C.-C. Wu,* ***F.-B. Wu*** *(fbwu@nuu.edu.tw)*, National United University, Taiwan

Ni-Al alloy coatings with stoichiometric Ni_3Al (γ') phase were deposited using magnetron co-sputtering technique with dual target arrangement. The desired composition ratio of Ni/Al close to 3/1 for the coatings through sputtering power modulation control was obtained. The as-deposited Ni_3Al coatings possessed either a nanocrystalline or a microcrystalline microstructure according to deposition sputtering powers. Through post annealing treatments, significant phase evolution was observed for the nanocrystalline Ni_3Al coating. On the other hand, the as-deposited Ni_3Al coating with well crystallized microstructure exhibited good thermal stability. A thermodynamic quasi-equilibrium state formed for the Ni_3Al coating deposited under high sputtering power was evident. The dependency of sputtering power and thermal histories on surface morphology was evaluated particularly. Through nanoindentation analysis, the nanocrystalline Ni_3Al coating exhibited a higher hardness than the well crystallized one. The variation in hardness was attributed to the crystallite size and microstructure evolution.

BP-38 Effect of Annealing on Wettability, Microstructure and Electrical Property of RuN Thin Films, ***C.-Y. Wu****, W.-H. Lee, Y.-S. Wang,* National Cheng Kung University, Taiwan*, S.-C. Chang, Y.-L. Wang (ylwang@tsmc.com)*, National Chia-Yi University, Taiwan

RuN thin films have been investigated as candidates for barrier layers in semiconductor Cu damascene processes. In this study, RuN thin films were deposited by the magnetron DC sputtering in N_2 and Ar atmospheres on Si and dielectric substrates. In order to study the thermal stability of RuN films, the as-deposited RuN films were annealed by rapid thermal annealing (RTA) and then the film resistance was in-situ measured by four-point probe that embedded in the RTA tool. After RTA annealing, an effusion of N occurred inducing changes in the crystallization of RuN and a sharp decrease in the sheet resistance. The x-ray diffraction data showed that the RuN phase was gradually disappeared and the Ru phases were enhanced. The RuN film had better barrier property than that of Ru, even though N was effused from RuN through annealing. The agglomeration of the RuN thin films was evaluated to guarantee the thermal stability during the post-deposition annealing. Besides, the agglomeration reaction of the RuN films under the nitrogen ambient in the RTA process and the different interactions of RuN between Si and dielectrics were also intensively investigated. It was found that the agglomeration behaviors were affected by the N content of the RuN films owing to the surface energy difference and interface lattice mismatch. Furthermore, the RuN films were able to act as a Cu plateable diffusion barrier layer for the advanced Cu-metallization technologies. Cu deposition may or may not occur competitively with the oxide reduction. In the case of the thin resistive oxide-covered RuN seed layers, the “terminal effect” further exacerbated the difficulties in obtaining a compact and fully coalesced Cu film because the rate of Ru oxide reduction was decreased along with the density of Cu nuclei. The Cu deposition must be accounted for Ru oxidation that is sensitive to its microstructure.

BP-41 Fabrication of Al Coated TiC Particles through Potential Hydrogen (pH), ***W.-R. Lee****, Y.-G. Jung, E.-H. Kim (udam99@changwon.ac.kr)*, Changwon National University, Korea

Light metal matrix needs to improve mechanical properties such as wear resistance, elastic modulus, and strength, for possible applications in automobile industry [1,2]. One of possible ways is to reinforce ceramic particle into the matrix. Therefore, in order to achieve these properties, the reinforcement phase must be well dispersed in the matrix. In this work, titanium carbide (TiC) particles were coated with aluminum (Al) to enhance the dispersion of the TiC particles into a molten metal based on Al, inducing the improvement of the mechanical properties and the thermal stability of the matrix. Aluminum nitrate ($Al(NO_3)_3$), as a precursor of Al, was added in the aqueous solution with the TiC particles. The coating of Al on the TiC particles is driven by attractive force between TiC particle with negative charge density and Al with cation in base aqueous solution. Heat treatment under H_2 gas was conducted to obstruct oxidation reaction of TiC particles coated with Al. Powder prepared was characterized by X-ray diffractometry, energy dispersive X-ray spectroscopy, and scanning electron microscope. The Al particle coated on the surface of TiC particles is significantly increased with decreasing the size of TiC particle, resulting from higher specific surface area. The content of Al on the surface of TiC particle is affected by the concentration of $Al(NO_3)_3$. The TiC particles of 4 and 40 μm are well-coated with Al particles, showing Al and TiC phases, whereas the TiC particle of 20 nm indicates three different phases such as Al, TiC, and TiO_2 (titanium oxide) formed by the oxidation of the TiC. The particle size is important factor to fabricate the Al coated TiC particle without oxidation reaction.

BP-42 Study by Optical Emission Spectroscopy of a Physical Vapour Deposition Process for AlCuFeB Deposition, *T. Duguet,* ***T. Belmonte*** *(thierry.belmonte@mines.inpl-nancy.fr), J.-M. Dubois, V. Fournée*, Ecole des Mines de Nancy, France

Complex metallic alloys (CMAs) represent an emerging field in materials science. They are defined as intermetallic compounds possessing a large unit cell containing a high number of atoms, usually ranging from some tens to a few thousands. We have shown recently, by resorting to different techniques under ultra-high vacuum (STM, XPS, LEED) that g-Al_4Cu_9 could be favourably used as a buffer layer to accommodate the strain between a quasicrystalline thin film and a metallic substrate [1]. In this work, we investigate the possibility to grow a quasicrystalline thin film in the Al-Cu-Fe-B system by PVD. Optical emission spectroscopy is chosen to identify the emissive species of the plasma in a PVD reactor equipped with three targets.

In a first step, we show the possibility to grow by PVD different phases in the Cu-Al system, especially the g-Al_4Cu_9 phase. We chose to deposit different thicknesses of each element and to anneal the deposited stack to get a homogeneous film with a controlled composition.

In a second step, Cu, Al, Fe, $Al_{63}Cu_{25}Fe_{12}$ and $Al_{59.5}Cu_{25.3}Fe_{12.2}B_3$ (in atomic percent) targets are used. Thin films are deposited in an Ar-10vol.%H_2 mixture at various powers and their composition is determined by Energy Dispersive X-ray analysis. Next, optical emission spectroscopy is used to identify the different emission lines in the plasma from 280 nm to 950 nm. UV emission of boron atoms could not be reached. We did not observe any difference, except in the intensity of the transitions, in the spectra for the $Al_{63}Cu_{25}Fe_{12}$ and $Al_{59.5}Cu_{25.3}Fe_{12.2}B_3$ targets. Finally, we discuss the possibility to control the composition of the layers and to monitor the process by OES.

[1] T. Duguet *et al.*, J. Phys. : Cond. Matter, 20 (2008) 314009.

BP-44 Reversible Resistive Switching Behaviors of Ga_2O_3 Memory Thin Films with Embedded Metal Layer, ***D.-Y. Lee*** *(b901300.ee94g@nctu.edu.tw), S.-Y. Wang, T.-Y. Tseng*, National Chiao Tung University, Taiwan

In this study, we investigate the effects of the embedded metal layer on reversible resistive switching (RS) behaviors of Ga_2O_3 memory thin films. The Ga_2O_3/metal/Ga_2O_3/Pt structures are fabricated in sequence followed by a 600°C post-annealing, where the 4 kinds of the embedded metal layers (Cr, Cu, Pt, and Mo) exhibit a thickness of 2 nm. According to the X-ray diffraction (XRD) patterns, the Ga_2O_3 films remain amorphous before and after post-annealing, which is also confirmed by the high-resolution transmission electron microscope (HR-TEM) observation. Moreover, secondary ion mass spectroscopy (SIMS) depth profiles indicate the metal diffusion within the Ga_2O_3 films. There is no high-voltage forming process required in all the memory cells, showing extra high voltage is unnecessary in the control circuits. Based on the results of the successive RS cycles, the memory cell with embedded Pt layer shows the most stable RS behaviors, compared with the cells with embedded other three metal layers. The endurance test is performed over 2000 cycles, and there is no data loss found in the non-destructive readout test under 0.3V. The aforementioned results demonstrate the possible application memory of the Ga_2O_3 memory thin films with embedded metal layer.

BP-45 Ion Energy Distribution Studies of Ions and Radical in Ar/H_2 Radio Frequency Magnetron Discharge During a-Si:H Deposition Using Energy-Resolved Mass Spectrometry, ***S.L. Mensah*** *(smensah@uark.edu), M. Gordon,* University of Arkansas*, H. Abu-Safe,* Lebanese American University*, H. Naseem*, University of Arkansas

Ion energy distributions of sputtered Si particles have been measured by an energy-resolved mass spectrometer, and the results are correlated with measured thin film properties. The plasmas have been generated in a simple magnetron chamber powered with 30-180W at 13.56MHz at pressures ranging from 5-30mTorr. Various H_n^+, SiH_n^+, SiH_n fragments (with n = 1, 2, 3) together with Ar^+ and ArH^+ species were detected in the discharge. SiH_n fragments, with n =1,2, most significantly affect film deposition, and H fragments most significantly affect the hydrogen.

In a pure argon discharge, the Ar^+ flux and the deposition rate increases with power.. However, the flux of Ar^+ decreases as that of ArH^+ increases with increase hydrogen concentration in the discharge. Plasma parameters, such as plasma potential and electron density and energy, were measured with the Langmuir probe and are in good agreement with the literature. The ion energy of SiH_n^+ fragments becomes bimodal with increasing hydrogen partial pressure. The roles of possible discharge particle collisions, neutral-neutral, ion-ion, and ion-neutral, and the kinetics leading to the formation of a-S:H are analyzed.

BP-46 Stress Level / Deposition Parameters Correspondence in FeSiN Magnetron Sputtered Thin Films, ***A. Mège-Revil****, J.F. Pierson (Jean-Francois.Pierson@mines.inpl-nancy.fr)*, Ecole des Mines de Nancy, France

The metastable γ'''-FeN phase has been discovered a few years ago. This phase crystallizes in the same cfc structure as TiN and CrN. The hard coatings community has not been giving it any interest yet, though it may be possible to create a nanocomposite structure by addition of silicon.

This study aims at depositing adherent γ'''-FeN thin films – with and without silicon – by PVD on various substrates. The FeSiN coatings were deposited by magnetron co-sputtering of distinct iron and silicon targets. Before this study, attempts to deposit FeN by PVD exposed in the literature resulted either in the synthesis of γ''-FeN films or of mixed γ''/ γ'''-FeN films. By using a higher pressure, thanks to a more important argon flow rate, the deposition of the γ'''-FeN phase alone was made possible. The silicon content was adjusted by the variation of the current applied to the Si target. Stress measurements were carried out on coatings deposited on silicon wafers. They confirmed the post-deposition observations of the coatings by showing that their poor adherence to glass substrates was due to very important tensile stress in silicon-free coatings. The introduction of silicon lowers the stress level.

This last phenomenon raises the issue of the localisation of Si atoms in the structure which is discussed here.

BP-47 Properties of Multi-Component CrBMoS Coatings by Pulsed Magnetron Sputtering from Powder Targets*,* ***Y. Zhou*** *(zhouyanwen@yahoo.com),* University of Science & Technology Liaoning, China*, P. Kelly,* Manchester Metropolitan University, United Kingdom*, Z. Zhao*, University of Science & Technology Liaoning, China

We report a new combinatorial approach to study organic thin films. This novel technique consists of in-situ spectroscopic ellipsometry and quartz crystal microbalance methods. In contrast to the quartz crystal microbalance, which is sensitive to the total mass attached to the surface, including the trapped solvent, spectroscopic ellipsometry only measures the amount of adsorbant on the surface. By using these two techniques in tandem, we are able to determine the thickness and water fraction of visco-elastic thin films.

We investigate cetyltrimethylammonium bromide (CTAB) thin films deposited onto a gold-coated quartz crystal as a model system. CTAB grown from a 2.5 mM solution demonstrates several phases in porosity evolution, including a temporary hold in water fraction as the film is rinsed off the substrate with water; these effects may be related to the structure of a CTAB bi-layer.

In addition, a variety of self-assembled monolayers (SAMs) of alkanethiols on gold-coated quartz crystals were used as model biomaterials to determine the water fraction of an adsorbed fibronectin layer. The porosity information was used to distinguish the proteins' conformation, dictated by the defined surface chemistries of the SAMs. Two protein concentrations in PBS buffer were studied (0.1 mg/mL and 0.01 mg/mL) to isolate how protein concentration affects the above variables.

BP-48 Characterization of Amorphous and Crystalline Zr-Cu-Ag-Al Metallic Thin Films with Different Thickness by Unbalanced Magnetron Sputtering, ***P.-N. Chen****, J.-H. Huang (jhhuang@mx.nthu.edu.tw), G.-P. Yu*, National Tsing Hua University, Taiwan

The $Zr_{43}Cu_{43}Ag_7Al_7$ system has been developed for a long time for producing bulk metal glass (BMG). The Zr and Cu based BMGs exhibit extremely high glass-forming ability (GFA) and show marvelous properties such as high yield strength, hardness and corrosion resistance, and good thermal and electrical conductivity. Although extensive studies have been performed on BMG, few studies has been reported on metallic glass thin film. In this study, the influence of film thicknesses on the mechanical, electrical properties, residual stress and corrosion behavior are investigated. The ZrCuAgAl metallic thin films with different thickness were deposited on Si and 304 stainless steel substrate in amorphous and crystalline structures by unbalanced magnetron sputtering (UBMS). The color of thin films was silver and the electrical resistivity was quite low. The structure of the ZrCuAgAl films was determined using X-ray diffraction (XRD). The thickness of thin film was obtained by scanning electron microscopy (SEM). The hardness of the film was measured using nanoindentation (NIP). The compositions of the film were obtained by X-ray photoelectron spectroscopy (XPS). The corrosion resistance of the ZrCuAgAl films was evaluated by potentiodynamic scan. The metallic glass thin films had good corrosion resistance in both aerated 0.5 M H_2SO_4 + 0.05 M KSCN solution and 5 wt% NaCl solution. With increasing thickness, the amorphous one had a higher residual stress than crystalline one, using laser curvature measurement.

BP-49 Effect of Intercalated Metal Layer (M) on Photocatalytic Capabilities of TiO_2/M/ITO Film Catalysts, ***K.R. Wu*** *(krwu@mail.nkmu.edu.tw),* National Kaohsiung Marine University, Taiwan*, C.-W. Yeh,* Kao Yuan University, Taiwan*, C.-H. Hung*, National Kaohsiung First University of Science and Technology, Taiwan

In this study, titanium dioxide (TiO_2) film is deposited on intercalated metal layer supported on indium tin oxide (ITO) glass substrate as a TiO_2/M/ITO film catalyst, where M is Ti or platinum (Pt) pre-sputtered thin layer. A Ti thin layer is chose as an intercalated metal layer which can promote the formation of $Ti_{1-x}O_2Sn_x$ phase in an oxidation-oriented photocatalyst. Alternatively, a Pt thin layer is used for fabricating a better p hotoelectrochemical photocatalyst. Structural properties characterized by X-ray diffraction (XRD) and Raman spectra show that the TiO_2/M/ITO catalysts exhibit primarily the crystallized anatase TiO_2 phase, regardless of types of the intercalated layers used by this technique. However, the most intense Raman peak shifts from a typical 144 cm^{-1} for the non- intercalated TiO_2/ITO film catalyst to a higher wave number of 147 cm^{-1} for the TiO_2/Ti/ITO film catalyst. Peak broadening is also observed. A shift towards the high wave number and broadening of the most intense $E_{g(1)}$ mode (144 cm^{-1}) are indications of noticeable tin-doping and/or a decrease in crystallite size and crystallinity of the anatase TiO_2 film. Under UV365 irradiation, the m ethylene blue (MB) degradation rate constant of the TiO_2/Ti/ITO film catalyst is the highest at 280×10^{-3} h^{-1} among three different types of catalysts, i.e. TiO_2/Pt/ITO and plain TiO_2/ITO. On the other hand, TiO_2/Pt/ITO film catalyst exhibits the highest photocurrent density of 280 $\mu A/cm^2$, but it has the lowest MB degradation rate constant of 90×10^{-3} h^{-1}. The superior photocatalytic activity of TiO_2/Ti/ITO film catalyst is attributed to the formation of $Ti_{1-x}O_2Sn_x$ phase at the Ti and ITO interface. However, the increase in resistivity of the TiO_2/Ti/ITO film catalyst causes the photocurrent response to be the least among the samples. The superior p hotoelectrochemical reaction of TiO_2/Pt/ITO film catalyst is the result of high work function and high electrical conductivity of the intercalated Pt layer that plays a diffusion barrier against tin ions from the ITO substrate. Hence, the electrical conductivity of the catalyst can be obtained, which is greatly beneficial to drive the transport of photogenerated electrons. The TiO_2/Pt/ITO film catalyst can be served as a good p hotoelectrochemical electrode for splitting water reaction.

BP-50 Improved Damp Heat Stability of Ga-Doped ZnO Thin Film by Pre-Treatment of PET Substrate, *D.-W. Kim, J.-H. Kang, Y.-S. Lim (yslim@kicet.re.kr),* ***M.-H. Lee****, W.-S. Seo,* Korea Institute of Ceramic Engineering and Technology, Korea*, H.-H. Park,* Yonsei University, Korea*, M.-G. Park, K.-H. Seo*, LG Display Co., Ltd., Korea

Transparent conducting oxide(TCO) thin film has been extensively investigated due to its numerous applications in the fields of flat panel displays, organic light emitting diodes, and photovoltaic devices. Indium tin oxide(ITO) thin films have been widely used for the applications because of its low resistivity and high transmittance. However, due to the high cost and the shortage risk of indium raw material, many researchers have explored alternative TCO materials to replace ITO. For the replacement, Ga-doped ZnO(GZO) is regarded as the most promising candidate.

The growth of highly transparent and conductive GZO thin film is possible by sputtering even at room temperature, so that plastic substrate, which might be the essential part of flexible display applications, could also be applicable to the process. For the plastic substrate, polyethylene terephthalate (PET) has been used due to its chemical stability, optical transparency and low cost, comparing to other plastic substrates such as polycarbonate, polyethylene naphthalate, polyehersulfone, and polyimide. However, GZO thin film grown on PET has very inferior damp heat stability due to the poor moisture resistance and high gas permeation of PET substrate. For practical applications of GZO thin film on PET, the damp heat stability is of great importance.

In this study, we report the improved damp heat stability of GZO thin film by pre-treatment of PET substrate. By degassing the PET substrate at high temperature prior to the thin film deposition, we tried to reduce the amount of outgassing moisture and impurity gas, which could deteriorate the electric properties of GZO thin film, during the deposition at the next step. The annealing temperature for the pre-treatment of the PET substrate was 100 ºC, which is below the glass transition temperature, and the annealing time was controlled by 20, 40 and 60 min. After the pre-treatment, GZO thin films were deposited by rf-magnetron sputtering method using a 5.5wt% Ga_2O_3 doped ZnO target at room temperature. After the deposition, all films were damp heat treated with 90% relative humidity at a temperature of 60 ºC for up to 150 hr in a climatic chamber. The results of 4-point probe and Hall measurement of the damp heat treated GZO thin film show that the electrical properties could be dramatically improved by pre-treatment of PET substrate. After 150 hr damp heat treatment, the sheet resistance variation of GZO thin film grown on 40 min-annealed PET substrate was about only 15%. The origin of the improvement was investigated by structural, compositional and electrical characterization, and the results will be discussed.

BP-52 Electric and Reliability Characteristics of Nitrogen-Incorporated Silicon Carbide Film Deposited by Chemical Vapor Deposition, ***L.Y. Cheng*** *(yjcheng@ncnu.edu.tw), T.-J. Hiu*, National Chi-Nan University, Taiwan

The influence of nitrogen flow on the electrical properties of Silicon-Carbide (SiC) barrier dielectrics prepared by chemical vapor deposition was reported. Experiment results showed that leakage current and dielectric constant was reduced with increasing nitrogen flow. The thermal stability of SiC film was greatly improved by doping nitrogen. The reliability of SiC barrier dielectrics with different nitrogen flows was investigated. An improved dielectric breakdown lifetime was observed due to better Cu barrier ability for nitrogen-incorporated SiC films. In addition, the Cu electromigration performance was slightly enhanced by capping SiC film with higher nitrogen flow because of the improvement bonding strength with Cu.

BP-53 Precipitate Formation and Effects on Electrical and Mechanical Properties of Fluorinated Silicon Oxide*, **J. Wu**, L.Y. Cheng (yjcheng@ncnu.edu.tw)*, National Chi-Nan University, Taiwan

Precipitates appear on fluorine-doped silicon oxide(SiOF) film when the film surface is exposed to atmospheric air. They are flake-type and hexagonal-shaped and show up rapidly after initiation, and then densely clustered. Energy-dispersive X-ary (EDX) analysis results of the precipitates show that mainly Si & O are detected. From the analysis of Raman spectra, the decreased intensities at about 600 cm^{-1} and 500 cm^{-1} post precipitation indicates the reduction of strained low-order ring structure in SiOF film. It is found that the dielectric constant of SiOF films initially increases at exposure to air and is attributable to the absorption of water, and then on the contrary a declining trend of the dielectric constant was observed after precipitation. From the Current-Voltage (I-V) characteristics, there is an apparent shift of the breakdown distribution to lower values of electric field for the SiOF films post-precipitation. Slight but appreciable reduction in hardness could be observed along exposure to air and precipitation. Precipitation on SiOF film at exposure to humid air is accompanied by reconstruction in structure, leading to further increase in film porosity and reduction in film rigidity.

BP-54 Film Properties of Copper Barrier Films with Different Deposition Temperatures, ***B.J. Wei****, L.Y. Cheng (yjcheng@ncnu.edu.tw), J.H. Wang*, National Chi-Nan University, Taiwan

Silicon nitride (SiN) and 3MS-base silicon carbide (SiCN and SiOC) films deposited by plasma-Enhanced Chemical Vapor Deposition (PE-CVD) have been investigated as copper barrier layer in terms of deposition temperature effect. Deposition characteristics, film composition, and integration issue under circuit fabrication processes were measured to evaluate the difference between various barrier films with varying deposition temperatures. Experimental results show that a SiN film was the best barrier film, however, higher dielectric constant was the major concern. On the other hand, a 3MS-base barrier film can reduce the dielectric constant to 3~5, depending on the deposition temperature. But the deposited film with the better thermal and chemical stability was obtained for the deposition temperature above 35 ºC.

BP-56 Triple Coatings: A Powerful Concept for Demanding Applications, ***M. Morstein*** *(m.morstein@platit.com), O. Coddet, P. Karvankova, A. Lümkemann,* Platit AG, Switzerland*, B. Torp,* Platit Inc.*, T. Cselle*, Platit AG, Switzerland

The concept of combining the beneficial properties of nanocomposite with those of non-nanocomposite PVD coatings in a single, multifunctional structure has been proven successful for various industrial applications. These triple-coating structures, especially when produced using the cylindrical rotating cathodes technology, provide a balanced mixture of hardness, toughness, abrasional wear resistance, heat barrier and frictional properties. Another advantage is the possibility of depositing a dedicated adhesion layer, thanks to the use of pure elements as the target materials.

The presentation will outline the potential of the triple coating concept based on three examples: Oxygen-containing triple coatings for turning applications, the new superhard TiXCo® family of coatings for tough hard milling and drilling, and the second generation DLC coatings for components and tools. The influence of different structures on overall coating properties and test performance will be discussed.

BP-57 Mechanical and Electrochemical Properties of Arc Ion Plated Titanium Dioxide on Polyetheretherketone, ***H.-K. Tsou***, Feng Chia University & Taichung Veterans General Hospital, Taiwan*, P.-Y. Hsieh, M.-H. Chi,* Feng Chia University, Taiwan*, C.-J. Chung (cjchung@seed.net.tw),* Central Taiwan University of Science and Technology, Taiwan*, J.-L. He*, Feng Chia University, Taiwan

The arc ion plating (AIP) technique is known to be capable of providing high film deposition rate and strong film adhesion, while titanium dioxide (TiO_2) is characterized by its high chemical stability, photocatalysis and biocompatibility nature. The present study employed AIP to deposit TiO_2 onto Polyetheretherketone (PEEK) at low temperature. It was aimed to investigate the microstructure, mechanical and electrochemical properties of the TiO_2 coatings as affected by coating variables for its some possible applications . The experimental results indicate that a crystallinic columnar film containing a controllable ratio of anatase to rutile phase can be prepared. Pencil hardness of the PEEK material graded as 4H was increased to over 9H by AIP-TiO_2 coating. Film adhesion of the AIP-TiO_2 coating can ultimately reach a critical load of 15 N and is associated with its deposition condition, but undergoing cohesive failure mode (of the scratch scar) regardless of its deposition condition. Polarization behavior of the TiO_2

coating in 3.5 wt.% NaCl electrolyte reveal that the AIP-TiO_2 coating presents a greater electrochemical inertness, if rutile phase exist. They are however close to the electrochemical behavior of graphite material in all cases.

Fundamentals and Technology of Multifunctional Thin Films: Towards Optoelectronic Device Applications
Room: Golden Ballroom - Session CP

Symposium C Poster Session

CP-1 Electro-Optical Property and Microstruture of Polymer Dispersed Liqid Crystal Doped with Various Reinforcing Materials, ***S.-W. Myoung***, *Y.-G. Jung, E.-H. Kim (udam99@changwon.ac.kr)*, Changwon National University, Korea

Polymer dispersed liquid crystals (PDLCs) which emerged in late 1980s are important technology in the development of switchable windows, electro-optic shutters, and especially displays because of their many advantages, viz., slim shape, low weight, no alignment layer, no polarizer, easy fabrication and so on, compared with conventional liquid crystal displays (LCDs) [1]. Hence, PDLCs for a display should have high contrast ratio, low driving voltage, and fast response time as well as low shrinkage. In this work, we incorporated different types o f reinforcing materials (RMs) such as hydrophilic silica (aerosil 200), polyhedral oligomeric silsesquioxane (POSS), and poly (dimetyl siloxane) (PDMS) into the conventional PDLC system to increase electro-optical properties by the increment of phase separation, resulting from the increase in elastic modulus of polymer matrix and the reduction of compatibility with LC, and the enhancement of conversion rate of monomer to polymer [2]. When additional amounts of RM are increased to a certain point, t he reactive mixture is homogeneously mixed before polymerization process. However, RM could be aggregated at above the optimum contents of RM, leading to the deterioration of electro-optical, mechanical, and thermal properties. Generally, as the contents of RM are increased, electro-optical properties viz., the contrast ratio, driving voltage, and rising time are improved because of the increase in LC droplet size and the reduction of anchoring strength between polymer and LC. However, when the contents of RM are higher, these properties are decreased due to probably poor phase separation between polymer and LC, caused by the aggregation of RMs. POSS with small-sized particles (1–2 nm) modified by organic substituent shows excellent properties in RMs used in this work.

CP-2 The Interface States Improvement of Pentacene Thin Film Transistors Through Self-Assemble Molecular Layers, *Y Wang (wangyw@cc.ncue.edu.tw),* Graduate Institute of Photonics, National Changhua University of Education, Taiwan R.O.C., ***C.-Y. Tsay***, Feng Chia University, Taiwan

In this article, we fabricated a series of pentacene based thin film transistor (TFT) with different surface treatment layers. The self-assemble molecular (SAM) layer was one of the most efficient tool to modified the insulator surface for pentacene deposition. Here, including the hexamethyldisilazane (HMDS), octadecyltrichlorosilane (OTS), and phenethyltrichlorosilane (PETS) were used to modify the silicon dioxide surface for the fabrication of pentacene TFTs. With the SAM layer, the oxide surface contact angles with dionized water have been changed and varied between 78.2° and 83.0°. The value was larger than the bare oxide suface, with contact angle about 50.3°. These values also implied that the surface with SAM layers have stronger interaction force with pentacene molecular. Hence, the pentacene on SAM layer may have a better film morphology and crystalline result. From the atomic force microscopes (AFM) result, we also observed the grain size of pentacene on SAM layer have a more dense structure. Finally, the interface trap density between pentacene/oxide junctions was extracted of the order of 10^{10} /cm^2eV through the conductance method. And the largest field effect mobility was calculated nearly 0.05 cm^2/vs. The sub-threshold slope have been improved to 0.86 V/dec. The more detail would be discussed in the manuscript.

CP-3 Residual Stess Relaxation in ZnO Thin Films Deposited by Magnetron Sputtering on Si, *F. Conchon,* ***P.O. Renault*** *(pierre.olivier.renault@univ-poitiers.fr), P. Goudeau, E. Le Bourhis,* University of Poitiers-France*, E. Sondergard, E. Barthel, S. Grachev, E. Gouardes, V. Rondeau, R. Gy,* Saint Gobain Research, France*, R. Lazzari,* INSP-France*, N. Brun*, LPS-France

ZnO is a material of technological importance for, among other things, 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.

By means of X-ray diffraction, we show in this communication that as-deposited ZnO films encapsulated or not by Si_3N_4 protective coatings are highly compressively stressed. Moreover, a transition of stress is observed as a function of the post-deposition annealing temperature. After a 800°C annealing, ZnO films are tensily stressed while ZnO films encapsulated by Si_3N_4 are stress-free. With the aid of in-situ X-ray diffraction under ambient and argon atmosphere, we argue that this thermally activated stress relaxation can be attributed to a variation of the chemical composition of the ZnO films. This work is done in the framework of an ANR project named Merethif.

CP-5 Hysteresis Effects on PVD Alumina Using an Inverted Cylindrical AC Magnetron Sputtering System, ***J. Mehta****, R. Kilaru, M. Gordon (mhg@uark.edu)*, University of Arkansas

Optical emission spectroscopy was used to study the hysteresis effects on Argon-Aluminum-Oxygen plasma in conjunc tion with the deposition of alumina. Preliminary results show definite evidence of hysteresis at 2 mtorr pressure, total gas flow of 40 sccm, and power of 4 kW between 55% and 70% oxygen partial pressure. Evidence was also seen at 2 mtorr pressure, total gas flow of 60 sccm, and power of 4.5 kW between 50% and 70% oxygen partial pressure. A comprehensive study was conducted at pressures between 2mtorr and 8 mtorr, at total gas flows between 40 sccm and 70 sccm, at powers between 4 kW and 6 kW, and at oxygen partial pressures between 0% and 100%. The findings have been correlated to the deposited films, some of which contain the corundum phase.

CP-6 Annealing Effects of ZnO Thin Film Growth on m-Plane Sapphire at Room Temperature by Atomic Layer Deposition, *C.-S. Ku,* National Synchrotron Radiation Research Center, Taiwan*, Y.-C. Chen, J.-M. Huang,* ***C.-M. Lin***, National Hsinchu University of Education, Taiwan*, H.-Y. Lee (hylee@nsrrc.org.tw)*, National Synchrotron Radiation Research Center, Taiwan

Zinc Oxide (ZnO) thin films growth by atomic layer deposition at 25°C on m-plane sapphire with total thickness ~200 nm examined by x-ray reflectivity (XRR). The X-ray diffraction (XRD) measurement showed polycrystalline structure for as-growth ZnO thin film. The annealing processes were treated on ZnO thin film with temperature range from 100°C to 700°C in vacuum. The XRR results showed film thickness will decreased for annealing temperature from 100°C to 400°C then reversed to increase until 700°C. However, the photoluminescence (PL) intensity rises rapidly from as-growth to 400°C and falling to 700°C. The PL near-band-edge (NBE) peak position showed red-shift from room temperature to 400°C then blue-shift slightly to 700°C. The green band emission intensity related to defect and vacancy was very weak respect to NBE and showed insignificance change with annealing temperature. The XRD also keep similar intensity ratio for each annealing temperature. We summarized the results and indicated ZnO thin film growth at room temperature showed batter optical properties with annealing process at 400°C.

CP-7 The Effect of Varying Inert Gas Species on the Depositon of Thin Conducting Silver Films via Magnetron Sputtering, ***G.T. West*** *(g.west@mmu.ac.uk), P. Kelly*, Manchester Metropolitan University, United Kingdom

Thin silver films are essential for applications that require high visible transparency along with good electrical conductivity, such as low-emissivity and solar control coatings. The nature of silver film formation, characterised by the coalescence of island-type structures, often necessitates a compromise between transparency and conductivity that could be mitigated by improvements in nucleation and growth mechanisms. For the applications outlined above which employ large-area dielectric substrates in continuous motion, it would be advantageous to influence film growth without resorting to conventional methods such as substrate heating or electrical biasing techniques.

Sputtering a silver target with ions from an inert gas plasma has differing effects on the nature and energy of particles bombarding both target and substrate as a function of gas species. The choice of inert gas affects the contribution of energetic reflected neutrals to the growth of the film, in terms of the energy delivered and the inclusion of inert gas into the coating. Bombardment of the target with ions of varying mass affects the sputter yield, and implantation at the substrate will also be influenced by mass-effects of ionic bombardment.

Glass substrates were pre-coated with zinc oxide before the deposition of thin silver films using DC and pulsed-DC magnetron plasmas generated from neon, argon, krypton and xenon source gases. The films were characterised in terms of their structural, optical and electrical properties by a variety of techniques including AFM, XRD, spectrophotometry and Hall-effect measurements. The results show the effect each source gas has on the growth and structure of silver coatings and the resulting optical and electrical performance of these films.

CP-8 Studies of the Structural Evolution and Film Properties of Pulsed Magnetron Sputtered Titania Coatings, ***P. Kelly*** *(peter.kelly@mmu.ac.uk), J. Kulczyk-Malecka, N. Farahani, G.T. West,* Manchester Metropolitan University, United Kingdom, *C. Hill, J. Stratton,* Millennium Inorganic Chemicals Ltd., United Kingdom, *G. Clarke,* Pilkington Technology Management Limited, United Kingdom, *I. Iordanova,* University of Sofia, Bulgaria, *V. Vishnyakov*, Manchester Metropolitan University, United Kingdom

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 many of the important functional properties of titania coatings, such as refractive index, photocatalytic activity, hardness, etc. are in turn, dependent on this structure. In this study, coatings have been deposited onto glass substrates by reactive sputtering from metallic targets and directly from oxide powder targets. The magnetrons were driven in mid-frequency (100 – 350 kHz) pulsed DC mode and in HIPIMS mode (frequency range 50 – 1000 Hz). The as-deposited coatings were analysed by scanning electron microscopy (SEM), X-ray diffraction (XRD) and micro Raman spectroscopy. Selected coatings were also annealed at temperatures in the range 100 – 800 C and re-analysed. The photocatalytic activity of the coatings was assessed through measurements of the degradation of organic dies, such as methyl orange, under the influence of UV light. The rate of diffusion of sodium atoms from the substrates through the annealed samples was also investigated by secondary ion mass spectroscopy (SIMS). It was observed that the 'low temperature' amorphous or nanocrystalline structure of the coatings evolved into a strongly anatase structure at annealing temperatures in the range 400 – 600 C, depending on the specific deposition conditions used, and that this structural transformation strongly influenced film properties. For the HIPIMS coatings, some evidence of nanocrystallinity was observed in as-deposited coatings, which was not observed for the pulsed DC coatings.

CP-9 Depositing Low Temperature Passivation Layers for Flexible Display Application, *P.-T. Liu (ptliu@mail.nctu.edu.tw),* ***Y.-T. Chou****, A.-D. Huang, B.-M. Chen, S.-Y. Tsai*, National Chiao Tung University, Taiwan

Hydrogenated amorphous silicon thin film transistors (a-Si:H TFTs) is mainly used as the switching device in active matrix liquid crystal displays (AMLCDs). For the requirement for light-weight, portable, and unbreakable in consuming electronics, the products replacing the glass substrates with flexible ones, such as electronic paper, personal digital assistant (PDA), global positioning system (GPS), and etc. have rapidly attracted lots of attention in recent years. In this thesis, we investigated the stability of a-Si:H TFTs under mechanical strain with and without silicon nitride (SiNx:H) passivation. The process temperature of these flexibledevice, including the passivation layer, was well-controlled below 200℃, and the substrate was using stainless steel foil. The strain stress was applied cylindrically parallel to the active channel path of TFTs. The stability measurement was performed by DC gate bias stress and lasted up to 104 seconds. By using electrical parameter fitting, the Vth metastability mechanism was dominated by state creation effect. Our result indicated the device with passivation layer was improved, and the Vth had less variation under both outward and inward bending. By exerting 190℃ post-annealing process after SiNx:H deposited, the Vth was shifted left and the reliability of flexible TFTs became better than without post-annealing process. That's related to the passivating effect of hydrogen ion under passivation layer and post-annealing process.

CP-10 Optical Properties of Multilayered Metal/Amorphous Carbon Coatings, *Y.-Y. Chang (yinyu@mail2000.com.tw), R.H. Yang, K.-C. Tseng,* ***C.-Y. Tsai***, Mingdao University, Taiwan

Transparent heat mirror coatings have attracted increased interest in reducing heat radiation loss through window panes from ecological and sustainable aspects. A multilayered coating with metal and amorphous carbon (a-C), possessing abrasion resistance and chemical inertness, has become a potential candidate for the dielectrics of these coatings. In this study, a series of metal/ a-C (metal= Ag, Ti, and W) multilayered coatings are deposited on conductive glass substrates using a twin gun magnetron sputtering system. High purity Ag, Ti, W, and graphite targets (99.99 at. %) are used for the deposition of the multilayered metal/ a-C coatings. The multilayered coatings are prepared in the form of a-C/metal/a-C/metal/glass structure. The sputtering power on the graphite target is 100 W. By adjusting the sputtering power (20W~100W) on the Ag, Ti and W targets and the deposition time, different layer thicknesses and periodic thicknesses of the multilayered coating are deposited. The effect of metal content (Ag, Ti, and W), layer thickness and periodic thickness on the optical properties of multilayered metal/ a-C coatings are investigated. In this study, chemical composition of deposited coatings is evaluated by a wavelength dispersive X-ray spectrometer (WDS). Field emission scanning electron microscope (FESEM) equipped with secondary electron imaging (SEI) and backscattered electron imaging (BEI) detectors is used to characterize the microstructure and layer thickness. X-ray diffraction (XRD) is used to characterize the crystal structure and the residual stress of the deposited films. A microscopic Raman spectrometry is employed to characterize the bond structure of a-C. Both transmission and reflection spectra are obtained using a UV-vis/IR spectrometer in the wavelength range of 220–2500 nm.

CP-11 Effects of Additive Gases and Plasma Post-Treatment on Electrical Properties and Optical Transmittance of ZnO Channel Layers in Transparent Thin Film Transistors, ***J.H. Bang****, W. Kim, H.S. Uhm, J.-S. Park (jinsp@hanyang.ac.kr)*, Hanyang University, Korea

Present 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/Vs). To resolve these problems, use of oxide semiconducting materials as a channel layer for TFT has recently been introduced. Among the various oxide materials, zinc oxide (ZnO) is one of the most promising candidates for the transparent TFT applications since it has good crystallinity by preparing at low temperature region and has a widely range conductivity from metallic to insulating. In addition, since the resistivity of as-deposited ZnO thin films is too high, various techniques to modify ZnO properties, such as co-doping with the additive gases in working gas, post annealing under ambient gas, and ion implantation, have been investigated extensively.

We have examined the effects of additive gases (such as hydrogen and oxygen) during growth and plasma (using argon or hydrogen) treatment after growth on the electrical properties and optical transmittance of ZnO channel layers in transparent TFTs. The ZnO films were deposited on various substrates (Corning 1737 glass, Si wafer, and aluminum oxide) at room temperature employing an RF magnetron sputter system with 4" ZnO (purity 99.99%) target by varying the mixing ratio of H_2 and O_2 additive gases. The deposited ZnO films were post-treated with Ar or H_2+Ar plasma in an inductively-coupled plasma CVD reactor. The morphology and cross-sectional structure of ZnO films were monitored by field-emission scanning electron microscopy (FESEM). The surface roughness and crystal orientation of ZnO films were measured by atomic force microscopy (AFM) and x-ray diffraction (XRD), respectively. Their electrical properties, such as resistivity, carrier concentration, and mobility, were measured at room temperature using the Van der Pauw method. In addition, the optical transmittance of ZnO films was measured using a UV/visible spectrophotometer operating in a spectra range of 300-1000 nm. The results showed that the material properties of ZnO films required for the channel layer of TFTs, such as approximately 10^3 Ωcm in resistivity, 10 cm^2/Vs in mobility, and 90 % in transmittance in the visible range could be achieved by controlling the mixing ratio of additive gases and these properties could also be improved further by post-treatment.

CP-12 Effects of Post Plasma Treatment on Material Properties and Device Characteristics in Indium Zinc Oxide Thin Film Transistors, ***W. Kim****, J.H. Bang, H.S. Uhm, J.-S. Park (jinsp@hanyang.ac.kr)*, Hanyang University, Korea

Transparent conductive oxides (TCOs) have recently gained much attention in a variety of technologies in passive applications such as transparent electrodes for liquid crystal displays (LCDs), organic light emitting diodes (OLEDs), and solar cells. The possibility to use TCOs in active applications such as transparent thin film transistors (TTFTs), UV sensors, and UV LEDs has also become a reality. High performance TFTs for active matrix display applications should have high electron mobility, high on/off current ratio, low threshold voltage, and low process temperature. However, these requirements cannot be fulfilled by conventional Si-based technologies. For this reason, many researchers have focused on oxide semiconductors including zinc oxide (ZnO), indium zinc oxide (IZO), zinc tin oxide (ZTO), and indium gallium zinc oxide (IGZO) as channel layers of TFTs. Especially, IZO thin films exhibit high electron mobility even when it is deposited at room temperature. It is also possible that IZO thin films are used both as channel layers and as source/drain (S/D) layers of TFTs.

We present experimental results that regard the effects of post plasma treatment on material properties of IZO thin films and device characteristics of IZO-based TFTs. The post-treatment was performed using with Ar or H_2 plasma in an inductively-coupled plasma CVD reactor. Since the high-speed stream of plasma bombards IZO films, it is possible to generate oxygen vacancies on the film surface and furthermore, hydrogen acts as a shallow donor within the IZO layer due to H^+ ion and O-H complex generated by H_2 plasma. Based on this phenomenon, we propose that S/D electrodes for IZO TFTs can be formed by selective plasma treatment without additional deposition of S/D layers. The fabrication of IZO-based TFTs was carried out by following procedures. A conducting IZO film was deposited on a glass substrate by RF sputtering for gate electrode. And then a SiN_x layer was grown using plasma-enhanced CVD as gate insulator. A semiconducting IZO film was deposited as channel layer and S/D electrode regions were opened by conventional photolithography process, and finally the sample was exposed to Ar or H_2 plasma. All the changes in electrical, structural, and optical properties of IZO films due to plasma treatment were monitored using various methods, such as Hall measurement, x-ray diffraction, and UV-Visible spectrophotometer. The device characteristics of IZO TFTs were also characterized in terms of plasma treatment conditions.

CP-13 Fabrication of Bottom-Gate Transparent Oxide TFTs Using a Novel Two-Mask Process, ***H.S. Uhm***, *J.H. Bang, W. Kim,* Hanyang University, Korea*, S.Y. Lee,* KIST, Korea*, J.-S. Park (jinsp@hanyang.ac.kr)*, Hanyang University, Korea

Recently, oxide semiconductors such as zinc oxide (ZnO), indium zinc oxide (IZO), zinc tin oxide (ZTO), and indium gallium zinc oxide (IGZO) have been recognized as the promising candidates for alternating a-Si:H thin films in TFT-LCDs. These materials represent surprisingly high electron mobilities (> 10 cm^2/Vs) even for amorphous films deposited at room temperature, which leads to higher switching speeds of TFTs. In addition to increasing the mobility, reducing TFT manufacturing steps has become an essential technology trend for many TFT-LCD makers in purpose of cost reduction and high throughput. In general, most a-Si:H TFT fabrication has been accomplished by means of 4- or 5-mask process. Since a-Si:H film is opaque, it cannot be located beneath the pixel electrode in conventional bottom-gate TFT structures. This leads to a complicated fabrication procedure because the entire process including a-Si:H channel, source-drain layers, and pixel electrodes has to be separately carried out. On the other hand, oxide semiconductors exhibit a high transmittance over 90 % in the visible region due to a wide band gap of 3-4 eV.

We propose a novel mask reduction method where only 2-masks are needed to produce a bottom-gate transparent oxide TFTs. The major spirit of our 2-mask process is to form simultaneously active layers, source-drain layers, and pixel electrodes via one photolithography process by applying a gray-tone mask (GTM) technique. We have introduced a new GTM design for forming a gray-tone of photo-resist on the channel region and for expanding the drain into the pixel area. The morphology and cross-sectional structure of transparent oxide TFTs were monitored by field-emission scanning electron microscopy (FESEM). Especially, the gray-tone profiles of photo-resist were carefully observed for ensuring the process feasibility with GTM. In order to evaluate DC characteristics, such as field effect mobility, on/off current ratio, threshold voltage, and sub-threshold swing, the output and transfer characteristics of fabricated oxide TFTs were measured using a semiconductor parameter analyzer. In addition, the optical transmittance of fabricated TFTs was measured using a UV/Visible spectrophotometer operating in a spectra range of 300-1000 nm.

CP-14 Preparation of Nano-Structured Alumina Thin Films by Microwave-Assisted Hydrothermal Process, ***J. W.-C. Yu***, *M.-S. Lin, Yi-Cheng Jaw, F.C.-N. Hong (wcyu75@hotmail.com)*, National Cheng Kung University, Taiwan

Nano-porous structured alumina thin films with anti-reflective property prepared by the sol-gel hydrothmal process were coated on glass substrates. Pseudo-boehmite nanocrystals precipitated alumina in few hundred nm thickness were formed during this process after conventional hydrothermal treatment. It was found that the commercial available microwave oven, which was used for porous alumina thin films formation in hydrothermal stage, exhibited rapid reaction time. Similar surface morphology and optical properties of formed thin film materials on the glass substrate were observed in comparison. Beside of the heating support reduced reaction time, microwave assisted reactions might be existed. Anti-reflective properties of alumina thin film by this process were obtained, due to itself unique nano-porous structure. The reflective effects of single side and dual side porous alumina thin films on the substrate were also investigated.

CP-15 Electrochromic Properties of Ni(V)O_x Films Deposited via Reactive Magnetron Sputtering with a 8V-92Ni Alloy Target, *J.-M. Ye (phonmeen@fcu.edu.tw), Y.-P. Lin, Y.-T. Yang, J.-T. Chang,* ***J.-L. He***, Feng Chia University, Taiwan

NiO_x has been extensively used as complementary counter electrochromic (EC) layer in smart windows. Reactive sputter deposition for obtaining NiO_x layer using metallic Ni targets has been very often considered, however, the ferromagnetic property of metallic Ni failed to be applied by conventional magnetron enhancement, particularly when considering large-area deposition. To overcome this, 8 at% V is alloyed into Ni target for eliminating the ferromagnetism, and Ni(V)O_x films is deposited via the reactive magnetron sputter technique in this study. Microstructure and the related EC properties were investigated.

Experimental results shows that the sputtering erosion of the non-ferromagnetic Ni(V) target surface becomes controllable as opposed to the pure Ni target. The Ni(V)O_x film deposited at the working atmosphere of 1.33 Pa and oxygen flow ratio of 40% exhibits the highest optical transmission change (colored to bleached). The half device assembled with a 200 nm-thick film presents the shortest response time (2 s for coloring, 3 s for bleaching) and the greatest optical transmittance change in visible region (69.5% for bleached, 42.0% for colored). This study demonstrates that alloying 8 at% V as a de-ferromagnetiser in Ni target does not observably affect the electrochromic properties of deposits.

CP-16 Resistive Switching in Transparent ITO/Cu_2O/TiO_2/ITO Stacked Structure, *L.-C. Chang (lcchang@mail.mcut.edu.tw), Y.-C. Peng, J.-H. Lu,* Mingchi University of Technology, Taiwan*,* ***Y.-C. Kuo***, National Taiwan Ocean University, Taiwan

Transparent, nonvolatile and reversible resistance switching of Cu_2O, TiO_2, Cu_2O/ TiO_2 thin films were studied by current-voltage measurements using ITO electrode and conductive atomic force microscopy. Crystalline cuprous Cu_2O, TiO_2, and ITO were prepared by radio frequency magnetron sputtering at room temperature. The transparent devices with various electrode sizes were fabricated through shadow mask. The stacked-structure-RRAM has a transmittance (including the substrate) in the visible region. The correlation between resistance switching behavior and film thickness is discussed.

CP-17 Cathodoluminescent and Photoluminescent Properties of Manganese-Doped Rhombohedral Zinc Germanate Prepared by Radio Frequency Magnetron Sputtering, *K.H. Yoon,* ***J.H. Kim*** *(joohan@dreamwiz.com)*, Chungbuk National University, Korea

Cathodoluminescent (CL) and photoluminescent (PL) properties of manganese-doped zinc germanate (Zn_2GeO_4:Mn) thin films have been investigated. The Zn_2GeO_4:Mn thin films were prepared by radio frequency (RF) magnetron sputtering in an argon-oxygen gas mixture atmosphere. X-ray diffraction (XRD) patterns of the as-sputtered Zn_2GeO_4:Mn films showed only a broad feature, indicative of an amorphous structure. After a post-sputter anneal at 700 °C for 1 hour in air ambient, the Zn_2GeO_4:Mn films were crystallized into a rhombohedral polycrystalline structure with a random orientation. The broad-band CL emission spectrum was obtained from the annealed Zn_2GeO_4:Mn films. The CL emission peak was centered at around 534 nm in the green range, which is accounted for by the $^4T_1 \rightarrow {}^6A_1$ transition in Mn^{2+} ions. The PL emission spectrum for the Zn_2GeO_4:Mn films was similar to the CL emission spectrum. In the PL excitation spectrum measured at room temperature, two discrete peak maxima were observed at 259 and 297 nm. The peak maximum at lower wavelength of 259 nm corresponds to 4.787 eV, which is related to band-to-band transition of Zn_2GeO_4. The peak at higher wavelength of 297 nm corresponding to 4.174 eV is considered to be due to the subband excitation.

CP-18 Effect of Buffer Layer on Preparation of Transparent Conducting Impurity-Doped ZnO Thin Films by dc Magnetron Sputtering, ***J.-I. Nomoto***, *J.-I. Oda, T. Miyata (tmiyata@neptune.kanazawa-it.ac.jp), T. Minami*, Kanazawa Institute of Technology, Japan

It has been reported that the various properties obtainable in transparent conducting impurity-doped ZnO thin films are affected by the deposition method, even when prepared under an optimized deposition condition. In particular, thin films deposited by conventional dc magnetron sputtering (dc-MS) with an oxide target exhibit non-uniform resistivity distribution and increase the obtainable resistivity in thin films that are deposited on moving large area substrates for practical applications. In this paper, we demonstrate a deposition technique newly developed for improving various properties of transparent conducting impurity-doped ZnO thin films prepared on low temperature glass substrates by dc-MS. The decrease of the obtainable lowest resistivity and the improvement of the spatial resistivity distribution on the substrate surface in impurity-doped ZnO thin film prepared by conventional dc-MS were successfully achieved by inserting a very thin buffer layer between the thin film and the glass substrate.

Al- or Ga-doped ZnO (AZO or GZO) thin films were prepared with thicknesses of 30 to 200 nm by a MS apparatus with an oxide target. The basic sputter depositions were carried out on OA-10 glass substrates at a temperature of 200ºC in a pure Ar gas atmosphere at a pressure of 0.4 Pa with a dc power of 200 W. For example, in the preparation of transparent conducting AZO thin film by dc-MS with an AZO target, first a very thin AZO film, deposited by a MS apparatus with the same target under different deposition conditions, was inserted as the buffer layer on the glass substrate . Then the transparent conducting AZO thin film was deposited to a desired total thickness by conventional dc-MS. The deposition of the buffer layer was found to be necessary to sputter the target surface whose oxidization was stronger than the target surface during conventional dc-MS deposition. Such a strongly oxidized target surface was attained with a target sputtered under an appropriate condition, for example, after the target was used in the sputtering for an appropriate time under an rf power supply or oxygen gas was introduced into the chamber. Since the buffer layer's optimal thickness was found to be approximately 10 nm, the obtainable lowest resistivity and resulting spatial resistivity distribution were evaluated by varying the thickness from 2 to 30 nm. The lowest resistivity of $4\ X10^{-4}\ \Omega$ cm was obtained in 100-nm-thick-AZO thin films inserted in an AZO buffer layer with a thickness of 10 nm, whereas the obtained resistivity of the AZO thin films inserted without the buffer layer exhibited $9\ X10^{-4}\ \Omega$ cm.

CP-19 Color Control of the Various Activator-Co-Doped La_2O_3:Bi Phosphor Thin Films Prepared by Magnetron Sputtering, ***T. Miyata*** *(tmiyata@neptune.kanazawa-it.ac.jp), K. Sahara, T. Minami*, Kanazawa Institute of Technology, Japan

We recently reported that intense blue emission in both PL and EL was observed from La_2O_3:Bi phosphor thin film. This paper describes the photoluminescent (PL) and electroluminescent (EL) characteristics in newly developed various activator (X)-co-doped La_2O_3:Bi (La_2O_3:Bi,X) phosphor thin films prepared by an rf magnetron sputtering (rf-MS) deposition method. The La_2O_3:Bi,X phosphor thin films were deposited on thick $BaTiO_3$ ceramic sheets by a combinatorial rf-MS deposition method using a powder target, which was a mixture of La_2O_3, Bi_2O_3, and oxide co-activator (Tm, Yb, Er, Eu, Tb, Dy, Ce, or Mn) powders calcined at 1200°C in air. Sputter depositions were carried out under the following conditions: atmosphere, pure Ar gas; pressure, 6 Pa; and substrate temperature, 250-350°C. The thickness of all the deposited oxide phosphor thin films was approximately 1.5 μm. After deposition, the phosphor thin films were postannealed in either an Ar gas or an air atmosphere for 60 minutes at temperature ranging from 700 to 1100°C. Multi-color PL emissions were observed from all La_2O_3:Bi,X phosphor thin films postannealed above approximately 800°C, regardless of the postannealing atmosphere . However, the PL emission color was considerably affected by the kind and the content of the co-doped activator . For example, multi-color PL emission consisting of blue broad peak due to the $6s^2$-$6s^1 6p^1$ transition in Bi^{3+} and some sharp peaks due to the transition in additional rare earth ions were observed from La_2O_3:Bi,Dy, La_2O_3:Bi,Er, and La_2O_3:Bi,Eu phosphor thin films under excitation at a wavelength of 302 nm. Note that PL emission due to the transition in rare earth ions was observed under the Bi^{3+} excitation wavelength. On the other hand, the color and intensity of the obtained EL emission were also considerably affected by the kind and the content of the co-doped activators. The thin - film EL (TFEL) devices were fabricated with an AZO/ZnS/La_2O_3:Bi,X/$BaTiO_3$/Al structure. The ZnS thin film, deposited by rf-MS, was introduced to improve the excitation efficiency of the hot electrons in the La_2O_3:Bi,X thin-film emitting layer. The EL emission in the wide area of the visible range was obtained in TFEL devices fabricated using La_2O_3:Bi,Er, La_2O_3:Bi,Dy, or La_2O_3:Bi,Eu emitting layers. The CIE color coordinates of the EL emission from La_2O_3:Bi,Er, La_2O_3:Bi,Dy, or La_2O_3:Bi,Eu TFEL devices were changed from (0.18, 0.24) to (0.29, 057), (0.18, 0.24) to (0.34, 042), or (0.18, 0.24) to (0.50, 041), respectively. Note that the CIE color coordinates of the EL emissions were controlled by the content of the co-activator.

CP-20 Determination of Dopant Concentration in Spiro2-CBP:Ir(ppy)$_3$ Co-Deposited Thin Films Used as Active Layer in Phosphorescent OLED, *Y. Angulo,* PUC-Rio, Brazil, *E. Gravina, R. Machado, C. Legnani, W. Quirino, C.A. Achete,* Inmetro, Brazil, ***M. Cremona*** *(cremona@fis.puc-rio.br)*, PUC-Rio, Brazil

Organic Light Emitting Diodes using Phosphorescent dyes (PHOLEDs) have demonstrated excellent performance of obtaining devices with internal quantum efficiencies of about 100% through radiative recombination of both singlet and triplet excitons.Transition metal compounds with organic ligands or organometallic compounds doped into appropriate host materials with vacuum thermal co-deposition process are generally used for this purpose. One of the most used compounds, the green phosphorescent *fac*-tris(2-phenylpyridine)iridium, Ir(ppy)$_3$, when doped into hosts such as 4,4′-N,N′-dicarbazole-biphenyl (CBP) with nominal concentrations of about 6-10 wt% allows the fabrication of PHOLEDs with very high external quantum efficiencies when compared with those obtained with fluorescent OLEDs. Actually, the dopant concentration values used during the film co-deposition process are nominal and there is no evaluation of the real content of Ir(ppy)$_3$ in the emissive layer. In this work, an accurate method to establish the real concentrations of Ir(ppy)$_3$ doped into 2,7-bis(9-carbazolyl)-9,9-spirobifluorene (Spiro2-CBP) as host using X-ray fluorescence (XRF) analysis is presented and discussed. The knowledge of the real concentration is critical for the performance optimization of the phosphorescent devices. XRF analysis is a powerful nondestructive physical method used for chemical elemental analysis of materials in the solid and liquid state and it is also quite common in research laboratories. The system used was the S4-Pioneer energy dispersive X-ray fluorescence system operated at 27 kV with a current of 100 mA and all the spectra were recorded at room temperature using a pentaerythrite (PET) crystal. For calibration purpose, a pellet of polyvinyl alcohol (PVA) was used as matrix for accurately weighted different amounts of Ir(ppy)$_3$ compound that were successively analyzed by XRF spectrometer. The measured XRF peak intensity is the sum of different contributions: the background and the $M_{\alpha1}$, $M_{\alpha2}$ and M_{β} iridium characteristic XRF lines. These intensities scaled by an overall scale factor and extracted by means of a non-linear fitting method based on Levenberg-Marquardt algorithm, can be plotted against the known mass concentration of Ir(ppy)$_3$. The curve obtained is used to determine the Ir complex content in the films. Preliminary results for 30 wt% nominal co-deposited Ir(ppy)$_3$:Spiro2-CBP films with a thickness of 100 nm provide an amount of Ir(ppy)$_3$ of 34±1 μg which corresponds to a concentration of 21.7 wt% in the film. The method was used for the direct determination of the Ir(ppy)$_3$ mass content in different co-deposited films.

CP-22 Effect of Concentration on Optical Properties of Cobalt Oxide Selective Coatings Prepared by Electrodeposition Method on Stainless and Copper Substrate, ***P.N. Shelke,*** Baburaoji Gholap College, India, *R.R. Hawaldar, S.D. Gunjal, R. Uddawant, K.C. Mohite (k.mohite@uoprak.ae), M.G. Takwale*, University of Pune, India

Thin films of cobalt oxide remain imperative by virtue their applications in rechargeable batteries [1], solar absorber coatings [2] and sensing [3]. Herein, cobalt oxide thin films were synthesized in two steps In step one, cobalt thin films were cathodically electrodeposited to stainless steel and copper substrates from CoSO4 (cobalt sulphate) and CoCl2 (cobalt chloride) precursor solutions at ambient conditions. These synthesized films were then transformed into Co3O4 thin films on annealing treatment in second step. The formation of cobalt and cobalt oxide was confirmed by X-ray diffraction studies. Oxidation state of cobalt in these compounds was confirmed by X-ray photoelectron spectroscopy (XPS). The influence on electrolyte composition and other parameters like pH, temperature, current density, deposition time as well as electrode distance were thoroughly investigated. Absorptance and emittance properties of these films were studied using UV-visible spectroscopy and Fourier transform infrared spectroscopy. Percentage absorptance (α) values ranged from 0.90 to 0.93 and emittance (ε) values ranged from 0.1 to 0.07 under optimized conditions of current density (21 mA/cm2) and when concentrations of CoSO4 and CoCl2 solutions were 0.98M and 0.28M, respectively.

Carbon and Nitride Materials: Synthesis-Structure-Property Relationships

Room: Golden Ballroom - Session DP

Symposium D Poster Session

DP-1 Optical and Electrical Response of Self-Assembled Single-Walled Carbon Nanotube Networks, ***I.-J. Teng*** *(eru.mse94g@nctu.edu.tw), L.-C. Wang, H.-L. Hsu, T. Wang, K.-L. Chen,* National Chiao Tung University, Taiwan, *S.-R. Jian,* I-Shou University, Taiwan, *C.-T. Kuo*, Min Dao University, Taiwan

We report the fabrication of self-assembled single-walled carbon nanotube (SWCNT) networks grown by using catalytic-CVD collaborating buffer layer-assisted process with a gas mixture of hydrogen–methane atmosphere. A simple and reproducible method of controlled fabricating self-assembled SWCNT networks is presented in this study. No pre-patterned catalyst process is applied to achieve the lateral-grown SWCNTs during the whole procedure. The electrical and infrared (IR) sensitive properties of the SWCNT network-based detector under cooled and un-cooled modes were both investigated. Results indicate that the variation of resistivity is significantly affected by the factors of network density and surroundings. In addition, the emission energy of the SWCNT networks exhibits around 1.03 eV by using photoluminescence (PL) spectroscopy at room temperature. The finding in our work provides a framework of optical and electrical properties of the self-assembled SWCNT networks for future optical detector applications.

DP-2 Coating of Carbon Nanotubes with Amorphous Carbon Nitride Thin Films and Characterization of Long-Term Emission Stability, ***Y.-R. Noh***, *J.-P. Kim, J.-S. Park (jinsp@hanyang.ac.kr)*, Hanyang University, Korea

Recently, carbon nanotubes (CNTs) are researched to develop a high resolution x-ray image system for medical applications such as early diagnosis of cancers using the superior properties of CNTs such as chemical stability, thermal conductivity, mechanical strength, and structural aspect ratio. For use of CNT-emitters as electron source for x-ray generation, a large number of investigations have been focused on how to enhance the emission current level and to reduce the turn-on field for electron-emission. In addition, the long-term emission stability should be ensured because the emission capability of CNT-based emitters may be degraded during operation due to several reasons such as weak adhesion and ionic etching of CNTs. In order to achieve desirable performances in emission current and stability, coating of CNTs with various materials have been studied. Among the coating materials, amorphous carbon nitride (a-CN$_x$) thin films have been proved by our previous work to improve the emission current and stability of CNT-emitters.

In this work, the effects of thermal treatment on CNTs, which were coated with a-CN$_x$ thin films, have been considered for the purpose of enhancing the long-term stability of CNT-emitters. The CNTs were directly grown on metal-tip (tungsten, approximately 500 nm in diameter at the summit part) substrates by inductively coupled plasma-chemical vapor deposition (ICP-CVD). The a-CN$_x$ thin films were coated on CNTs by RF magnetron sputtering. Thermal treatment on a-CN$_x$ coated CNT-emitters was performed using a rapid thermal annealing (RTA) system by varying temperature (300-800°C), atmosphere (N$_2$, O$_2$ or none), and process time. Morphologies and microstructures of a-CN$_x$ films were analyzed by field-emission scanning electron microscopy (FESEM), high-resolution transmission electron microscopy (HRTEM), and x-ray photoelectron spectroscopy (XPS). The stability property of the a-CN$_x$/CNTs hetero-structured emitters was measured using a high vacuum (below 10^{-7} Torr) field-emission measurement system. For characterization of emission stability, the fluctuation and degradation of the emission current were monitored in terms of operation time. The results were compared with a-CN$_x$ coated CNT-emitters that were not thermally heated as well as with the conventional non-coated CNT-emitters.

DP-3 The Gas Sensing Study of Nanocomposite Material Based on Functionalized Carbon Nanotubes, ***L.C. Wang***, National Chiao Tung University, Taiwan, *K.-T. Tang (kttang@ee.nthu.edu.tw)*, National Tsing Hua University, Taiwan, *C.-T. Kuo*, MingDao University, Taiwan, *S.-R. Yang*, Chung-Shan Institute of Science & Technolog, Taiwan

The purpose of this study was to develop the gas sensing film with nanocomposite material. In this case, a process was successfully developed to synthesize the polymer-base materials by filling the functionalized carbon nanotubes (CNTs) into the free volume of the polymer films. The raw materials included poly (n, n dimethylamino propylsilsequioxane, or SXNR) polymer and the multiwalled carbon nanotubes (MWNTs, 40 ~ 60 nm in diameter and a few µm in length) synthesized by thermal chemical vapor deposition (CVD). The MWNTs were functionalized in the solution of HNO$_3$/H$_2$O$_2$ (volume ratio 2/1) to oxidize CNTs to improve their hydrophilic property by forming carboxylic acid and hydroxyl groups on the surface. The gas sensing sensitivity of the synthesized nanocomposites was evaluated by the Surface Acoustic Wave (SAW) gas sensor device to examine their gas absorption/desorption response time and weight increase in the atmosphere of ethanol and dimethyl methylphosphonate (Dmmp) vapors. The results indicated that the functionalized CNTs could improve the response time of gas sensing than unfunctionalized CNTs. (The gas sensing mechanism of the nanocomposites will be discussed in the text, which may relate to degree of dispersion of CNTs in the polymer matrix.)

DP-5 HF-CVD of Nano (NDC) and Micro (MDC) Diamond Coatings onto CrN/Cr Bi- Layers: Morphology, Adhesion and Wear Resistance, *R. Polini, M. Barletta (barletta@ing.uniroma2.it)*, Università di Roma Tor Vergata, Italy, *G. Cristofanilli*, Università di Roma Tor Vergata, Itlay, ***D. Bellisario***, Università degli Studi di Roma, Rome

CrN/Cr bi- layers have been used recently to promote the growth of high quality Hot Filament Chemical Vapor Deposition (HFCVD) diamond coatings onto Co-cemented tungsten carbide (WC- 6wt.% Co) substrates.

Yet, adhesion and wear resistance of diamond coatings on CrN/Cr interlayers can be very poor. In the present investigation, the influence of the crystalline size of the diamond coatings on their adhesion and wear endurance is looked into.

Films of CrN/Cr were deposited onto 10x10x3 mm WC- 6wt.% Co samples using a PVD arc plant. The CrN/Cr interlayer was achieved by progressively decreasing the nitrogen concentration inside the deposition chamber from 100% to 0% of the gas phase, and increasing the argon concentration. This way, when the nitrogen was completely replaced by the argon in the gas phase, a resulting layer of metallic-Cr was superimposed on the underlying graded CrN layer.

Nano - and micro- crystalline Diamond Coatings were deposited by HFCVD onto untreated and Fluidized Bed Machined (FBM) CrN/Cr interlayers. Nanodiamond Coatings (NDC) were characterized by a smoother morphology and they showed improved wear resistance. However, the superimposition of Nanodiamond Coatings (NDC) onto CrN/Cr interlayers corrugated by Fluidized Bed Machining (FBM) was found to be the most promising choice, leading to the formation of highly adherent and wear resistant coatings.

DP-6 Effect of Nickel Incorporation on Structural, Nanomechanical and Biocompatible Properties of Diamond Like Carbon Thin Films Prepared by Low Energy Biased Target Ion Beam Deposition, *P. VijaiBharathy*, Bharathiar University, India, *D. Nataraj (de.natraj@gmail.com)*, Bharathair University, India, ***Y.-Y. Chang***, Mingdao University, Taiwan, *D. Mangalaraj*, Bharathiar University, India, *S.-M. Yang*, National University of Kaohsiung, Taiwan, *Y. Qiaoqin*, University of Saskatchewan, Canada, *L. Yang, T.J. Webster*, Brown University

Surface and compositional modification by incorporating metals in DLC matrix leads to tune its properties suitable for biomedical applications. The purpose of this study is to evaluate a new surface coating for bone-related implants by combining the hardness, inertness and biocompatibility of DLC and nickel. For this purpose, trace amount (less than 3at %) of nickel was incorporated into DLC matrix using biased target ion beam deposition technique. The nickel concentration in DLC matrix was adjusted by altering the target bias voltage ranging from -300V to -700V. Film characteristics were investigated using Raman, X-ray photoelectron spectroscopy (XPS) and High resolution Transmission electron microscopy (HRTEM). Mechanical properties were investigated using Nanoindentation method. Biocompatibility of the Ni-DLC thin films were investigated using Osteoblasts cell adhesion test. From XPS and Raman analysis it is clear that the nickel incorporation induce more graphite-like bonding in DLC matrix. From XPS analysis, the presence of Ni, NiC$_x$ and NiO$_x$ phases in the DLC matrix was noticed. HRTEM proves that Ni particles are in the form of nanoclusters having a diameter of ~3nm. Nanoindentation results confirmed that the hardness of the Ni-DLC composite films gets decreased with the increase in nickel concentration. Cell culture tests using the human osteoblasts bone marrow cells were performed to determine the effect on cell growth with respect to that of nickel content in DLC matrix. By the addition of nickel into the DLC matrix, it was found that there is no adverse effect on the cellular growth and reactions as compared to that of Si and glass samples. Therefore, nickel incorporated DLC thin films could be a promising alternative coating material for bone related biomedical applications.

DP-7 Silicon Modified DLC Coatings Deposited by PACVD and PVD Sputter Techniques, ***M. Keunecke*** *(martin.keunecke@ist.fraunhofer.de), I. Bialuch, K. Bewilogua*, Fraunhofer IST, Braunschweig, Germany, *D. Hofmann, S. Kunkel*, AMG Coating Technology GmbH, Hanau, Germany

Amorphous hydrogenated carbon (a-C:H or DLC) coatings are widely used in several industrial applications. These coatings are commonly prepared by plasma activated chemical vapor deposition (PACVD). The mainly used technique for deposition a-C:H coating in industrial scale bases on a glow discharge in a hydrocarbon gas like acetylene or methane using a substrate electrode powered with medium frequency (m.f. - some 10 to 300 kHz). A relatively new and promising technique is the deposition of a-C:H coatings by a reactive magnetron sputter deposition with acetylene as reactive gas.

Modified a-C:H-coatings can extend the range of applications. An interesting modification are the Si-modified a-C:H coatings. These a-C:H:Si (Si-DLC) coatings exhibit low coefficients of friction against steel counterpart, good wear resistance and are predicted to extend the operation temperature range to higher temperatures.

Using these two mentioned techniques a-C:H:Si coatings were prepared, characterized and compared. The chemical composition of the coatings was investigated by electron microprobe analysis. The mechanical properties like resistance against abrasive wear, plastic hardness, adhesion and friction coefficients were determined. Cross sectional SEM images showed the growth structure and surface morphology of the coatings.

DP-8 Wear Resistance and Interfacial Studies of Cu-Doped Diamond-Like Carbon on Aluminum Alloy, *J.-Y. Jao*, ***Y.-C. Liu***, *S.-Y. Shiu, F.-S. Shieu, L.-S. Chang*, National Chung Hsing University, Taiwan, *H.-C. Shih (hcshih@mx.nthu.edu.tw)*, National Tsing Hua University, Taiwan

Copper-doped diamond-like carbon (DLC) films with varying Cu concentrations were deposited on 7075 aluminum alloy substrates using filtered cathodic vacuum arc (FCVA) system. The incorporation of Cu into the DLC thin films have great influence on their microstructure, surface morphology, interfacial qualities, chemical composition and mechanical properties of the resulting films. It is found that the friction coefficient of the thin films is lower than 0.1 and the residual stress between the DLC thin films and aluminum alloy substrates can be substantially decreased after the effective doping of Cu into the films, which implies that the Cu-DLC films are suitable to be used as a protective coating on aluminum alloys.

DP-9 Structural, Nanomechanical and Biocompatible Properties of Titanium Incorporated Diamond Like Carbon Thin Films, *P. VijaiBharathy,* Bharathiar University, India, *D. Nataraj (de.natraj@gmail.com),* Bharathair University, India, *Q. Yang,* University of Saskatchewan, Canada, *D. Mangalaraj,* Bharathiar University, India, *J.S. Albero,* University of Alicante, Spain, *T.J. Webster,* Brown University, *Y.-Y. Chang,* Mingdao University, Taiwan, ***Y. Tang***, University of Saskatchewan, Canada

Titanium (Ti) incorporated diamond like carbon (Ti-DLC) thin films with different Ti concentration were deposited onto silicon wafers using biased target ion beam deposition technique. The structure of the films was characterized by Raman spectroscopy, X-ray photoelectron spectroscopy (XPS) and high resolution transmission electron microscopy (HRTEM). The mechanical properties of the films were investigated using nanoindentation and the biocompatibility of the films was investigated using osteoblast cell adhesion testing. Raman and XPS results show that the incorporation of Ti induced more graphite-like bonding in DLC matrix. XPS results show that the incorporated Ti did not react with carbon to form TiC but was oxidized to form TiO_2 at the very surface of the films. HRTEM results reveal that the incorporated Ti formed nanoparticles with an average size of approximately 5 nm distributing in the DLC matrix. Nanoindentation analysis shows that the hardness of the DLC films decreased with the incorporation of Ti in the films . Osteoblast cells spread well on Ti-DLC surfaces indicating the non-toxic nature of the films. In addition, the incorporation of Ti into DLC increased cell growth, indicating improved biocompatibility. In summary, the incorporation of low concentration of Ti into DLC films increases the biocompatibility than DLC film, thus Ti-DLC would be a new alternative coating for biomedical implants coating applications.

DP-10 Reaction Mechanism and Characteristics of High-Temperature Oxidation of sp^3 Rich Diamond-Like Carbon Films Synthesized by the Cathodic Arc Evaporation Process, *D.-Y. Wang (jackaljr@mdu.edu.tw),* ***J.-L. Lu****, W.-C. Chen, M.-H. Shih*, MingDao University, Taiwan

The diamond-like carbon (DLC) film has been widely used in the cutting and forming industries with its high hardness, low friction coefficient, high wear resistance, and chemical inertness. In this study, Diamond-like carbon (DLC) films were synthesized by the cathodic arc evaporation (CAE) process. The unique process takes advantage of the cathodic arc plasma to trigger the chemical decomposition reaction for DLC thin films. The energetic metal plasma catalyzed the decomposition of hydrocarbon gas (C_2H_2), and induced the formation of the metal doped and hydrogenated DLC thin films. The formation mechanism of DLC was analyzed by the plasma diagnostic. The main features of the plasma diagnostic from the CAE process include Cr、CN and C when CrN transform to DLC.

The oxidation behavior of sp^3-rich DLC films was investigated by using thermal gravimetric analysis (TGA) and differential scanning calorimeter (DSC). In this study, a significant weight loss results from the carbon oxidation between 330 and 460^{o}C. According to the TGA curve, weight gain of specimen changed only slightly as the temperature increased from 500 to 800^{o}C due to the thermal oxidation of underlying CrN and CrC_xN_y interlayers. The peak temperatures were read from the first derivative curve (DDSC) of the DSC curve, DDSC can observe three change-point of temperatures at 350, 390 and 440 ^{o}C. Finally, used TGA and DSC calculate the activation energy and the oxidation kinetics.

All the oxidation characteristics of the films were identified by transmission electron microscopy (TEM), X-ray diffraction (XRD), scanning electron microscopy (SEM), Raman spectroscopy and X-ray photoelectron spectroscopy (XPS).

DP-11 UV/O_3 Treatment of a-C:O and a-C:N Thin Films, *W. Kulisch (wilhelm.kulisch@yahoo.de),* University of Kassel, Germany*, F. Danneil, H. Vasilchina, S. Ulrich,* ***M. Stueber****,* Forschungszentrum Karlsruhe, Germany*, G. Ceccone, D. Gilliland,* European Commission JRC, Italy*, C. Popov*, University of Kassel, Germany

The effect of an UV/O_3 treatment (185 and 254 nm emission) on the surface properties of a-C:O and a-C:N films deposited by reactive d.c. magnetron sputtering of a graphite target in the presence of O_2 and N_2, respectively, has been investigated. As-grown and treated samples have been investigated, among others, by X-ray photoelectron spectroscopy (XPS), electron probe microanalysis (EPMA), Fourier transform infrared spectroscopy (FTIR), atomic force microscopy (AFM), and contact angle measurements against purified water. In addition, the surface energy has been determined by the method of Owens, Wendt and Kaelble. EPMA measurements show that the presence of O_2 and N_2 in the sputtering atmosphere leads to the incorporation of up to 17% oxygen and 33% nitrogen, respectively, into the amorphous carbon films. FTIR spectra provided additional information on the bonding environment of the carbon atoms in these species. Their presence has a pronounced influence on the contact angle against water although all as-grown films were moderate hydrophobic with contact angles between 68 and 85°. 30 min UV/O_3 treatment in air rendered all surfaces highly hydrophilic with contact angles below 10°. XPS measurements showed that the oxygen concentration at the surface has increased by 10% or more as a result of the treatment. The surface energy rises from 60 mN/m to 78 mN/m, which is due to a drastic increase of the polar component of the surface energy.

DP-12 Electrical Properties of Liquid-Phase Deposited Carbon Nitride Films, ***H. Kiyota*** *(hkiyota@ktmail.tokai-u.jp), M. Higashi, T. Kurosu*, Tokai University, Japan

Since theoretical prediction of tetrahedral β-C_3N_4 by Liu and Cohen, carbon nitride has been of great interest in developing superhard and wide band-gap material. For electronic applications, carbon nitride is a promising low-κ material for multilevel interconnection of ULSI circuits because of the high resistivity and low dielectric constant. Deposition of carbon nitride has been attempted by conventional vapor deposition techniques such as chemical vapor deposition and reactive sputtering. Recently, we have attempted the liquid-phase deposition of amorphous carbon and carbon nitride to develop alternative deposition techniques for carbon related materials. In this work, we have studied electrical properties of liquid–phase deposited carbon nitride films which were deposited by the application of a DC bias voltage to Si substrates immersed in acrylonitrile (CH_2CHCN) . The apparatus used for deposition consists of a glass vessel, two electrodes, and a DC power source. A 20 × 40 mm^2 n-type Si (100) wafers were mounted on the both of two electrodes. Typical deposition parameters were a bias voltage of 3 kV, a current density of 1 mA/cm^2, a liquid temperature of 70°C, and a deposition period of 1 h. Continuous and uniform films were grown by the application of both negative and positive bias voltages. X-ray photoelectron spectra of the deposited films show the presence of C, N, and O atoms as major components in the films. Furthermore, sodium is detected for the samples deposited by the negative bias application during the 1st deposition period after changing the reactant liquid. To measure electrical properties of carbon nitride films, Al electrodes with a diameter of 1 mm were formed onto the films by using a high-vacuum evaporation system. Ohmic contact onto the backside of Si was formed to fabricate metal-insulator-semiconductor (MIS) diode. Resistivity of the film was determined to be higher than 10^{11} Ω cm at 300 K. Capacitance and conductance of MIS diodes were measured as the functions of bias voltage at frequency between 120 Hz and 1 MHz. The samples contaminated by sodium show instable behavior in their capacitance-voltage characteristics. However, the *C-V* characteristics can be stabilized after bias-aging treatment, indicating that the incorporated sodium acts as mobile ionic charge in the insulating CN_x film. We attempted to prevent the mobile charge contamination of carbon nitride films, and found that sodium concentration of the film decreases rapidly by repeating the deposition period. Based on the *C-V* results, dielectric constants of the carbon nitride, interface trap densities, and energy diagram of MIS structure are also discussed.

DP-13 Corrosion Performance of Diamond-Like Carbon (DLC)-Coated 316L SS in Simulated Body Fluid Environment, ***E. Gil de Fuentes*** *(lindagil@cantv.net),* Universidad Nacional Experimental Politecnica (UNEXPO), Venezuela*, M.H. Staia, R. Fragiel, E.S. Puchi,* Universidad Central de Venezuela (UCV), Venezuela*, D.E. Chicot*, Université des Sciences et Technologies de Lille, France

Diamond-like carbon (DLC) films have several advantages in biomedical applications such as high hardness, chemical inertness and low friction. Furthermore, SS 316L substrates coated with DLC films have been reported to have a good biocompatibility and high corrosion resistance. In the present investigation, the coatings were deposited in an industrial facility onto a SS 316L substrate by means of closed field unbalanced magnetron sputter ion plating. The chemical bonding structures of the DLC films were characterized by means of Raman spectroscopy and the electrochemical behavior were evaluated by means of electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization in a 0.89% NaCl solution of pH 7.4 at a temperature of 37ºC, simulating the body fluid environment. The porosity and protective efficiency of DLC coatings were obtained using potentiodynamic polarization tests. Moreover, the delamination area and volume fraction of water uptake of DLC coatings as a function of immersion time were calculated using electrochemical impedance spectroscopy. The DLC films showed high impedance, high polarization resistance and high breakdown potential, which were attributed to the high sp^3 content and the uniformity of these films. The excellent chemical inertness of the DLC films makes them promising corrosion resistant coating materials for such applications.

DP-14 Pulse Plasma Nitriding and a-CN_x:H Coating Deposition on Hot Work Steel Samples, ***M. Zlatanovic*** *(jzlatanovic@beotel.net),* School of Electrical Engineering, Serbia*, N. Popovic*, Nuclear Science Institut Vinca, Serbia

Samples made of hot work steel grade H11 were nitrided at various pulse plasma process parameters. The influence of the nitrogen content in nitrogen-hydrogen plasma, substrate temperature, treatment time, pulse duty cycle and frequency on diffusion and compound zone formation was investigated. After plasma nitriding at selected process parameters a carbon containing gas was introduced in process chamber which resulted in transition from diffusion to deposition processing mode. The obtained surface structures were characterized by the optical microscopy, microhardness measurements, calotest method, Raman and IR spectroscopy, XRD analyses and SEM microscopy. Deposited hydrogenated carbonitride films were covered by the electrically conductive particles of different size partially incorporated in the coating. The origin and grows of spherical particles was discussed comparing some properties of rf and pulse plasma surface treatment. The experiments demonstrated possibility of a continuous diffusion\deposition pulse plasma processing intended for tribological applications.

DP-15 Surface Optical Raman Modes in Nano-Crystalline $In_xGa_{1-x}N$ Thin Films Prepared by Mixed Source Modified Activated Reactive Evaporation, ***S. Meher*** *(samir@physics.iitm.ac.in), K.P. Biju, M.K. Jain*, IIT Madras, Semiconductor Laboratory, India

Nano-crystalline *c*-axis oriented $In_xGa_{1-x}N$ thin films were prepared by modified activated reactive evaporation (MARE) technique using a simple mixed source evaporation of indium and gallium metals. In MARE technique, the substrate is placed in conjunction with the RF cathode itself instead of the ground electrode and hence subjected to high energy nitrogen ion bombardment. The high energy of nitrogen ions enables room temperature growth of the films without any intentional substrate heating. X-ray diffraction (XRD) pattern reveals the average crystallite size to be ranging from 6-12 nm. The indium composition (x) calculated from the XRD peak shift using Vegard's law was found to be 0.8, 0.63 and 0.38 respectively for the three films. Atomic force microscopy (AFM) was used to study the surface roughness of the InGaN alloy films. The average transmittance in the near infrared region which corresponds to the strong free carrier absorption was found to increase with increase in gallium incorporation in the alloy. The band gap values obtained by fitting the absorption edge with Urbach formula which includes the effects caused by In-Ga segregation in InGaN alloy system was found to be in good agreement with the values obtained from photoluminescence (PL) spectra. Raman scattering was used to probe the surface optical (SO) phonon modes in these InGaN nano-crystalline thin films. SO phonon modes are mostly observed in polar crystals, when the average crystallite size is about one order of magnitude smaller than the wavelength of the incident laser radiation (488 nm in the present case). In such cases, the lattice vibration is confined to the surface which gives rise to a wavenumber in between the transverse optical (TO) and longitudinal optical (LO) phonon modes. In the present case, SO phonon modes were observed at 566 cm^{-1}, 580 cm^{-1} and 628 cm^{-1} respectively for x = 0.8, 0.63 and 0.38 $In_xGa_{1-x}N$ alloy films. Additionally, A_1 (TO) and A_1 (LO) modes are also clearly visible for the x = 0.8 and 0.63 films. But, for x = 0.38 film, A_1 (TO) mode vanishes and E_2 (high) mode appears. These A_1 (LO), A_1 (TO) and E_2 (high) modes correspond to the hexagonal wurtzite structure. The presence of surface roughness in these nano-crystalline InGaN alloy films is mainly responsible for perturbation of the surface potential which in turn makes the SO phonon modes observable. This type of electron-phonon interaction in such confined systems has significant influence on the electronic and optical properties of semiconducting nanomaterials which in turn plays an important role in device applications.

DP-17 Improving Surface Smoothness of Gallium Nitride Nanowires by Introducing Hydrogen Plasma, ***T.-H. Wu****, F.C.-N. Hong (wcyu75@hotmail.com)*, National Cheng Kung University, Taiwan

In the present study, we have found that the surface diffusion is suppressed by introducing hydrogen gas into the plasma-enhanced chemical vapor deposition (PECVD) apparatus during the growth of GaN nanowires. The formation of GaHx (x=1, 2, 3) species due to the reaction between gallium atoms and hydrogen plasma reduced the surface diffusion length of Ga-containing growth species, and thus decreased the amount of growth species adsorbed on the nanowire surfaces which results in the elimination of the nucleation on nanowire surface and improves the surface smoothness of the nanowire. The stacked-cone nanostructures and nanobelts appeared under low-hydrogen or no-hydrogen conditions in the PECVD system, but were completely absent under high hydrogen conditions. The mechanism of the improvement of nanowire surface smoothness will be presented as well as the effect of hydrogen plasma on modifying the mechanism of GaN nanowire growths.

DP-18 Resistive Switching Effect in Zirconium Oxynitride Thin Film Deposited by Unbalanced Magnetron Sputtering, ***C.H. Lee*** *(ericalee0713@gmail.com), J.-H. Huang, J.-P. Yu*, National Tsing Hua University, Taiwan

Resistance switching random access memory (RRAM) is one of the promising next generation memory devices. RRAM shows advantages such as highly scalable, low power operation, simple structure, and fast response. The resistive phenomenon is based on the electrically stimulated change of the resistance of metal-insulator-metal (MIM) memory cell. Various models were proposed for the reversible and reproducible resistive switching phenomenon; however, resistance switching mechanisms have not been clearly clarified. The most convincible mechanism is the formation and disruption of conductive filaments which may be composed by plenty of ionic and electronic defects. The resistance switching behavior of zirconium oxide as an insulator film was wildly investigated for resistance memory. Zirconium oxynitrides, being a mixture of ZrN, Zr_2ON_2 and ZrO_2 phases, are expected to have more defects to form the conductive filaments and therefore the mechanism of switching resistivity or the failure of the device can be better studied in this class of materials. In this study, Zr(N,O) films with a thickness of 100 nm were deposited on $TiN/SiO_2/Si$ substrates at 450°C using unbalanced magnetron sputtering. The working gases consisting of argon and nitrogen gases were introduced at fixed flow rates. The reactive gas oxygen ranging from 0 to 1.5 sccm were used to deposit the resistive switching layer Zr(N,O) with different oxygen contents. The I-V characteristics of the TiN/Zr(N,O)/TiN device were analyzed at room temperature. Film thickness and microstructure were observed by a field-emission scanning electron microscope. The crystal structure was characterized by X-ray diffraction. The composition depth profile of the thin film was analyzed by Auger electron spectrometer. Results of this study confirmed that Zr(N,O) used as the insulator film possesses better properties of reversible and reproducible resistance switching than pure ZrO_2 thin film.

DP-20 Effect of Carbon on the Tribological Performance of Nano-Structured AlTiCN Films, ***H.-Y. Kao****, Y.-Y. Chang (yinyu@mail2000.com.tw)*, Mingdao University, Taiwan

Ternary AlTiN and AlTiCN 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 C_2H_2 activated by the AlTi alloy plasma in the evaporation process was used to deposite the AlTiCN coatings. At a total gas pressure of 2.0 Pa, a mixture of reactive N_2 and C_2H_2 with different C_2H_2 flow rate from 0 sccm to 150 sccm was introduced into the chamber to form the AlTiCN 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 AlTiN films. A nanocomposite structure of coexisting metastable hard AlTiCN crystallites and amorphous carbon phases was found in the coatings, those possessed smaller crystallite sizes than the ternary AlTiN film. Scratch tests and Rockwell indentation were performed to determine the interfacial adhesion between substrate and AlTiCN films. Mechanical properties, such as hardness and elastic modulus, were measured by nano-indentation test. Sliding friction and wear investigations were performed by using a micro sliding wear test with loading of mN range. The effects of carbon concentration on the microstructure and mechanical properties of AlTiCN coatings were studied.

DP-21 The Effect of Sulfur on the Structure of Nanomaterials Synthesized in Organic Liquids, ***A. Arai****,* Toyo University, Japan*, H. Gamo,* Toppan Printing Co. Ltd., Japan*, S. Shibasaki,* Toyo University, Japan*, A. Ando,* National Institute for Materials Science, Japan*, M. Nishitani-Gamo (mngamo@toyonet.toyo.ac.jp)*, Toyo University, Japan

We have recently developed a novel catalytic method for synthesizing a wide variety of nanomaterials, such as a carbon nanotubes (CNTs) in organic liquids [1]. The method realized a simple, speedy and high-purity growth of carbon naomaterials in organic liquids. In this method, there is no need for a vacuum reactor. A catalytic decomposition of the organic liquid yields carbon nanomaterials. At the interface between the liquid and the catalyst-supported substrate surface, a large gradient of the temperature exists. This nonequilibrium condition at the substrate surface is a characteristic feature of the liquid phase synthesis method.

It has been interesting for us that the effect of the added sulfur in the gas phase on the structure of a new carbons grown by the chemical method. We have reported that the added H2S in the gas phase enhanced the sp3 formation both in the case of CVD diamond and the carbon nanotube [2-3]. In the case of the liquid phase growth system, how affect the sulfur on the morphology and structure of the carbon nanomaterials is also interesting in the viewpoint of realizing a controllable process for the new carbons.

In this study, we investigated the effect of sulfur on the morphology of the grown materials by using a varied mixture of 1-octanethiol (CH3(CH2)7SH; OcSH) and 1-octanol (CH3(CH2)7OH; OcOH) for a carbon source.

The mixture of OcSH and OcOH was used as an organic liquid source. The cobalt (Co) catalyst-supported silicon (Si) substrate was electrically heated at the temperature in 1073 K in organic liquid. We used thermally oxidized Co-sputtered Si substrate for the growth experiment. The substrate was heated at 1073 K for 10 min in air. The morphology of grown materials was observed by scanning electron microscopy (SEM).

Both in the case of the ratio of OcSH to the mixed organic liquids were 10 % and 50 %, the thick fibriform materials and the film-like materials were obtained. In the case of the ratio was 5 %, the obtained nanomaterials were fibriform materials. Contralry to the former case, the film-like materials was not growned. The density of the fibriform materials was increased with decreasing of the OcSH content in the mixed organic liquid.

The content of OcSH, namely, the amount of sulfur in the liquid phase resulted in a wide variety of morphologies in the grown nanomaterials with different density.

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DP-22 The Investigation of Scratch Behaviour of Composed Structured TiBN Hard Films Deposited on Cold Work Tool Steel at the Different Nitrogen Rates, *H. Cicek,* Atatürk University, Turkey, ***O. Baran*** *(obaran@erzincan.edu.tr),* Erzincan University, Turkey, *Y. Totik, E. Aslan, I. Efeoglu*, Atatürk University, Turkey

Low adhesion between film-substrate is greatest disadvantage of hard coatings. It is expected that TiBN coatings exhibited high hardness and adhesion. Due to these excellent properties has been increasing interest in TiBN coatings. In this study, TiBN films were deposited on AISI D2 cold work tool steel and silicon wafers by CFUBMS. The structural, mechanical and adhesion properties of this films are analyzed by XRD,SEM, micro+nano hardness tester and indentation+scratch tester, respectively. TiBN films deposited by sputtering exhibited dense and a columnar structure. From TiBN films at the nanocomposite structure were obtained TiB2 (101) phase as dominant,TiN(200) as less specific and amorphous BN phases does not reflected. The highest critical load obtained with scratch test results were identified as 102N.The highest hardness and the highest elastic module values were obtained at the lowest nitrogen flow rate.

Tribology and Mechanical Behavior of Coatings and Thin Films
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Symposium E Poster Session

EP-2 Coating Performances When Dry Machining Refractory Titanium Alloys, ***M. Nouari*** *(Mohammed.Nouari@insic.fr), M. Calamaz, F. Girot*, Ecole des Mines de Nancy, France

In machining process, the tool-chip contact is characterized by intense thermo-mechanical loading. The coupling between thermal and mechanical loads may lead to tool failure, especially when machining refractory titanium alloys. Within such environments the efficiency of the coating material plays an important role in preserving the structural integrity of the cutting tool. The current study emphasizes the role of coating materials in enhancing wear resistance of the cutting tool and improving the tool-chip contact. The change in wear mechanisms with machining parameters such as cutting speed and coating material is discussed. The cutting tests were performed using an instrumented planer machine. Experiments were conducted on the Ti-6Al-4V titanium alloy (workpiece) and cemented carbide tool (tool substrate). Four coating materials were considered: (i)- diamond (thin layer, about 2-3µm), (ii)- diamond+TiB$_2$+CrN/DLC (Diamont Like Carbon) (about 3,5µm), (iii)- diamond (thick layer), (iiii) Diameco$^+$ (3µm). The performance of each coated tool was analyzed and compared to the uncoated one in terms of friction coefficient, contact length and tool wear. A study on the transient phenomenon of the tool degradation has been carried out according to the contact conditions which have been found strongly depended to the machining parameters.

EP-3 Study of Self-Lubricated Coatings Deposited onto Radial and Angular Bearings, ***N.M. Renevier*** *(nrenevier@uclan.ac.uk),* University of Central Lancashire, United Kingdom, *D.G. Teer*, Teer Coatings Limited, United Kingdom

Bearings are widely used in the automotive industry (gear box, wheel, steering power, crankshaft, etc) and play an essential role in the automotive reliability and performance. Extensive studied have been carried previously out on hard coatings and Me-CH coatings[1], this paper will report new results obtained with self-lubricated coatings that have shown exceptional results on other automotive parts. An experimental study was performed to assess the effect of self-lubricated coatings on the behaviour of radial and angular bearings that are designed to support thrust and/or radial loads. The bearings having large contact angles can support heavier thrust loads. They are suitable for a wide range of applications including high speed machine tool spindles or gear boxes. Self-lubricated coatings were deposited onto AISI 52100 bearing steel for laboratory tests and onto bearings for industrial tests. A laboratory pin on disc test rig was used and the tribological propertie s (friction-wear) were measured in various controlled environmental conditions (dry and lubricated). The surfaces were analysed by SEM-EDAX as well as STM/ AFM. The 4 best candidates were retained for the next industrial bearing test. Parameters such as vibration, friction/wear and temperature have been used to monitor bearing performance and the results are reported in the paper.

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EP-5 Mechanical Properties Evaluation of HFCVD Diamond-Coated WC-Co Substrates With Hard Chromized Interlayers, ***C.-C. Chou*** *(cchou@mail.ntou.edu.tw),* National Taiwan Ocean University, Taiwan, *J.-W. Lee,* Mingchi University of Technology, Taiwan, *H.-H. Lin, Y.-I. Chen, Y.-C. Chu*, National Taiwan Ocean University, Taiwan

Chromized interlayers produced by pack chromization on WC-Co substrates were tested and identified to be a potential microstructure for improving tribological performance of diamond coatings in the previous study [1]. However, interlayer's thickness as well as time and temperature of the chromization process were found critical to the formation and adhesion of the diamond films on WC-Co substrates. The microcracks on a chromized interlayer of the WC-Co substrate reduce the adhesion of the interlayer itself and the composited diamond coating as well. The time and temperature of the chromization process enhance cobalt's diffusion which interferes with the nucleation and growth of diamond film. To clarify cobalt binder's influence, the mentioned process parameters were mainly studied basing on substrates with 12 wt.% cobalt content which was two times higher than those used in [1]. Scratch tests were implemented to verify the strength between chromized interlayers and substrates. Daimler-Benz Rockwell-C indentation tests were then conducted to evaluate the adhesion properties of chromized interlayer and the later diamond-coated structures on the substrates. Phases and structures of diamond films were verified by X-ray diffraction and Raman spectrum. In conclusion, the optimal process parameters of chromized interlayer and the accompanied microstructure of the diamond coatings were addressed.

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EP-6 Correlation Between PVD Coating Strength Properties and Impact Resistance at Ambient and Elevated Temperatures, ***K.D. Bouzakis*** *(bouzakis@eng.auth.gr),* CERTH, Greece and IPT, Germany, *M. Pappa, G. Skordaris,* Aristoteles University of Thessaloniki, Greece / Fraunhofer PCCM, Germany, Greece, *E. Bouzakis,* Fraunhofer PCCM, Germany, Greece, *S. Gerardis*, Aristoteles University of Thessaloniki, Greece / Fraunhofer PCCM, Germany, Greece

The performance of PVD films depends on the operational temperature of the coated tools or components. In this paper, the correlation between the mechanical properties and the impact resistance of a TiAlN coating at various temperatures will be introduced. Nanoindentations were conducted at ambient and elevated temperatures by a nanoindentation device, enabling measurements at temperatures up to 400oC in an inert gas atmosphere. The obtained results were evaluated using appropriate FEM algorithms for determining the films' stress-strain constitutive laws, which depend on the temperature. Moreover, perpendicular impact tests on the coated cemented carbides inserts were conducted at temperatures up to 400oC for investigating the film's impact behaviour. The developed impressions were recorded by scanning electron microscopy and white light confocal measurements. The results demonstrated a non-linear temperature dependence of the film fatigue properties and a significant improvement at approximately 150oC of these properties. This fact can be attributed to dislocations movements and stress concentrations avoidance in the coating material, induced by the temperature raise. Finally, a good correlation versus the temperature was revealed between the yield stress by nanoindentations determined and the fatigue endurance stress via impact tests.

EP-8 Coefficient of Friction and Wear of Sputtered a-C Thin Coatings Containing Mo*, **P. Novak*** *(petrnov@kfy.zcu.cz), J. Musil, R. Cerstvy,* University of West Bohemia, Czech Republic

The paper reports on preparation of ~2000 to 3000 nm thick a-C coatings containing Mo, interrelationships between their mechanical properties, coefficient of friction (CoF) μ and wear k and the effect of Mo content in the a-C coating on these interrelationships. The Mo-C coatings were prepared by sputtering using an unbalanced magnetron (UM) equipped with a graphite targets (Ø=100 mm, 99.9% purity) fixed to the UM cathode with Mo ring of different inner diameter $Ø_i$. The content of Mo in the a-C coating was controlled by $Ø_i$. It is shown that (1) CoF μ and wear k of the coating strongly depend not only on its hardness H but also on its effective Young's modulus $E^*=E/(1-\nu^2)$, the ratio H^3/E^{*2} characterizing the resistance of coating to plastic deformation and elastic recovery We and (2) the nc-Mo_2C/a-C coatings with low amount of Mo composed of Mo_2C nanograins dispersed in a-C matrix exhibit low values of $\mu\approx0.07$ and $k\approx10^{-7}mm^3/Nm$ measured using CSM tribometer with WC ball at rotation speed v=0.05m/s, total sliding length l=1000 m and load L=2N; here E and ν is the Young's modulus and the Poisson ratio, respectively. The CoF μ and wear k of a-C/Mo_2C coatings are compared with those of nc-TiC/a-C coatings with C/Ti>2 containing a low amount of nc-TiC nanograins.

EP-9 Challenges and Applications of Elevated Temperature Nanoindentation to 750°C*, **B. Beake*** *(ben@micromaterials.co.uk), P. Aden,* Micro Materials Ltd, United Kingdom*, N. Schwarzer,* Saxonian Institute of Surface Mechanics, Germany*, G.S. Fox-Rabinovich,* McMaster University, United Kingdom*, W. Helle*, LOT Oriel GmbH, Germany

Nanoindentation testing can become increasingly challenging at elevated temperature, particularly when the test temperature increases to 750°C. Effective thermal control and good experimental design are critical to obtaining reliable hardness and elastic modulus measurements. The importance of controlling the sample and indenter temperatures during the test and the experimental conditions to ensure that indentation creep does not influence elastic modulus measurements (particularly on metallic samples) are discussed. There are additional challenges in nanoindentation testing above the oxidation temperature of diamond, and the steps that can be taken to obtain reliable measurements in the temperature range 500-750°C are described.

Applications in thin film research, including cutting tool coatings (TiAlN, AlCrN, AlTiN, TiAlCrSiYN etc) and DLC will be presented. The optimum combination of hardness and toughness/plasticity varies with the severity and nature of the cutting conditions. For improved performance in interrupted cutting the plasticity index (plasticity index = plastic work/total work) is critical, with high values (i.e. *not* extremely high H/E) resulting in extended tool life. Nanoindentation at elevated temperature showed that the hardness of the coatings generally decreased and the plasticity index rose with increasing temperature. In high-speed turning hot hardness is the dominant factor whilst for interrupted cutting high hot hardness should be combined with improved plasticity for longer tool life.

Analytical modelling with Film Doctor software has shown that the temperature field modifies the von Mises stress distribution in contact applications. For example, optimisation of DLC coatings for applications involving friction requires 1) accurate experimental determination of the variation in coating and substrate mechanical properties with temperature 2) determination of the temperature field in the application 3) determination of the stress field in contact taking the temperature field into account.

EP-12 Tribological Behavior of Thick-Layered TiCN Coatings*, **H.-M. Lin**, J.-G. Duh (jgd@mx.nthu.edu.tw)*, National Tsing Hua University, Taiwan

Great emphases recently have been placed on such material characteristics as hardness and toughness in developing protective hard coatings. This study paper thus aims to investigate indentation behavior with a higher loading for the thick-layered TiCN coatings deposited by plasma enhanced magnetron sputtering (PEMS). Some literatures had been evidently proved that TiCN coatings can effectively prevent fractures from growing. The thick layer of TiCN exhibited its cracks after indentation. Deposited as thick as 20 μm, the TiCN coatings thus required a comparatively larger loading of 20 mN for an easy observation by SEM. Both wear and scratch experiments were employed to 20-μm thick layer of TiCN coatings. Besides, scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDS) and X-ray diffraction (XRD) were also used to investigate microstructures and morphologies of the TiCN coatings. The results indicated that fracture toughness of the TiCN coatings could be precisely predicted from merely observing how their cracks grew with varying loadings in the indentation.

EP-16 Cracking Behaviour vs. Wear Behaviour of CrSiN Nanocomposite Coatings*, **T. Schmitt*** *(Thomas.Schmitt@ec-lyon.fr), J. Fontaine,* Ecole Centrale de Lyon, France*, P. Steyer, G.P. Pot,* INSA de Lyon, France*, F. Sanchette,* CEA, France*, C. Esnouf,* INSA de Lyon, France

Nowadays, ternary nanocomposite coatings are known for their high mechanical and oxidation resistance. Such films are composed of different phases, usually a nanocrystallised phase embedded into a thin amorphous one. This leads to the formation of an isotropic nanosized hard composite. The aim of this study is to understand the wear mechanisms of CrSiN nanocomposite coatings. Deposition was performed in an industrial arc evaporation PVD chamber, using specially designed Cr-Si targets. Single-layered CrN and CrSiN (2.8 at.% Si) coatings and the corresponding CrN/CrSiN multilayers (10 and 100 nm periods) were considered. Microstructure was investigated by XRD, SEM and TEM. Wear behaviour is investigated through tribological tests using a reciprocating ball-on-flat tribometer. Due to our specific configuration, using coated balls and uncoated flats, tests show a high severity, owing to increase cinematic length for the coating. Silicon addition leads to a detrimental decrease of the wear resistance in the case of singe-layered coatings, whereas the use of the multi-layered structure improves the durability. In order to better understand the mechanisms involved, mechanical properties were investigated by means of nanoindentation and SEM *in situ* tensile tests. Neither the hardness nor the strain to failure (H/E) could account for such wear results. On the contrary, cracking behaviour, discussed according to the Kelly-Tyson's model, is able to elucidate the high wear resistance of the multi-layered films.

EP-18 Evaluation of Hardness and Mechanical Property of Cr_2N/Cu Multilayered Thin Films by Molecular Dynamics Simulations*, **J.-C. Huang*** *(jchuang@mail.me.tnu.edu.tw)*, Tungnan University, Taiwan

Multilayered thin film nanostructures have received a lot of attention for applications such as in high-density storage systems, magnetic media, protective coatings and microsystem technologies. However, there are many multi-layered thin film products with mechanical weakness, which dominates the performance of the materials. It is necessary to investigate the processing and mechanical properties of multilayered thin films for improvement of their reliability. In this work, the molecular dynamics simulation method was used to investigate the hardness and mechanical property of Cr_2N/Cu multilayered thin films under nanoindentation. The indentation load-displacement curves were employed in this work. The results showed that the hardness and mechanical property of Cr_2N/Cu multilayered thin films differed under different film thickness. In addition, the film thickness also shows very strong influence on the interaction energy between Cr_2N thin film and Cu thin film.

EP-19 Direct Measurement of the Glass Transition Temperature of a Thin Polymer Film*, **S. Pavan*** *(sophie.pavan@ec-lyon.fr), J.-L. Loubet,* Ecole Centrale de Lyon, France*, M. Ben Saad, J. Mallégol*, ArcelorMittal Research Liège, Belgium

Polymer films are increasingly used as protective coatings for metallic substrates. Appropriate mechanical characterization methods are thus necessary, at micro and nano-scale and taking into account time- and temperature dependent effects. A dynamic nano-indentation technique has been developed, allowing the measurement of hardness, elasticity and loss factor (tan δ) of visco-elastic analysis of polymer thin films. In order to determine the glass transition temperature, indentation is performed at different temperatures, in the range from -40 to 80°C, thanks to a climatic chamber hosting the apparatus.

The glass transition temperature determined by our technique is in close agreement with Dynamic Thermo Mechanical Analysis (DMTA) performed on free polymer films, mainly when taking into account time-temperature shift between both experiments. The great advantage of this nano-indentation technique lies in the ability to characterize the polymer films directly on their substrates, without any specific preparation.

Different studies have been carried out using nanoindentation as an investigation technique. In these studies, we have considered polyester thin films (20 μm thick) deposited on steel substrates. Films submitted to different UV weathering conditions (accelerated tests as well as natural exposure) were compared. The evolution of mechanical properties with aging conditions was determined.

EP-20 Tribological and Corrosion Behavior of TiAlN/Pt and TiALN/TiAL Multilayers, ***M. Flores*** *(maflores@cucea.udg.mx), E. Rodriguez, J. Garcia*, Universidad de Guadalajara, Mexico

In the present work we report the results of studies about the influence of Pt layers on the corrosion, wear and friction of TiALN coatings deposited on 316L stainless steel by magnetron sputtering. The coatings investigated were TiAlN//Pt, TiALN/TiAL multilayers and TiN. The thickness of the Pt layers was from 50 nm to 200 nm and the period of TiALN/TiAL and TiAlN/Pt multilayers were from 250 to 500 nm. The friction and wear tests were performed on a ball-on-flat tribometer and conducted in dry (unlubricated) conditions at room temperature. The loads used were 5N and 10N, the oscillating frequency was 5 Hz. The corrosion was studied using open circuit potential measurements and potentiodynamic polarization in ringer solutions. The structure of multilayers was studied by means of XRD. The surface topography and wore surface were studied by means of optical microscopy and profilometry. The results indicate that coefficient of friction (COF) of TIALN coatings decreased when metal layers are introduced and the corrosion resistance of TiAlN coatings is improved when Pt layers are deposited.

EP-21 The Performance TiAlN + AlCrN Coated Grade in Milling of ADI, ***W. Mattes*** *(mattes@unerj.br)*, SENAI-SC, Brazil, *A.C. Bottene*, USP, Brazil, *R. da Silva*, UNERJ, Brazil

The aim of this investigation is to study the performance of the new generation of the TiAlN + AlCrN coated grade and to map the influence of cutting conditions on the tool life in milling of ADI (Austempered Ductile Iron). The results show that chipping is the main wear mechanism which determines the tool life in dry condition and notch wear in wet condition for this application. This due to the different stress mechanisms and preexisting cracks in the coating. The wear development shows clearly that the coating TiAlN + AlCrN has the best ability to delay the chipping growth. It was also found that a high content of Al in the coating TiAlN + AlCrN was especially favorable compared to a TiAlN multilayer with lower Al content AlCr coating. This is due to fine grains and low compressive stress level in the coating which increase the coating ability to withstand the mechanical and thermal impact. It was also found that the use of coolant decreases the tool life with 60-80% compare to dry milling.

EP-23 Towards Redefining the Geometry of the Rockwell Stylus to Improve the Scratch Test, ***N.M. Jennett*** *(nigel.jennett@npl.co.uk)*, National Physical Laboratory, United Kingdom, *G. Favaro*, CSM Instruments, Switzerland, *N. Randall*, CSM Instruments

The scratch test is widely used in industry to test the adhesion and resilience of coatings. It is well known that the scratch test is highly sensitive to variations in the stylus geometry. Inconsistencies in scratch test results are a problem for quality control and acceptance testing and it is believed that the majority of test variability comes from variability in the geometry of the styli obtained from manufacturers and the change in geometry that occurs due to wear from contact with hard and/or rough surfaces. In 2002 the EC project REMAST (SMT4-CT98-2238) certified a European Certified Reference Material ref. BCR692 specifically to enable a rapid verification of stylus geometry (and instrument calibration). This has demonstrated that many Rockwell styli do not have a spherical tip and that the average radius of the tip can vary greatly. Part of this problem is that the measurement methods in ISO6508 are poorly defined.

In this paper we present work from the international cooperative research of VAMAS Technical Working area 22 project 6 " Improved specification of scratch test stylus geometry". We have taken 10 styli from three manufacturers (30 total) and a reference 1 mm diameter ruby ball and measured them using Confocal microscopy, 2D profilometry and shadow-projection cross-section methods. The radii of the styli spherical caps were measured as a function of the width of data taken about the indention axis and show clearly how the effective radius of the indenter at different indentation/scratch depths can change significantly. Scratch testing on BCR692 demonstrates clearly that these differences are related to a variation in scratch test performance. Differences between measurement methods are discussed in the light of the radius values obtained and recommendations are made for an improved geometry specification for the scratch test stylus in the revision of ISO6508 currently underway.

EP-24 Temperature Dependent Comparison of Silver Molybdate and Silver Tungstate as Solid Lubricants to Understand Double Metal Oxides, ***D. Stone****, D.P. Singh, J. Liu*, Southern Illinois University Carbondale, *C. Muratore, A.A. Voevodin*, Air Force Research Laboratory, *Q. Ge, S.M. Aouadi (saouadi@physics.siu.edu)*, Southern Illinois University Carbondale

Double oxide phases that combine a transition metal and a noble metal have recently become a subject of investigation as potential lubricious materials for high temperature tribological applications. In this paper, two selected double metal oxide phases, namely silver molybdates and tungstates, were produced in thin film and powder forms using magnetron sputtering and hydrothermal methods, respectively. The lowest frictional properties of these materials were measured at 600°C to be 0.1 and 0.4 for the $Ag_2Mo_2O_7$ and α-Ag_2WO_4 phases, respectively. Hence, a systematic investigation was carried out to understand the changes in chemistry and crystal structure of these materials with increasing the temperature up to 600°C using in-situ Raman spectroscopy and differential scanning calorimeter. In addition, simulations were performed to investigate their structure using ab-initio molecular dynamics (AIMD) method within the density functional theory framework. The structural and chemical information obtained using computational and experimental studies was correlated to their high temperature tribological performance.

EP-25 Influence of Different Plasma Nitriding Treatments on the Wear and Crack Behaviour of Forging Tools Evaluated by Rockwell Indentation and Scratch Tests, ***H. Paschke*** *(hanno.paschke@ist.fraunhofer.de), M. Weber, P. Kaestner, G. Bräuer*, Fraunhofer IST, Germany

Forging tools have a short lifetime compared to cold forming tools e.g. for sheet metal forming. The high local surface temperatures with alternating chilling conditions due to the spray cooling with water based cooling lubricants is provoking fatigue of the tool material. Crack initiation and crack growth due to thermal shock exposure often cause spalling of the tool steel material in the surface near regions. These are starting points for extensive wear. Hard coatings like CrN, TiAlN only have a minor influence on this behaviour and will spalling together with flakes of the surface near material. This is the reason why forging tools are mostly uncoated up to now.

Nitriding can increase the hardness and wear resistance at elevated temperatures and has become state of the art for hot forming tool steels in forging applications. Coincidental a decrease of the ductility can occur and will reduce the crack resistance of the tool surface especially under thermal shock conditions.

The main wear mechanism of hot forming tool steels will be discussed. Exemplary for plasma nitrided forging tools, the hot working steel 1.2367 which is used for the production of automotive components was analyzed. The influence of the nitriding parameters like temperature, nitrogen supply and the plasma excitation on the nitriding depth, the maximum hardness and the crack sensitivity will be presented.

It could be shown that the crack sensitivity of nitrided samples can be evaluated by the Rockwell indentation test as well as the scratch test, which both are normally used for the adhesion measurement of hard coatings. The application of these characterisation methods showed significant differences in the crack formation in dependency on the discussed nitriding processes.

Comparative application tests in the production of automotive components show the influence on the wear behaviour and lifetime of forging tools in an industrial environment.

EP-26 Nanocrystalline Diamond Films Coatings for Tungsten Carbide Tools, *V.P. Adiga*, University of Pennsylvania, *C.D. Torres, P.J. Heaney, A.V. Sumant*, University of Wisconsin-Madison, *K. Sridharan*, Argonne National Laboratory, *F.E. Pfefferkorn*, University of Wisconsin-Madison, ***R.W. Carpick*** *(carpick@seas.upenn.edu)*, University of Pennsylvania

Tungsten carbide (WC) micro end mills exhibit a high wear rate, and when cutting soft materials such as aluminum, the chips tend to adhere to the cutting tool increasing the cutting force and leading to clogging and eventually tool failure. Diamond has outstanding properties such as high hardness, high thermal conductivity, chemical inertness, extremely low friction, low wear, and low adhesiveness, making it an ideal coating for cutting tools. However, it has been a challenge to grow uniform, conformal diamond films on WC tools with good adhesion due to the presence of cobalt which suppresses the diamond nucleation and reduces adhesion between the tool and diamond film. We present results for nanocrystalline diamond (NCD) films deposited onto WC micro end mills, using two types of pretreatments namely, (1)tailoring the surface preparation by selective removal of Co using acid etching followed by ultra-dispersed diamond (UDD) nanoparticle seeding in an ultrasonic agitation bath, and (2) carbon ion implantation (CII) of the tool surface prior to diamond growth. Both approaches have all led to a high density of diamond nucleation sites at the surface and enhanced tool performance against Al. We will present macroscopic measurements that explore how the diamond-work-piece adhesion depends on the surface preparation technique. We will also discuss the dramatic reduction of adhesion between Al and the tool that is observed when the diamond coating is present. To understand the origin of this behavior in more detail, atomic force microscopy was used to measure the work of adhesion for Al when in contact with both bare WC and NCD. It was observed that adhesion between Al and diamond is far lower than for

Al and WC, illustrating that the macroscopic reduction of adhesion during micro machining is manifested at the nanoscale single asperity level.

EP-28 Impact of Uniaxial Strain on GIFBE in Partially Depleted SOI n-MOSFETs, ***C.-H. Dai*** *(m953050006@student.nsysu.edu.tw), T.-C. Chang*, National Sun Yat-sen University, Taiwan

The influence of tensile mechanical strain on gate-induced floating-body effect (GIFBE) in advanced partially depleted SOI n-MOSFETs was investigated. Both drain current and mobility enhance after applying strain due to the reduction of average transfer effective mass. However, it was found that the GIFBE becomes serious under the mechanical strain. To explain this phenomenon, we first clarify the mechanism of GIFBE using different operation condition. The experiment results indicate that the GIFBE can be attributed to the anode hole injection (AHI) rather than the widely accepted mechanism of electron band (EVB) tunneling. Based on the AHI model, the enhanced GIFBE under the mechanical strain is mainly due to the narrowing of band gap induced by the strain in the poly-gate.

EP-29 Numerical Approach for the Description of Different Fracture Modes for Zr/ZrO$_2$ system - Deterministic and Probabilistic Aspects, ***L. Li*** *(li.li@utc.fr), D. Brancherie, J. Favergeon, J.M. Roelandt*, University of Technology of Compiegne, Roberval Laboratory, France

The presence of an oxide layer allows to separate the metal substrate from its external environment, and therefore helps protecting it from corrosion. Once this layer is damaged, its protective role disappears, and the corrosion of the metal alloy accelerates. The phenomenon of oxide layer damage is strongly influenced by the processing conditions, environnemental sollicitations, thermic and mechanical. In fact, depending on the conditions the material is subjected to, different fracture modes may appear: in particular, the periodic crack pattern in the oxide layer or the debonding of the oxide layer.

All these damage phenomena (cracks or debonding) are strongly influenced by the presence of defects in the oxide layer. To take into account the probabilistic aspect, a statistical analysis of numerical results obtained for random sampling of limit stress distributions is carried out to characterize the inter-crack distance in the oxide layer.

We propose here a numerical approach capable of reproducing these fracture modes for Zr/ZrO$_2$ system.

For the description of the periodic crack pattern in the oxide layer, a strong discontinuity model is used. The advantage of this method is to overcome the mesh dependency of the computed solution and to handle automatically the propagation of the crack. An adaptation of the strong discontinuity model is necessary to describe the multi-cracking. In fact, the competition of several cracks can lead to numerical instabilities associated to the presence of bifurcation points. To ensure the convergence of solutions, we introduce a viscous perturbation to regularize the numerical solution.

For the description of the debonding of the oxide layer, cohesive elements are introduced in the model. Several laws and criteria of damage were considered to reflect the interface decohesion. The numerical results show that the cohesive elements have an effect to release stress around the periodic cracks in the oxide layer, pushing the cracks further and thus increasing the inter-crack distance.

To consider the initial state of the oxide layer linked to the processing conditions, we add the residual stress in the oxide layer. We calculate the residual stress with analytical methods or some finite element simulation of the oxidation process.

The influence of every parameters: limit stress in the oxide layer, decohesion at the interface metal/oxide, substrate behavior and residual stress in the oxide layer are evaluated in terms of the inter-crack distance.

Finally, the parameters of the numerical models are identified from the results of experimental tests.

EP-30 The Effect of Surface Wettabiity on Friction and Wear of Nanopatterned DLC Film, *Y.J. Jang (jang@ume.mech.nagoya-u.ac.jp),* ***H. Kousaka****, N. Umehara*, Nagoya University, Japan

In this work the effect of surface wettability of nanopatterned diamond-like carbon (DLC) films on friction and wear behavior with sliding friction has investigated. Nanopatterned DLC films with surface roughness ranging from 5 to 9 nm were prepared by deposition of DLC film on the Si (100) substrate with nanoscale Cu dots. The following different surface wettability DLC films have been chosen: super-hydrophobicity (θ =164˚, RMS roughness = 9 nm), hydrophobicity (θ_{water}=96˚, RMS roughness = 5 nm) and hydrophilicity (θ_{water}=13˚, RMS roughness = 7 nm). Tests with these DLCs have been carried out with a ball-on-disk tribometer with hydrophilic Si_3N_4 ball coupling in air with 45~50 % relative humidity (R.H.) levels. The super-hydrophobic DLC film deposited using the 2.45 GHz surface wave-excited plasma CVD technique has been investigated with tetramethylilane (TMS: $Si(CH_3)_4$) gas. The hydrophobic/hydrophilic DLC film deposited using the r.f. magnetron sputtering and Ion implantation. The most important result achieved with the tribological tests and the FE-SEM examinations is that with couplings of a hydrophilic and a superhydrophobic DLC, self-lubrication has a greatly positive effect. The worn surface of the DLC film was smoothed significantly with decrease in surface energy, with sliding in air and water showing the lowest friction coefficient such as 0.065, 0.023. On the other hand, as wetting angle decreases, abrasive wear might have occurred when sliding in air due to the entrapment of large hard wear debris particle within the rubbing interface before being removed, leaving rough grooves on the worn surface. The role of air in reducing wear particle size of the super-hydrophobic DLC film has been attributed to the formation of low surface energy surfaces with self-cleaning effect.

EP-31 Liquid Cyrstals onto Boron Nitride/Diamond-Like Carbon Multilayered Films for Ultralow Friction Applications, ***V.B. Amaral*** *(Vinicius.Amaral@csiro.au),* Commonwealth Scientific and industrial Research Organisation, Australia*, T. Amann, S. Meier, M. Konig, A. Kailer*, Fraunhofer IWM, Germany

Abstract: Low friction systems that involve coatings such as the boron nitride and diamond-like carbon films can be used for high-performance engines or systems, that operate at high temperatures, low or high pressures, or in hostile environments. The present work is intended to show the application of liquid crystals (LCs) as lubricant fluids, among diamond-like carbon (DLC) and amorphous hydrogenated boron nitride (a-BNH) coatings to develop a low-friction tribological lubricant system. Tribological tests were performed to measure the friction coefficient and the resistance of the coatings against wear and the friction coefficient in contact to 100Cr6 (AISI E 52100) steel. The same tribological test was carried out with a configuration that led to the measurement of electrical resistivity of the coatings. To characterize the films, light microscopy, atomic force microscope and Raman spectroscopy were used. As a result of the work, systems with a coefficient of friction (COF) lower than 0.005, stable for temperatures up to 90°C and with high electrical resistance were obtained.

Characterization: Linking Synthesis Properties and Microstructure
Room: Golden Ballroom - Session FP

Symposium F Poster Session

FP-1 Growth and Optical Properties of Uniform Tungsten Oxide Nanowires Bundles via a Two-Step Heating Process by Thermal Evaporation, *Y.T. Hsieh,* National Tsing Hua University, Taiwan*, M.W. Huang,* National Chung Hsing University, Taiwan*, C.C. Chang,* ***C.H. Chien****, H.C. Shih (zziz.tw@gmail.com)*, National Tsing Hua University, Taiwan

Uniform tungsten oxide ($W_{18}O_{49}$) nanowires with diameters of 15–20 nm and lengths of several micrometers were synthesized by thermal chemical vapor deposition (CVD) without using any catalyst via a two-step heating process in a tube furnace. Typical temperatures of this two-step process are 8 00 and 1000°C, respectively. The first-step heating was found crucial for the growth of small and uniform nanowires because it made the crystal cluster uniformly distributed on the p-type Si(100) wafer surface. 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 spectroscopy (EDS), Raman, UV-visible, and cathodoluminescence (CL) spectroscopy. 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. Blue emission was observed in both the UV-visible and CL spectra, indicating that the $W_{18}O_{49}$ nanowires exhibited a red-shift at an optical absorption wavelength due to oxygen deficiencies. The crystallinity and size distribution of the nanowires influenced the band gap. In the CL spectra, the blue emission was at shorter wavelengths than reported previously, which is attributed to the nanoscale size effect.

FP-3 Modulated IR Radiometry of Magnetron Sputtered Optically Active Coatings with Au Nanoparticles Dispersed in an Amorphous TiO_2 Dielectric Matrix, ***F. Vaz*** *(fvaz@fisica.uminho.pt), F. Macedo, R.T. Faria Jr., M. Torrell,* Minho University, Portugal*, A. Cavaleiro,* University of Coimbra, Portugal*, K.H. Junge, J. Gibkes, J. Pelzl, B.K. Bein*, Ruhr-University, Germany

Optically-active Au:TiO_2 thin films were prepared and characterized with the aim to establish a correlation between the Surface Plasmon Resonance Effect (SPR) and the films' effective thermal transport properties. Variations of the optical activity and of the SPR effect of the films were obtained by dispersing Au nanoclusters in an amorphous TiO_2 dielectric matrix, by varying the films' Au content and by annealing the as-deposited films, thus tailoring the size, shape, and number of Au nanoclusters [1].

Different series of films containing amounts of gold of 10 - 30 at.% were deposited by dc reactive magnetron sputtering. Thermal annealing was carried out in vacuum atmosphere, using temperatures of 300 - 800ºC. A heating rate of 5 ºC/min., one hour at the desired temperature, and free cooling was applied in all annealing processes.

The depth profiles of the effective thermal transport properties of the films, measured by frequency-dependent Modulated IR Radiometry [2], exhibit a structure characterized by two characteristic lengths: At higher modulation frequencies, corresponding to smaller structures, the effects related to the Au nanoclusters are sensed, whereas at lower modulation frequencies, the thermal properties of the films as a whole are measured. Preliminary results show that the significant variations of the crystalline phase and of the clusters' shape and size are correlated with the changes observed in the evolution of the thermal depth profiles, as a function of the increased annealing temperature.

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[2] F. Macedo, A. Gören, A.C. Fernandes, F. Vaz, J. Gibkes, K.H. Junge, J.L.N. Fotsing, B.K. Bein, *Potential of Modulated IR Radiometry for the On-Line Control of Coatings*, Plasma Proc. Polym. 4, (2007) S857-864.

FP-4 The Effect of Thermal Annealing on the Structural Properties of ZnO Thin Films, ***E. Broitman*** *(broitman@andrew.cmu.edu), H-J. Hsieh,* Carnegie Mellon University*, B.H. Howard,* National Energy Technology Laboratory, U.S. Department of Energy*, J.B. Miller*, Carnegie Mellon University

Zinc oxide (ZnO) is a semiconductor material with great potential in catalysis, photonics, and chemical sensing applications. Here we report the structural properties of ZnO thin films prepared by spin-coating a sol-gel precursor solution containing zinc acetate dihydrate and monoethanolamine in isopropanol solvent onto glass subtrates. By varying precursor concentration and number of spin-coats, film thicknesses between ~20 and 250 nm were obtained. Annealing at temperatures up to 500°C was correlated to the structural, optical and morphological properties of the films.

The surface topography of the calcined films (characterized by high-resolution FIB-SEM), the optical absorption (measured by FTIR), and the extent of their c-axis orientation (characterized by XRD) varied with annealing and precursor solution concentration. At annealing temperatures of 100°C and below, films exhibited the structure of a lamellar ZnO precursor, Layered Basic Zinc Acetate (LBZA). At higher temperatures, LBZA released loosely bound water and acetate groups, and Zn-OH groups condensed to form a film consisting of stacked ZnO nanograins (~20 nm diameter) having wurtzite structure. Micron-scale wrinkle patterns, in the form of skeletal branches, were observed in many of the films annealed at 500°C. A minimum of surface wrinkles and a maximum in c-axis orientation were observed at intermediate precursor concentrations.

A simple model is presented to correlate wrinkle generation with the release of mechanical stress, which results from the removal of the solvent during the annealing process.

FP-5 Residual Stress Gradients in Shot Peened TiN and TiCN Coatings Characterized by High Temperature X-ray Diffraction, ***M. Bartosik*** *(matthias.bartosik@stud.unileoben.ac.at),* Montanuniversität Leoben, Austria*, R. Pitonak,* Boehlerit GmbH & Co.KG, Austria*, J. Keckes*, Montanuniversität Leoben, Austria

Residual stress gradients in shot peened TiN and TiCN coatings deposited by chemical vapor deposition are characterized using in-situ X-ray diffraction in a temperature range of 25-1100°C. The stress gradients are determined using the $\sin^2\psi$ method and evaluated by applying inverse Laplace transformation. The experimental results show a tensile stress of about 0.6 GPa across the whole thickness of 9 µm in the as-deposited coatings. By shot peening high compressive stress can be produced up to a depth of about 2 µm. In the rest of the coating however the original tensile stress remains. The magnitude of the compressive stress strongly depends on the pressure used during the shot peening process. In-situ experiments indicate, however, that the temperature at which the relaxation of the peening-induced compressive stresses starts is influenced by the stress magnitude itself: in coatings with higher compressive stress a lower temperature is required to initiate relaxation processes.

FP-6 The Preparation and Photo-Sensing of Thermal Evaporated ZnS Nanowires, ***Y.-W. Cheng*** *(pizzway@hotmail.com)*, Chinese Culture University, Taiwan

In this study, we reported that the high-density ZnS nanowires were synthesized on a Si substrate using thermal evaporation at a synthesizing temperature of 1000°C for 1 hr. A field emission scanning electron microscope (FESEM), a MAC glancing incident X-ray spectrometer with an incident angle of 0.5°, an *x*-ray photoelectron spectroscopy (XPS), a high-resolution transmission electron microscope (HRTEM) with an energy dispersive *x*-ray spectrometer (EDS) and a photoluminescence (PL) spectrometer were used to characterize the as-prepared ZnS nanowires, which shows that the ZnS nanowires are single crystalline hexagonal wurtzite structure. The photo-sensing measurement shows that the ZnS nanowire-based photodetectors have both high sensitivity and low response time, which demonstrates that ZnS nanowires have potential application in future UV photodetectors.

FP-7 Characteristics of Linear Polarization Selector and Polarization-Discriminatory Inverter Fabricated by Oblique Angle Deposition, ***Y.J. Park****, J.J. Kim, S.J. Park, C.K. Hwangbo (hwangbo@inha.ac.kr)*, Inha University, Korea

Oblique angle deposition (OAD) is widely used for fabricating thin-films with nanoengineered microstructures. The films deposited in this technique show the optical anisotropy originating from the microstructures and the porosity of the films increase due to shadow effects. These controls can be utilized to engineer thin films for specific applications such as three-dimensional photonic crystals, gradient index optical filters, broadband antireflection coatings, and linear polarizer, etc.

In this study, we investigate the optical and structural properties of linear polarization selector and polarization-discriminatory inverters. They are realized as a combination of quarter-wave plate, Bragg reflector and opposite quarter-wave plate. The two quarter-wave plates of opposite zigzag structure and the Bragg reflector of helical structure are fabricated by electron beam evaporation using OAD technique. The linear polarization selector transmits the normal incidence p-polarized light with wavelength lying in the Bragg regime, and reflects the s-polarized light as the p-polarized lights. The linear polarization-discriminatory inverters show that the incident linear polarized light becomes opposite linear polarized lights with Bragg effect at output.

FP-8 Effect of Substrate Bias and Nitrogen Flow Rate on the Microstructure and Properties of TaN_x Thin Films, *C.-K. Chung (ckchung@mail.ncku.edu.tw), N.-W. Chang, T.-S. Chen,* ***S.-C. Chang****, B.-H. Wu*, National Cheng Kung University, Taiwan

Ta-N thin films have been extensively studied as diffusion barriers for Cu interconnection in ultra large integrated circuits (ULSI). In this paper, we investigated the relationship between the microstructures, resistivity and hardness of the TaN_x thin films using direct-current reactive magnetron sputtering . The TaN_x thin films were deposited on the Si (100) substrates at different substrate bias and nitrogen flow rate ($FN_2\% = FN_2 /(FAr+FN_2)$ x 100%). The effect of bias and FN_2% on the microstructure, morphology, composition, resistivity and hardness of the TaN_x films were measured by grazing incidence X-ray diffraction (GIXRD), scanning electron microscopy (SEM), energy dispersed spectrum (EDS), four-point probe and nanoindentation, respectively. GIXRD patterns show that the TaN_x films at zero bias and low FN_2 % were quasi-amorphous in nature. As the bias increased, the crystalline orientation of TaN (200), (220), (311) were observed at low FN_2 %. The formation of phases in the films at 0-10 FN_2 % changed from metallic body center cubic Ta (0 FN_2 %) to quasi-amorphous Ta_2N, then sequentially to polycrystalline face center cubic TaN. The evolution of microstructure resulted in the variation of morphology, electrical and hardness of films . The quasi-amorphous TaN_x film has smoother surface morphology than polycrystalline one. The resistivity of films at zero bias increased from 104.97 to 899.61 µΩ -cm with increasing FN_2 % . The resistivity at constant FN_2 % also increased with increasing bias due to ion bombardment. The hardness of thin films was between 13.02 to 17.68 GPa. The quasi-amorphous TaN_x films at low FN_2 % are much harder compared to the polycrystalline films at high FN_2 %. But bias effect here is insensitive for hardness variation . A TaNx film with high hardness, low resistivity and smooth morphology can be obtained at 5 FN_2% and bias 100 V for application of diffusion barrier in ULSI.

FP-10 Stress Development in Amorphous Si Thin Films: an *in situ* Study, ***A. Fillon*** *(amelie.fillon@etu.univ-poitiers.fr), G. Abadias, A. Michel, C. Jaouen*, University of Poitiers, France

Thin film silicon materials exhibit different structures, from amorphous to crystalline, which opens a wide range of applications, e.g. solar cells or MEMS devices. Comparatively to polycrystalline metallic thin film growth, stress evolutions in amorphous materials has been much less studied. However, a more simple behaviour may be expected due to the lack of elastic anisotropy and epitaxial strain. The purpose of this work is to study the stress development during magnetron sputtering growth of *a*-Si thin films. By varying the kinetic and energetic conditions, we attempt to clarify the origin of the compressive steady state stress observed in these amorphous layers.

In-situ stress evolution during deposition of amorphous Si was studied. The stress measurements were made in real-time during growth using a technique for substrate curvature measurement known as the multiple-beam optical stress sensor. The *a*-Si thin films were grown at room temperature on single crystal Si(001) substrates by either dc or rf magnetron sputtering in an ultra high vacuum system (~2. 10^{-6} Pa) using Ar as working gas. Different target powers and Ar pressures were used to vary the deposition rate in the range 0.01 to 0.15 nm/s.

In a large range of pressure (< 0.44 Pa), a steady-state compressive incremental stress of ~-1.2 GPa is observed during growth of the *a*-Si layer and hardly independent on the deposition rate and substrate bias voltage. This suggests that the atomic peening mechanism does not play a significant contribution to the stress generation. Rather, the stress build-up is ascribed to surface stress effect, especially in the absence of epitaxial inheritance, similarly to what has been proposed by Floro et al [1] for *a*-Ge grown by thermal evaporation. At higher pressures, a stress relaxation is observed at larger film thickness, which can be related to a change in surface morphology and roughness, as revealed from ex-situ atomic force microscopy observations and X-ray reflectivity.

[1] J.A. Floro, P.G. Kotula, S.C. Seel and D.J. Srolovitz, Phys. Rev. Lett. 91, 096101 (2003).

FP-11 In-Situ Impedance Spectroscopy Studies into the Effects of Electric Field Distribution During Plasma Electrolytic Oxidation of Al, ***C.-J. Liang***, *A. Aleksey (A.Yerokhin@sheffield.ac.uk),* University of Sheffield, United Kingdom*, E. Parfenov,* Ufa State Aviation Technological University, Russia*, A. Matthews*, University of Sheffield, United Kingdom

In-situ impedance spectroscopy is a new method to acquire fundamental characteristics of plasma electrolytic oxidation (PEO) processes. In this technique, a variable frequency current waveform is used as a perturbation signal to obtain impedance characteristics of the electrolyser during the PEO processing. Previous studies have demonstrated feasibilities of this technique when operating in both the large and the small signal PEO modes [1;2]. It was however noticed that strong voltage electric fields have significant effects on characteristics of impedance spectra. In this research, to comprehend the effects of electric field distribution in the electrolyser, PEO processes were studied in equidistant and non-equidistant cell geometries.

During experiments, the voltage and current waveforms were acquired and processed using specially developed software to derive characteristics of impedance, admittance, and phase angle. To assist data analysis, the characteristics were refined to eliminate process-inherent wild points and noise, as well as to smooth and convolute data. The COMSOL software package was used to model and represent the distribution of electric field in the cells; these distributions were then correlated with immittance in the PEO electrolyser obtained by the impedance spectroscopy.

The modeling shows to be effective for estimation of the effects associated with electric field distribution in different geometry cells, thus promoting a better understanding of the PEO technique.

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FP-12 Composition and Structural Analysis of Ti-C(O,N) Sputter Deposited Thin Films, ***J.M. Chappé*** *(jeanmarie@fisica.uminho.pt), L. Cunha, C. Moura,* Universidade do Minho, Portugal*, J.F. Pierson,* Ecole des Mines de Nancy, France*, N. Martin,* Institut FEMTO-ST, France*, F. Vaz*, Universidade do Minho, Portugal

Ti-C(N,O) thin films were synthesized on silicon substrates by direct current reactive magnetron sputtering of a titanium target while acetylene and a mixture of oxygen and nitrogen (3:17 ratio) were injected into the deposition chamber. Tuning the (oxygen + nitrogen) / carbon ratio in the film from 0.2 to 1.5 allowed obtaining a smooth evolution of the film properties. The acetylene flow rate was kept constant at 5 sccm while the (O2 + N2) flow rate was controlled in order to obtain a series of samples exhibiting extended behaviors from oxycarbide to titanium carbide compounds.

Composition analysis by electron probe microanalysis was performed to quantify the titanium and metalloid concentrations in the films. Similarly the composition was related to the deposition rate of the Ti-C(N,O) films. X-ray diffraction experiments revealed a face centered cubic structure for all the films but with a significant reduction of the lattice parameter from a = 4.336 Å to 4.292 Å as well as the grain size dropped from 40 to 20 nm, as the (O2 + N2) flow rate changed from 0 to 4 sccm. The structural analysis showed that the titanium carbide structure produced without O2 + N2 injection led to a progressive substitution of carbon by oxygen and/or nitrogen atoms in the lattice. Moreover, the (111) preferential orientation vanished when the O2+N2 gas mixture was supplied into the sputtering process. DC electrical conductivity of the films was gradually modified with the increase of the O2 + N2 gas mixture flow rate. Measurements versus temperature showed that a metallic to semiconducting evolution was observed, which was discussed taking into account the variations in chemical composition and the correspondent structural modifications in the films.

FP-13 Study of Crystallization and Microstructure Evolution of TiO_2 Thin Films and Powders by XRD Total Pattern Fitting, ***R. Kuzel*** *(kuzel@karlov.mff.cuni.cz), Z. Matej, L. Nichtova*, Charles University in Prague, Czech Republic

Evolution of microstructure of different TiO_2 samples with temperature and time was studied both after post-annealing and by in-situ measurement in XRD high-temperature chamber.

Coplanar XRD grazing incidence measurements (2θ scans) in parallel beam setup were evaluated by total pattern fitting by using of a new own software Mstruct. This is an extension of flexible modular system of Crystal Objects and Fox program [1] for studies of real structure of thin films. It includes the effects and corrections necessary for thin film diffraction geometries. Diffraction peak positions are determined by variable lattice parameters and zero shift error, and by possible residual stresses introduced in terms of weighted Reuss-Voigt model. Correction of peak positions for refraction is necessary for very low angles of incidence. Peak intensities calculated by the fObjCryst library from a known crystal structure model. They can be modified by absorption and the texture correction obtained from the known model of ODF after numerical integration over all crystallites with diffracting {hkl} planes perpendicular to direction of the measured diffraction vector, or they can be varied independently, if the texture is unknown. Peak profiles are given by numerical convolution of the known instrumental function described by the pseudo-Voigt function and physical profiles including several free parameters (models). The size broadening is described by the model of log-normal distribution of spherical crystallites or distribution given by a histogram, the strain broadening either by phenomenological microstrain or dislocation model. Stacking faults and twins can be included too. Individual layers in the system are characterized by their thickness and linear absorption coefficient.

It was shown that crystallization of *amorphous* films occurs above 220°C depending on their thickness and in all cases relatively large crystallites (> 100 nm) grow quickly from the very beginning of crystallization. By contrast as-deposited *nanocrystalline* films (crystallite size ~ 5 nm) or nanocrystalline powders showed the fine microstructure stable to quite high temperatures (above 500°C) before the strain relaxation and crystallite growth was observed.

During the crystallization of amorphous films tensile residual stresses were generated. They were of simple uniaxial character and strongly increase with decreasing film thickness. Their values obtained by the total pattern fitting and independently by the direct XRD stress measurement agreed well.

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FP-15 Comparative Study of Three Methods to Measure Thickness of PVD Coatings, ***M.A. Quiñones-Salinas*** *(maqs73@hotmail.com), R.D. Mercado-Solis,* Universidad Autonoma de Nuevo Leon, Mexico*, J. Smolik, A. Mazurkiewicz*, Institute for Sustainable Technologies, Poland

In thin hard coatings, thickness continuity is a very important factor for quality. The aim of this work was to compare the capabilities, advantages and disadvantages for measuring PVD coating thickness of three available analytical methods: Glow Discharge Optical Emission Spectroscopy (GDOES), Scanning Electron Microscopy (SEM) and the Kalotester Method. For this purpose, three mono-layer [CrN, TiN, TiAlN] and two multi-layer [Cr/CrN)x8, (CrN/TiN)x3] coating structures were deposited on tool steel by the arc evaporation method and their thickness was measured using the three methods. The complete method procedure for each analysis is described and discussed in this paper. Finally, advantages and disadvantages in the use of these three methods are concluded from this comparative study. The highly precise measurements obtained by SEM analyses is the main advantage of this method, however sample preparation is time consuming. GDOES method provides quick results but not highly accurate, especially when measuring multi-layered structures. SEM and GDOES analyses are usually expensive, being this one main disadvantage of these methods. The Kalotester method is the fastest and is inexpensive but not highly accurate. It was concluded from this work that no single method is better than the others. It will have to be a decision of the user which method to choose bearing in mind that the analysis will inevitably involve a compromise between time, cost and accuracy.

Applications, Manufacturing, and Equipment
Room: Golden Ballroom - Session GP

Symposium G Poster Session

GP-1 The Effects of Low Friction Coating on the Tribological Behaviors of the Piston Ring, *B.C. Na (bcna@katech.re.kr),* ***J.H. Seo,*** Korea Automotive Technology Institute, Korea*, D.S. Lim*, Korea University, Korea

The piston ring contact in a typical automotive engine is an example of a highly loaded. Therefore, for piston ring design several aspects are important. Among them are function, cost, NVH, fuel economy, durability, and impact on other design aspects of the engine.

Continuously contacting with piston ring, the face of cylinder liner, brings about abnormal wear such as unfairwear or earlywear. because the engine get more powered and one requirement for a good fuel economy is to achieve a low level of mechanical friction.

In this study, modern low friction coatings at the piston ring interface aimed to investigate the potential. The coated specimens for piston ring wear test were producted by using PVD coating (WC/C, CrN+ WC/C, CrN +DLC). The profile of coated specimens were observed by non-contact type optical surface measuring system and the friction-wear behaviors of coated specimens were investigated by using piston ring wear tester. Piston ring wear test was performed to analyze the friction and wear behavior. The results showed that the application of low friction coatings effectively improved tribological performance of the piston ring .

GP-2 Nano-Columnar Amorphous Carbon Coating Design For Molding Dies of Optical Elements*,* ***T. Aizawa*** *(taizawa@sic.shibaura-it.ac.jp),* Shibaura Institute of Technology, Japan*, T. Fukuda,* Mitue Mold Co. Ltd., Japan*, E. Iwamura*, Arakawa Chemical Co. Ltd., Japan

Toward high qualification of oxide glass molding, reduction of separation temperature and adhesive stress of mold material from deforming glasses is keenly noticed as a challenging issue in technology. Geometric inaccuracy or unacceptable deviation in tolerance significantly increases with increasing the separation temperature. Even in using CrN coating, adhesive stress exceeds 1 MPa during the molding process.

Our developing nano-columnar amorphous carbon coating is applied to this oxide-glass molding die to solve this mold-glass mechanical interaction. This nano-columnar coating has vertical aligned nano-structure in the direction of thickness with higher density inter-columnar region; this coating deforms elastically up to 8 to 10 % of film thickness via nano-indentation test. Atomic force microscopy, Raman spectroscopy and high resolution TEM reveal that this coating is composed of two phase composite where amorphous carbon column is covered by graphitic inter-granular regions. Owing to distributed elastic modulus, this coating can afford to retard the onset of mold-die separation from deforming glasses and to reduce the adhesive stress. In addition, thermal stability of this coating is enhance by optimization of interlayer between nano-columnar layer and die surface.

The isothermal molding stamping is utilized to evaluate the engineering durability of this nano-columnar coated WC/(Co) die in molding the meniscus oxide glass lens. The holding temperature is controlled to be just below the glass transition temperature (Tg). Two types of oxide glasses with Tg = 673 and 773 K are employed to investigate the effect of temperature transients on the molding behavior. In both cases, geometric deviation of molded glass lens is much reduced owing to this elastically deforming nano-columnar coating.

GP-3 Structural and Mechanical Properties of Multilayered AlTiN/ZrN Coatings, *Y.-Y. Chang (yinyu@mail2000.com.tw),* ***C.-C. Hung****, W.-Y. Chang*, Mingdao University, Taiwan

Transition metal nitrides, such as ZrN and AlTiN, have been used as protective hard coatings due to their excellent tribological properties. In this study, ZrN, AlTiN and multilayered AlTiN/ZrN coatings with superlattice structure were synthesized by cathodic-arc evaporation with plasma enhanced duct equipment. Zirconium and AlTi alloy cathodes were used for the deposition of AlTiN/ZrN coatings. During the coating process of multilayered AlTiN/ZrN, ZrN was deposited as an interlayer. With different cathode current ratios [AlTi/(Zr+AlTi)] of 0.4, 0.5, and 0.6, the deposited multilayered AlTiN/ZrN coatings possessed different chemical contents and periodic thicknesses. The nanolayer thickness and alloy content of the deposited coating were correlated with the emission rate of cathode materials. In this study, field emission scanning electron microscope (FESEM) equipped with secondary electron imaging (SEI) and backscattered electron imaging (BEI) detectors, and X-ray diffraction (XRD) were used to characterize the crystal structure and the residual stress of the deposited films. The composition of deposited coatings was evaluated by a wavelength dispersive X-ray spectrometer (WDS). High resolution transmission electron microscope (HRTEM) and scanning transmission electron microscope (STEM) were used for nanolayered structure analyses of the multilayered AlTiN/ZrN coatings. Hardness, Young's modulus and fracture toughness of the deposited coatings were determined by nano-indentation and Vickers indentation methods. The effect of alloy content (Al, Ti, and Zr) on the microstructure and mechanical properties of AlTiN/ZrN coatings were studied.

GP-4 Effect of Embedded Metal Layer on $SrZrO_3$ Resistive Switching Memory Films*,* ***C.-C. Lin*** *(chunchieh@mail.ndhu.edu.tw), W.-T. Ho,* National Dong Hwa University, Taiwan*, C.-Y. Lin*, National Chiao Tung University, Taiwan

$SrZrO_3$ (SZO) resistive switching memory films have been extensively studied owing to their possible application in nonvolatile memory. However, pure SZO memory films with unstable resistive switching characteristics, such as a variation of switching voltages, could restrict their application. In our previous studies, vanadium oxides were added into the SZO sputtering target for depositing a doped SZO film which performs better resistive switching behavior, but the fabricating process was quite complicated. In this study, we propose the improvement of resistive switching characteristics in SZO films by an embedded metal layer. By introducing an embedded metal layer within the SZO films, the improved stability of the resistive switching characteristics is investigated. The embedded metal layer is proposed to diffuse into and dope the SZO film to produce a space charge region, reducing the effective resistive switching region. Besides, the memory tests, such as retention time, endurance, and non-destructive readout, are also investigated in this study.

GP-5 Low Temperature Synthesis of Amorphous Carbon Films by Using Microwave Plasma Jet*,* ***Y. Tachimoto*** *(spand-sofic@hotmail.co.jp),* Keio University, Japan*, A. Shirakura,* Kanagawa Academy of Science and Technology, Japan*, H. Kodama,* Aoyama Gakuin University, Japan*, T. Horiuchi,* Kanagawa Industrial Technology Center, Japan*, T. Suzuki*, Keio University, Japan

Amorphous carbon (a-C:H) films have been synthesized inside polyethylene terephthalate (PET) bottles to improve gas barrier properties. Low pressure synthesis of a-C:H, generally applied for coating PET bottles, requires high vacuum related cost being difficult for applying inexpensive products, such as plastic bottles. Therefore, we started to study cost effective and high productive atmospheric pressure plasma CVD process. In this study, a-C:H films to PET substrates by using microwave plasma jet under ambient atmospheric pressure at low temperature. The optimum flow rates of C_2H_2 as a source gas and N_2 as a carrier gas were determined for flat and smooth a-C:H film formation on PET substrates. PET substrates with optimally synthesized a-C:H films have 2.5 times higher oxygen barrier property than untreated substrates. Furthermore, a-C:H films inside PET bottles were successfully synthesized using atmospheric plasma jet with a specially designed nozzle.

GP-6 A New Method for Inner Surface Modification by Plasma Ion Implantation Based on Internal ICP Discharge*, Z.J. Wang, X.B. Tian (xiubotian@163.com), 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) into the inner surface of a cylindrical pipe has been investigated and demonstrated the larger difficulties especially for small diameter tubes. A new technology is proposed for the inner surface treatment in our lab. In this novel technique, an inductively coupled radio-frequency coil is utilized as internal plasma source. The coil also acts as a grounded electrode to eliminate the overlapping effect of plasma sheath in the tube to increase the bombardment energy of incident ions. The influence of gas pressure, RF power and geometry of the helical inductive coupler on the plasma distribution in tubes has been investigated. Wear resistance and corrosion resistance of the inner surface modified by nitrogen ion implantation have also been studied. The experimental results indicate that steady discharge is sustained with uniform plasma density in the interior of the pipe based on this new technique. The plasma density increases with increasing RF power and the best uniformity has been achieved with RF coil turns of 35 and RF power of 250W for the tube 200mm in length and 30mm in diameter. The wear resistance and corrosion resistance of the internal surface have been enhanced significantly by plasma immersion ion implantation. The experimental results demonstrate the feasibility and superiority of this new method for ion implantation into inner surface of a cylindrical pipe with a small diameter.

GP-8 Self-Organised Nanostructuring of Composite Coatings at High-Temperatures for Drag Reduction and Self-Cleaning*, **P. Schaaf** (peter.schaaf@tu-ilmenau.de), S. Günschmann,* Ilmenau University of Technology, Germany*, J. Wilden, V.E. Drescher,* TU Berlin, Germany*, M. Hopfeld*, Ilmenau University of Technology, Germany

Coated and nanostructured surfaces gain much importance for improving the efficiency of high temperature applications (e.g. in turbines). By embedding ceramic particles with a negative thermal expansion coefficient (NTEC) into a metallic matrix, a reversible thermal activation of a nanostructured surface can be established. At high temperatures a defined drag reducing surface microstructure ("shark-skin") is formed in the the coating surface, while a self-cleaning effect at low temperatures (in idle period) is achieved by the reversal of the deformation. A feedstock powder produced by high energy ball milling and consisting of nanocrystalline yttrium oxide and tungsten oxide particles embedded into a conventional MCrAlY alloy was used for the investigations. By using different thermal spray and cladding techniques the powder is deposited onto different substrates. In a next step the coating is implanted with oxygen, yttrium, or xenon to induce the formation of $Y_2W_3O_{12}$ particles inside the coating in the desired morphology. $Y_2W_3O_{12}$ is a ceramic with a strong negative thermal expansion coefficient and is stable also at temperatures above 1373 K. The effects on phase formation and morphology changes are analyzed in detail. Results of phase formation, surface micro-morphology, microstructure and properties of these high-temperature coatings are presented.

The work is supported by the German Research Foundation (DFG) within Priority Programme 1299 (HAUT).

GP-9 Comparison of Crystalline La_2CuO_4 Thin Film Synthesis with Different Processes*, **N. Tranvouez** (Nolwenn.Tranvouez@mines.inpl-nancy.fr),* Ecloe des Mines, France*, J.-F. Jean-FrançoisPierson, F. Capon,* Institut Jean Lamour, France*, J.Ph. Bauer*, Ecole des Mines de Nancy, France

Several studies have been conducted on the superconducting properties of $La_2CuO_{4+\delta}$, elaborate by different methods. Although sputtering processes are widely used for the deposition of high quality oxide films, only few publications are focused on the lanthanum cuprate sputtered films. Moreover, the literature does not report information about the effect of the deposition process on the structure and the properties of $La_2CuO_{4+\delta}$ films. In this presentation, we aim to show the effect of different depositions processes on the film composition, structure and properties.

Within the first process, lanthanum cuprate films were deposited by co-sputtering of metallic copper and lanthanum targets in various Ar-O_2 reactive mixtures. The oxygen flow rate introduced into the deposition chamber was optimised to fully oxidise the sputtered atoms. The atomic ratio La/Cu in the film was adjusted by the variation of the pulsed DC current applied to the copper target. Within this process, the experimental window range for successful $La_2CuO_{4+\delta}$ deposition was found to be very narrow. The second process, namely, reactive sputtering of a composite La-Cu target, shows easier control on the film composition. The La/Cu atomic ratio is strongly dependent to that of the composite target. In the third process, lanthanum and copper oxide multilayers have been synthesized by reactive sputtering. The La/Cu atomic ratio was controlled by the thickness of each layer

Whatever the deposition process, an annealing step in air at 600°C was necessary to obtain the crystalline La_2CuO_4 phase. Finally, the influence of the substrate nature (silicon, $SrTiO_3$, fused silica, stainless steel) on the film properties was investigated.

GP-10 Effect of Copper Acetate on Structure and Mechanical Properties of Plasma Electrolytic Oxidation Coatings on Al*, **A. Aleksey** (A.Yerokhin@sheffield.ac.uk),* University of Sheffield, United Kingdom*, A. Lhermeroult,* ENSIACET, France*, A. Pilkington,* RMIT, Australia*, A. Matthews*, The University of Sheffield, United Kingdom

This paper deals with the effects of Cu^{2+}cations on structure and mechanical properties of Plasma Electrolytic Oxidation (PEO) coatings on Al. The coatings were prepared on BS Al-6082 aluminium alloy using the pulsed bipolar PEO mode in silicate-alkaline electrolyte with addition of 0 to6 g/l of copper acetate $Cu(CH_3COO)_2$. In order to investigate the coating morphology, chemical and phase composition, SEM observations EDX and XRD analyses were carried out. Residual stresses have also been studied using the XRD $\sin^2\psi$ method. The mechanical behavior was investigated using nanoindentation, scratch and impacts tests.

It was found that the addition of copper acetate increases the proportion of α-Al_2O_3 at the expense of γ-Al_2O_3 constituent. Cross-sectional SEM studies and EDX analysis revealed that copper tends to segregate in the outer porous region of the coating. Residual stresses and Young's modulus as well as alpha phase proportion do not follow a uniform trend on copper concentration. With addition of 1g/l of copper acetate, a slight decrease in these characteristics is observed but for the coating formed with 2g/l of copper, they are enhanced to finally suffer a significant drop at 6 g/l.

Mechanical tests indicated that incorporation of copper has direct effect on the coating resistance to impact wear and its adhesion to the substrate; these both decrease with the increase of copper content in the coating. On the contrary, the coating hardness increases with Cu concentration. In conclusion, the optimum combination of structural and mechanical characteristics of the coatings was found at an addition of 2g/l of copper acetate to the base electrolyte.

GP-15 Effect of Plasma Nitriding Pre-Treatment on Steel Surface Deformation Under Nitride Based Multilayer Coating (BELCOAT SS for Stamping Mold of Ultra High-Tensile Steel)*, **T. Okude** (okude.toru@kobelco.com), D.T. Yasunaga, K. Yamamoto,* Kobe Steel Ltd., Japan*, T. Kashi, K. Imai,* Kams Co. Ltd., Japan*, Takazawa, J. Yshida*, Nippon Koshuha Steel Co. Ltd., Japan

Significant damages occur to the forming molds and stamping molds when ultra high-tensile steel sheets is implemented in the production process. To improve the lifetime of such stamping molds, conventional thermal diffusion processes to form carbide materials such as VC, NbC or TiC [1] have been used. While these carbide diffusion coatings show relatively good wear resistance at moderate stamping condition, their durability is not satisfactory for stamping of ultra high-tensile steel at minimum lubrication condition. Another drawback of such diffusion processes is their treatment temperature, which is usually close to 1000ºC. Conventional cold working die steel, such as D2, are tend to be thermally distorted by such high temperature treatment resulting in a size deviation of the final stamped products.

A novel nitiride based multilayer coating (BELCOAT-SS[2]) was deposited by AIP process on the conventional D2 steel. Deposition temperature is less than 450ºC, which is significantly lower than conventional diffusion carbide forming process and almost no dimentional change was observed by the coating process. Primarily, coatings basic properties such as hardness and adhesion were compared with conventional carbide diffusion coatings. Hardness of the BELCOAT-SS is approximately 32 to 35 GPa, whereas 35 GPa is measured for the VC and TiC.

Adhesion was evaluated by scratching the coated surface by using spherical diamond indenter with progressive load up to 100 N. Film cracking was observed at around 20 to 30 N in the case of carbide coating and no film cracking was observed up to 50 N in the case of BELCOAT-SS.

GP-16 Characterisation of PAPVD Coatings on Duplex-Treated Hot-Work Tool Steel*, M.A. Quiñones-Salinas (maqs73@hotmail.com), **R.D. Mercado-Solis**,* Universidad Autonoma de Nuevo Leon, Mexico*, J. Smolik, A. Mazurkiewicz*, Institute for Sustainable Technologies, Poland

In many engineering applications the selection of a coating is largely dependent on its physical and mechanical properties such as hardness, elastic modulus and adhesion to the substrate. In addition, the through thickness continuity and structural integrity of the coatings are of paramount importance, particularly in multi-layer coating structures. The aim of this paper is to establish and compare the physical and mechanical properties of five different coating structures through a comprehensive characterisation of mono- and multi-layered coatings produced by discontinuous duplex treatment processes (ion nitriding + PAPVD coatings).

In this work, various PAPVD coating structures [CrN, (Cr/CrN)x8, (CrN/TiN)x3, TiN, TiAlN] were deposited on an AISI H13 hot-work tool steel substrate after ion nitriding. The thickness of the individual component layers of the coatings was measured and microscopic observations were performed after the deposition process to assess continuity and integrity of the coatings. Nano indentations were performed in order to obtain the elastic modulus and the hardness of the coatings. Elemental through-thickness profiling concentrations within the coating structures were determined using Glow Discharge Optical Emission Spectroscopy (GDOES). Finally, coating adhesion was determined using the scratch test method. Changes in the acoustic emission and in the tangential force were recorded during the scratch tests to establish the progressive stages of failure of the coatings until complete removal. Scratch tests data was complemented by microscopic observations of the scratches at each failure stage.

Based on the analysis, it was concluded that the TiN and TiAlN coating systems exhibit comparatively higher hardness and Young's modulus than the other PAPVD coating systems. In terms of adhesion, the Cr-based coatings produced higher levels among which CrN was highest. The results of this investigation may provide useful information for the selection of coating systems for an intended engineering application, based on coating's properties.

GP-17 Nitriding of the CoCr Alloy as a Method for Improving the Adhesion of Hard Biocoatings, *J.A. Ortega-Saenz,* ***M.A.L. Hernandez-Rodriguez*** *(mhernandez@gama.fime.uanl.mx),* Universidad Autonoma de Nuevo Leon, FIME, Mexico*, R. Michalczewski,* Institute for Terotechnology, Poland*, J. Smolik,* Institute for Sustainable Technologies, Poland*, M. Szczerek*, Institute for Terotechnology, Poland

This paper concerns the process of the composite: 'nitrided layer-PAPVD coating' creation on substrates CoCr alloy intended for biotribological applications. The irregularities and imperfections of the surfaces and the dynamic nature of human motion results in high stresses. The difference in modulus of elasticity between ceramic coating and biocompatible CoCr alloy substrate results higher susceptibility of coatings to fracture under cyclic loading and biotribology conditions. In order to diminish this effect and improve load carrying capacity of the system, the nitriding process was studied in this work.

Five nitriding processes with varying nitriding potential ($p(N^+/H^+)$ =1, 1.5, 2, 2.5 and 3) were selected for optimising. Modulus of elasticity and nanohardness of nitrided layers were measured by nanoindentation. Crossections were examined by means of scanning electron microscopy (SEM) in order to determine the thickness and the uniformity of the affected zone. The change in surface roughness was studied with the help of 3D roughness parameters obtained by atomic force microscopy (AFM). It was found that the most suitable properties of the surface layer were achieved by nitriding at $p(N^+/H^+)$ =2.5.

According to this result, CrN as well as multilayer TiN/CrN coatings were deposited onto the substrates with and without nitiriding for evaluation of the nitriding effect on the adhesion. CoCr alloy nitrided were included for comparison. All these conditions were characterized by means of several analytical methods: AFM, nanohardness, SEM, X-ray diffraction (XRD), GDOES and scratch test.

The scratch test has revealed the improvement of adhesion of the PAPVD coatings due to nitriding of the CoCr alloy substrate.

GP-18 Tribology of Duplex Process of Plasma Nitriding Plus Hard Nanostructured Coating of Wear Resistance Applications in Tool Steels, ***M. Arizmendi*** *(ana.arizmendi@cimav.edu.mx), G. Vargas,* Centro de Investigacion en Materiales Avanzados, S.C., México*, A. Chavez*, CINVESTAV-SALTILLO, Mexico

Nowadays the subject of recycling plastics (like Polyethylene terephthalate (PET) bottles) is very important from the environmental point of view. However the tools used into mill to cut plastic are not very efficient due to their poor mechanical and wear properties. Between them, the blades manufactured of D2 steel are commonly used. This paper looks at the tribology of nanostructured WC–Co based coatings placed on a plasma nitriding surface of D2 tool steel to increase their wear resistance properties. The tribological performance of the coatings will be related to their mechanical and wear properties as well as deposition parameters microstructure and actual composition. Wear resistance of these coatings was studied through pin-on-disk experiments. These results also were compared with the same procedure on a surface of CPM10V steel from the point of view of the performance in the cutting real process. Iin this paper results demonstrated that this kind of coating nanostructures improves several times the wear resistance and the life time of tool steel increases at least in 500%.

GP-19 Fundamentals of Voltastatic Method for Kinetic Studies of High-Voltage Plasma-Assisted Anodising in Alkaline Solutions, ***L.O. Snizhko***, Ukrainian State University for Chemical Engineering, Ukraine*, A. Aleksey (A.Yerokhin@sheffield.ac.uk),* University of Sheffield, United Kingdom*, N.L. Gurevina,* Ukrainian State University for Chemical Engineering, Ukraine*, E. Parfenov,* Ufa State Aviation Technological University, Russia*, A. Matthews*, University of Sheffield, United Kingdom

The interest to the growth processes of anodic oxide films on valve metals, especially Al, Mg, Ti and Zr, has been recently revived due to rapid development of high-voltage plasma-assisted electrochemical surface treatments in alkaline electrolytes known as Plasma Electrolytic Oxidation (PEO). The films formed by this method possess superior protective properties and show many promises for functional applications. It is suggested that, unlike conventional anodising, formation of PEO coatings in alkaline electrolytes occurs via hydration of anodically dissolved metal ions followed by hydroxide precipitation, with subsequent dehydration and sintering by plasma discharge. Unfortunately, available electrochemical techniques are not accommodated for diagnostics of such processes.

In this study, the voltastatic method was adopted and applied for kinetic investigations of the growth processes of anodic oxide films on magnesium and aluminium. In alkaline solutions the current maximum is present on anodic voltastatic transients, which is characteristic of the processes controlled by the formation and growth of new phase nuclei. At the early stages of the coating formation process, the most probable mechanism takes into account an active metal dissolution with hydroxide formation in the near-to-the electrode electrolyte region. This is associated with 3-dimentional nucleation process during re-deposition of the dissolved metal hydroxide phases.

The theory of voltastatic method for small (100 to 800 mV) and high (400 to 600 V) voltages was developed and diffusion coefficients (D) of cations though the film were evaluated. It was shown, that values of D are strongly dependent on the electrolyte nature and the voltage magnitude. Under small polarisation, the order of diffusion coefficient corresponds to that in solid state. Under high voltages however, the values of D approach those observed for diffusion in liquids. This provides direct proof and allows to evaluate essential characteristics of plasma state at the electrode.

New Horizons in Coatings and Thin Films
Room: Golden Ballroom - Session HP

Symposium H Poster Session

HP-1 Cobalt Nanocrystals Embedded in Silicon Oxide Fabricated by Incorporating Oxygen Elements During Sputtering Process, ***C.-W. Hu*** *(cwhu.ee94g@gmail.com),* National Chiao Tung University, Taiwan*, T.-C. Chang,* National Sun Yat-Sen University, Taiwan*, C.-H. Tu,* National Chiao Tung University, Taiwan*, Y.-H. Huang,* National Tsing Hua University, Taiwan*, C.-C. Lin,* National Chiao Tung University, Taiwan*, M.-C. Chen,* National Sun Yat-Sen University, Taiwan*, F.-S. Huang,* National Tsing Hua University, Taiwan*, S.M. Sze, T.-Y. Tseng*, National Chiao Tung University, Taiwan

In the experiment, the $CoSi_2$ thin film deposited by sputtering in O_2 ambient has been studied to fabricate the Co nanocrystals memory device. Based on the difference of the oxidation free energy between the Co and Si elements, a selective oxidation process during the thermal annealing enhance the formation of cobalt nanocrystals embedded in silicon oxide. The charge-storage ability of the formed Co nanocrystals has also been studied by fabricating the capacitance structure. In addition, more factors such as annealing temperature and oxygen flow rate are discussed for the nanocrystals formation. It is found that the Co nanocrystals show a larger size and lower density at high temperature annealing. The size and density distribution of nanocrystals affect the performance of the memory device. In the study of oxygen content, the XPS analyses have confirmed that the compositions of nanocrystals were changed by different oxygen flow rate during sputtering process. An inappropriate oxygen flow causes the in-complete oxidation or over-oxidation, which degenerate the charge storage ability of the Co nanocrystals device.

HP-2 High Power Impulse Magnetron Sputtering of Zirconium, ***J. Rezek*** *(jrezek@kfy.zcu.cz), J. Lazar, J. Vlcek*, University of West Bohemia, Czech Republic

High power impulse magnetron sputtering of zirconium was investigated at a high average target power density in a period, being approximately $100Wcm^{-2}$. The depositions were performed using an unbalanced circular magnetron with a directly water-cooled planar zirconium target of 100mm diameter. The repetition frequency was 500Hz at duty cycles ranging from 4 to 10% and an argon pressure of 1Pa. Time evolutions of the discharge characteristics were measured to provide information on absorption of energy in the discharge plasma and on transfer of arising ions to a substrate (located 100mm from the target) at an average target power density in a pulse up to $2.22kWcm^{-2}$. Time-averaged mass spectroscopy was performed at the substrate position. High fractions (21-32%) of doubly charged zirconium ions were found in total ion fluxes onto the substrate at decreasing fractions (from 23 to 3%) of singly charged zirconium ions when the average target power density in a pulse increased from 0.97 to $2.22kWcm^{-2}$. It was shown that ion energy distributions are extended to high energies (up to 100eV relative to ground potential) under these conditions. The rise in the values of the average target power density in a pulse resulted in a decrease of the deposition rate of films from 590 to 440nm/min.

HP-3 Impact of Strain Engineering on InGaAs NMOSFET with a InGaAs Alloy Stressor, ***H.P. Sun***, *S.-T. Chang (stchang@dragon.nchu.edu.tw), C.-C. Lee*, National Chung Hsing University, Taiwan

Strain engineering has been widely adopted to extend scaling limits and the device performance of MOSFETs. To sustain further enhancement in device performance, new materials and novel device structures are needed. The high electron mobility of III–V compound semiconductor makes them an attractive candidate as MOSFET channel material for high-speed applications beyond the sub 32 nm technology node. National University of Singapore (NUS) research group had reported the first demonstration of a strained InGaAs with In mole fraction of 0.53 channel n-MOSFET featuring in situ doped InGaAs with In mole fraction of 0.4 source/drain (S/D) stressors (Please refer to a conference paper by Prof. Yee-Chia Yeo at Symposium on VLSI Technology Digest, pp. 244-245, 2009). To realize the full potential of the III–V compound-based MOSFETs, channel-strain engineering will be an important direction. The effect of strain on electron transport in many III–V compound-based semiconductors, e.g., gallium arsenide (GaAs) and indium gallium arsenide (InGaAs), is need to further study. However, the integration of the process-induced strain in III–V compound-based MOSFETs to exploit the effect of local stressors, such as the lattice-mismatched S/D for mobility enhancement, is also needed to explore. In this work, we report the results of electron mobility calculations and device simulations for novel InGaAs with In mole fraction of 0.53 NMOSFETs with InGaAs S/D stressors using In mole fraction of 0.4 under various geometry structures. The lattice mismatch between InGaAs alloy S/D and InGaAs channel is exploited to induce tensile strain in the channel for mobility enhancement. The stress distribution in the InGaAs channel regions in NMOSFETs with various lengths and widths were studied using 3D ANSYS simulations. The mobility enhancement was found to be dominated by the tensile stress along the transport direction and compressive stress along the growth direction in wide width devices. Stress along the width direction was found to have the least effect on the drain current in wide length and width cases. Impact of width on performance improvements such as the drive current gain was also analyzed using 3D TCAD simulations.

HP-4 Ir Nanocrystals Lying on Asymmetric SiO_2/Si_3N_4 Tunnel Barrier With Large Memory Window for Nonvolatile Memory Application, ***T. Wang***, *C.J. Chen, I.-J. Teng, C.M. Liu*, NCTU, Taiwan, *C.-T. Kuo (kuoct@mdu.edu.tw)*, Min Dao University (MDU), Taiwan

Recently, metallic nanocrystals have been widely investigated for high programming/erasing (P/E) efficiency and low power consumption nonvolatile memory application [1-2]. Metallic nanocrystal nonvolatile memory has many advantages, such as smaller operating voltage, a wide range of available work functions, and larger charge capacity. In addition, for possibility breaking the scaling limits of thickness of the tunnel oxide, multi-stacked tunneling layer has been also extensively studied [3-5] . Multi-stacked tunneling layer provided asymmetric tunnel barrier (ATB) and it could enhance the P/E efficiency. In this work, iridium-nanocrystals (Ir-NCs) lying on SiO_2/Si_3N_4 (3-nm/3-nm) tunnel layer stacks have been demonstrated and compared its characteristics with SiO_2 (6-nm) as tunnel oxide in the application of nonvolatile memory. Two type of metal-insulator-semiconductor (MIS) capacitor stacks of Al/SiO_2/Ir-NCs/Si_3N_4/SiO_2/P-Si/Al and Al/SiO_2/Ir-NCs/SiO_2/P-Si/Al were analyzed by scanning electron microscope (SEM), high resolution transmission electron microscopy (HRTEM), capacitance-voltage (C-V) measurement, and current-voltage (I-V) measurement, respectively. SEM images showed the mean size of Ir-NCs and density was approximately 5 nm and 1×10^{12} cm^{-2}, respectively. Due to the bi-stacked tunneling layer improving P/E efficiency, significant hysteresis window of 11.6 V have been observed with a sweep voltage of +/- 10 V. The hysteresis window was larger than the single tunneling layer. And then, data storage decay percentage of the bi-stack (SiO_2/Si_3N_4) after 10^4 sec was only less 5 percentages than the single (SiO_2). Furthermore, the endurance of these devices shows excellent characteristics by P/E voltage stressing at +/- 9 V, 100 msec. In summary, Ir-NCs nonvolatile memory with bi-stacked tunneling layer provided high P/E efficiency, sufficient data retention and good device endurance.

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HP-5 Structure and Properties of Nanocrystalline TiN Thin Film Produced by High Power Impulse Magnetron Sputtering: Effect of Ionization Rate, ***C.-Y. Su***, *J.-H. Huang (jhhuang@mx.nthu.edu.tw)*, National Tsing Hua University, Taiwan, *G.-P. Yu*, National Tsing Hua University, *J.-Y. Wu*, Institude of Nuclear Energy Research, Taiwan

Magnetron sputtering has been widely used in surface coating industry; however, there are a few shortcomings that limit the applications on high added-value products. The most significant one may be the low ionization rate (about 5%) that causes poor adhesion and low denseness of the thin film. The newly developed High Power Impulse Magnetron Sputtering (HIPIMS) technique is for overcoming the shortcomings of traditional magnetron sputtering. HIPIMS technique can produce thin film with very high ion to neutral ratio, similar to ion plating method; moreover, the ionization rate can be controlled by adjusting HIPIMS power and frequency. In this study, TiN thin film, 600 nm thick, was deposited on Si wafer by HIPIMS with different power and frequency, and the ionization rate of the target material was monitored. The plasma density was measured by a flat Langmuir Probe. The microstructure, composition, and mechanical properties of the TiN thin film were characterized to understand the effect of ionization rate. The preferred orientation was characterized by X-ray diffraction. Field-Emission Scanning Electron Microscopy was used to observe the microstructure. The composition depth profile was analyzed by Auger electron spectroscopy. Nanoindentation was used to measure the film hardness. The composition of the film was determined by X-ray photoelectron spectroscopy. The packing factor was calculated from the results of Rutherford backscattering spectroscopy. The results showed that the structure and properties of the TiN thin films are quite sensitive to the ionization rate. TiN films presented a dense columnar structure when the target material was highly ionized, which led to excellent mechanical properties. However, under the conditions that the ionization rate was too high, the deposited film had very high residual stress that even caused the spallation of the film. On the other hand, a nearly pure Ti film was obtained at the lower ionization rate.

HP-6 Effects of Seed Layer Precursor Type on the Synthesis of ZnO Nanowires using Chemical Bath Deposition, ***W.-Y. Wu*** *(wanyu@mail.mse.ncku.edu.tw)*, National University of Tainan, Taiwan, *T.-L. Chen, J.-M. Ting*, National Cheng Kung University, Taiwan

A two-step process was used to grow aligned ZnO nanowires on the glass substrates. The process involves first the deposition of a ZnO nanocrystal seed layer using spin coating, followed by the growth of aligned ZnO nanowires using chemical bath deposition (CBD). The characteristics of the seed layers were controlled by using different precursors and spinning coating conditions. During the CBD, the bath pH value was varied. T he seed layers and the nanowires obtained were examined using scanning electron microscopy, transmission electron microscopy (TEM). Effects of the seed layer characteristics and the CBD bath pH value on growth and characteristics of obtained ZnO nanowires were then investigated. The obtained ZnO nanowires also show interesting photoluminescence spectra in which near band-edge emission occurs at 380 nm.

HP-7 X-Ray Images Obtained from Cold Cathodes Using Carbon Nanotubes Coated with Gallium-Doped Zinc Oxide Thin Films, ***J.-P. Kim***, *Y.-R. Noh*, Hanyang University, Korea, *K.-C. Jo, S.Y. Lee*, KIST, Korea, *H.-Y. Choi, J.-U. Kim (jukim@keri.re.kr)*, KERI, Korea, *J.-S. Park*, Hanyang University, Korea

X-ray tubes using cold cathodes as electron source attract 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. In order to achieve high resolution x-ray images, CNT-based emitters must have a large current capacity and, at the same time, ensure a stable prolonged-operation of current emission. Furthermore, x-ray images may strongly depend on the emission performance of CNT-based electron sources. Recently, coating of CNTs' surface with wide bandgap materials has been attempted to obtain a stable and uniform emission current from CNT-emitters. However, this manner may cause the increase of turn-on voltage for electron emission and also the decrease of tunnelling probability.

In this study, we present x-ray imaging data obtained from cold cathodes using gallium-doped zinc oxide (GZO) coated CNT-emitters. Multi-walled CNTs were directly grown on conical-type (250 μm in diameter) metal-tip substrates at 700°C by inductively coupled plasma-chemical vapor deposition (ICP-CVD). GZO films were deposited on the grown CNTs at room temperature using a pulsed laser deposition (PLD) technique. Field emission scanning electron microscopy (FESEM) and high-resolution transmission electron microscopy (HRTEM) were used to monitor the variation in morphologies and microstructures of CNTs before and after GZO-coating. Energy-dispersive x-ray spectroscopy (EDX) was used to extract the relative atomic content in GZO films. Effects of GZO-coating on the electron-emission performances of fabricated CNT-emitters were examined by characterizing turn-on fields for electron-mission, maximum emission currents, and field enhancement factors. The CNT-emitters with a triode in structure were installed in the x-ray tube which was composed of gate-electrode meshes and electrostatic lens inside. The x-ray tube was housed in a vacuum chamber pumped down to 3×10^{-7} Torr. X-rays radiated from the anode (Cu) was extracted passing through a beryllium (Be) window where the specimen was in contact with. The relationship between the electron-emission performance of GZO-coated CNT-emitters and the x-ray imaging data was also elucidated.

HP-8 Fabrication and Photo-Sensing Properties of Sb-Doped SnO$_2$ Nanowire Sensors, ***P.-S. Lee*** *(g9731581@oz.nthu.edu.tw)*, National Tsing Hua University, Taiwan

Recently, one dimensional (1-D) tin oxide nanostructures, including nanowires, nanorods and nanobelts, have attracted considerable attention because of their application in constructing nanoscale devices. In order to enhance and modulate the various properties, SnO$_2$ nanostructures are frequently doped with appreciate elements, such as indium (In) and antimony (Sb). In this present work, Sb-doped SnO$_2$ nanowires were synthesized on an Al$_2$O$_3$ substrate using a thermal evaporation. It is found that both the diameter and Sb concentration of the nanowires increases with increasing growth time (0.5-4 hr). The morphology and microstructure of Sb-doped SnO$_2$ nanowires were characterized by a field emission scanning electron microscope (FESEM) and a transmission electron microscope (TEM). The composition and chemical bonding nature were investigated by *x*-ray photoelectron spectroscopy (XPS). The photo-sensing measurements were carried out using a volt-amperometric technique, which shows that both the reaction and response time of the nanowires decrease with increasing growth time.

HP-9 Indium Layer Through Different Process in High-Quality CuInSe$_2$ Film for Solar Cell, ***T.-W. Chang***, *W.-H. Lee (leewen@mail.ncku.edu.tw), G.-S. Lyu*, National Cheng Kung University, Taiwan

Different process of fabricated Indium layers was by Thermal Evaporation, Sputter, and electrodeposited to make high-quality CuInSe$_2$. The great method was found in this work. First, the precursor layer of copper was sputtered onto the Mo-coated glass. The same thickness of indium layer through different process was deposited on the precursor layer of copper. Then, the layer of selenium was electrodeposited on the indium layers, and annealed by rapid thermal processing (RTP). The method of rapid thermal processing reduces selenium dissipation. We deposit CIS respectively to control ratio, and to fabricate the superior structural properties of these selenized films were also clearly reflected by X-ray diffraction. Field-Emission-Scanning electron microscopy indicates that the ordered copper indium diselenide thin-film 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. Mobility of the CIS film was indicated by Hall Measurement.

HP-10 Reactive High Power Impulse Magnetron Sputtering of Titanium Oxide Thin Films, ***M. Audronis*** *(martyn@gencoa.com)*, Gencoa Ltd., *V. Bellido-Gonzalez*, Gencoa Ltd, *P. Korgul, A. Matthews*, The University of Sheffield, United Kingdom

Many of the technologically important metal oxide thin films (e.g. Al$_2$O$_3$, TiO$_2$, etc.) are sputter deposited from metal targets in a reactive gas atmosphere, usually argon and oxygen, i.e. using reactive magnetron sputtering to ensure industrially relevant coating deposition rates. High Power Impulse Magnetron Sputtering (HIPIMS) is known to provide a highly ionised flux of sputtered material and is thought to provide enhanced coating structure-property relationship control (through self-species plasma/ion assistance), as compared to DC or mid-frequency AC/pulse-DC magnetron sputtering. It is therefore desirable to use HIPIMS in a reactive deposition mode in order to apply its advantages in metal oxide thin film fabrication.

This paper reports on the deposition process and structural and compositional properties of titanium dioxide thin films produced by reactive HIPIMS. A new plasma emission monitoring based reactive sputtering process control system (developed specifically to aid stable and reproducible reactive HIPIMS processes) was used for coating deposition. Coating morphology and structure were investigated by field emission gun scanning electron microscopy, atomic force microscopy and X-ray diffraction. Coating chemical composition was investigated by electron probe micro-analysis and glow discharge optical emission spectroscopy, while their mechanical (hardness and elastic modulus) properties were investigated by nano-indentation testing. Processing parameters are correlated to the film properties.

HP-11 Forming CuInSe$_2$ Using Two-Step Electrodeposition of CuSe$_\chi$ and InSe$_\chi$ Layers, ***S.-Y. Hu***, *Y.-X. Su, W.-H. Lee*, National Cheng Kung University, Taiwan, *S-.C. Cheng, Y.-L. Wang (ylwang@tsmc.com)*, National Chia-Yi University, Taiwan

One-step electrodeposition is the most well-known technique to form CuInSe$_2$ (CIS) for solar cell applications. However, the composition of CIS films is hard to control in a ternary solution. In this study, the deposition potential and electrolyte concentration were confined in a narrow range to control the atom proportion of CIS films. Two-step electrodeposition of CuSe$_\chi$ and InSe$_\chi$ precursors provide another route to form CIS film, which was able to control the deposition amount of copper (Cu) and indium (In) without considering the huge variation of their reduction potentials. For CuSe$_\chi$ deposition, the reduction potential of Cu is smaller than that of selenium (Se) such that the deposition amount of Cu is more than that of Se at the same electrolyte concentration. Increasing the deposition potential and the concentration of SeO$_2$ raised the percentage of Se. Higher electrolyte concentration also led to a smooth and dense CuSe$_\chi$ film. The sheet resistance of CuSe$_\chi$ film decreased and the micro-structure became smoother after thermal annealing. The existence of CuSe leads to easier formation of InSe and low-resistance CuSe$_\chi$ films could decrease the terminal effect to improve the uniformity of subsequently InSe$_\chi$ electrodeposition. The deposition potential ranged from –0.8V to –0.9V. The content of In would be too low when the deposition potential was under –0.8V, and when the potential was larger than –0.9V, electrolysis occurred and produced mass SeO$_2$ film on the surface. The ratio of Cu/In was verified by energy dispersive spectrometer (EDS) and easily controlled by electrodeposition coulomb in each step. After two-step electrodeposition, rapid thermal annealing was employed to form CuInSe$_2$. The treatment was carried out at 550°C for 70S. The formation of CuInSe$_2$ was verified by X-ray diffraction.

HP-13 Gas Sensing Properties of SnO$_2$ Nanostructured Films by Electrophoretic Deposition, ***S.-C. Wang*** *(scwang@mail.stut.edu.tw), M.-R. Chen*, Southern Taiwan University, Taiwan, *R.-K. Chiang*, Far East University, Taiwan, ROC, *C.-Y. Tsay, C.-K. Lin*, Feng Chia University, Taiwan

In this study, the nanosized SnO$_2$ powder was synthesized by a novel thermal decomposition method and electrophoretic deposited on a patterned Al$_2$O$_3$ substrate for the gas sensing property measurement. The phases and microstructure of the powders were characterized by the XRD, SEM, TEM and BET. Tin oleate complex and 1-octadecanol were used as the precursors, which were thermally decomposed and assembled as octahedron hollow or solid Sn$_6$O$_4$ (OH)$_4$ agglomerate powder at the temperature of 200°C in N$_2$ atmosphere. After heat treatment at 700°C for 1h in air, the powder was transformed to crystalline SnO$_2$ nanoparticle in a size of 50 nm. The SnO$_2$ electrodes with promising gas sensing properties were prepared by electrophoretic deposition using an isopropyl alcohol colloid. The nitrogen-adsorption and desorption isotherms and the relatively gas sensing properties of CO gas were characterized and discussed in details.

HP-15 Parameters Influencing the Deposition Rate During High-Power Impulse Magnetron Sputtering, ***S. Konstantinidis*** *(stephanos.konstantinidis@umons.ac.be), M. Palmucci, A. Balhamri, J.-P. Dauchot, M. Hecq, R. Snyders*, Université de Mons, Belgium

High-Power Impulse Magnetron Sputtering (HiPIMS) is a plasma-based thin film growth technique. Short (several µs) high-power (several kW/cm²) pulses are delivered to the plasma allowing a high ionization degree of the sputtered metal atoms. As a consequence, ion bombardment assists film growth. However, it is commonly found that the deposition rate is lower in HiPIMS than in conventional dc magnetron sputtering (dcMS) processes. This would indicate a different plasma-surface interaction mechanism during HiPIMS.

In our study, plasma composition was characterized by Time-Resolved Optical Emission Spectroscopy (TR-OES) and the amount of material deposited was determined by X-Ray Fluorescence (XRF). HiPIMS and dcMS discharges were operated with a titanium target in argon or neon with a working pressure set to 5 or 10 mTorr.

TR-OES analysis shows a decrease of the argon signal at the end of the pulse ; apparently indicating the rarefaction of the argon gas during the pulse. In contrast, neon signal only presents a weak saturation for long pulses. TR-OES results would suggest that gas heating (induced by the sputtering wind) and the gas rarefaction thereof has a smaller amplitude during HiPIMS in neon. On the other hand, Ti^+ signal strongly increases during the pulse in both cases, demonstrating the high ionization rate of the sputtered material. Strong argon rarefaction and the increased number of metal ions would allow the sputtering process to evolve from argon-sputtering to metal-sputtering i.e. self-sputtering. In the case of titanium, self-sputtering is less efficient than argon sputtering. This could be an explanation to the decrease of the deposition rate, as observed by XRF. In neon, the gas rarefaction would be less pronounced and metal ions would contribute to the sputtering process to a smaller extent. The reduction of the deposition rate in neon, as compared to the dcMS discharge, is therefore less pronounced than in argon.

HP-17 Fabrication of AlN Nanowires for Optical-Sensing Properties, ***T.Y. Lu*** *(c0c987@gmail.com)*, National Tsing Hua University, Taiwan

Recently, research on the growth and properties of low-dimensional nanomaterials has attracted increasing attention because of their application in constructing nanoscale devices. In order to enhance and modulate the various properties, nanostructures have been doped with appreciate elements frequently. In this study, Zn-doped AlN nanowires were synthesized on the Si substrates using the thermal chemical vapor deposition method. It is found that both the diameters and Zinc concentration of the nanowires increase with increasing growth time (1-4 hrs). The microstructure of Zn-doped AlN nanowires were characterized by field emission scanning electron microscope (FESEM) and transmission electron microscope (TEM). The composition and chemical bonding energy were investigated by *x*-ray photoelectron spectroscopy (XPS). The optical properties of AlN nanowires were analysed by Raman spectroscopy and cathodoluminescence(CL). The optical-sensing measurements were carried out by using a volt-amperometric technique, which shows that both the reaction and response time of the nanowires decrease with increasing growth time.

HP-18 High Density of SiC Nanoparticle Formation from Three-Layer Si/C/Si on Si (100) Using Rapid Thermal Annealing, *C.-K. Chung (ckchung@mail.ncku.edu.tw), T.Y. Chen,* ***C.-W. Lai****, C.C. Peng, B.-H. Wu*, National Cheng Kung University, Taiwan

The density of nanoparticle SiC (np-SiC) film formed by conventional furnace annealing (FA) of Si/C/Si multilayers at 900 °C is about 10^8 cm^{-2}. In this paper, rapid thermal annealing (RTA) were used to investigate the formation of high density of np-SiC film from thermal reaction of Si/C/Si multilayers on Si(100) substrates deposited by ultra-high-vacuum ion beam sputtering. Two kinds of Si/C/Si multilayer thickness, namely 10/100/10 nm and 10/100/50 nm, were designed to study the annealing and thickness effect on the reaction of np-SiC formation by RTA. The evolution of microstructure and reaction between C and Si was examined by grazing incidence X-ray diffraction (GIXRD) for phase identification, high resolution field emission scanning electron microscope (HR-FESEM) for surface morphology and the depth profile of Auger electron spectroscopy (AES) for interdiffusion behavior. The density of np-SiC on surface formed by RTA at 750 °C than was about 10^{10} cm^{-2} which is two orders higher than that by FA at 900 °C . Efficient thermal energy is the diving force for the crystalline np-SiC formation through interdiffusion between C and Si. The lower formation temperature of np-SiC by RTA may be attributed to RTA enhanced SiC nucleation and crystallization behavior at high heating rate. The annealing method also influences the particle size . Smaller particle size less than 100 nm can be obtained by RTA. The particle size, distribution and density are concerned with the bottom layer thickness.

HP-19 Roughness-Enhanced Thermal-Responsive Surfaces by Surface Initiated Polymerization of Polymer on Ordered ZnO Pore-Array Films, ***C.-J. Chang*** *(changcj@fcu.edu.tw), E.-H. Kuo*, Feng Chia University, Taiwan

Reversible switching of the wettability on a thermal-responsive surface can be achieved by changing the temperature. ZnO pore-array films consisting of growth-hindered vertically-aligned ZnO nanorods were fabricated by the process including microsphere lithography and hydrothermal procedures. Then, a self-assembly 3-amionpropyltriethoxysilane monolayer formed on the pore-array surface, followed by the graft polymerization of poly(N-isopropylacrylamide) (PNIPAm) on the surface. The microstructure of the ZnO pore-array films, silane monolayer and grafted PNIPAm were characterized by contact angle, XPS and AFM measurements. The surface can exhibit hydrophilicity at low temperature. At higher temperatures, the compact and collapsed conformation of PNIPAm chains induced by intramolecular hydrogen bonding in PNIPAm chains leads to low surface free energy and large water contact angle. The nanostructures on the ordered ZnO pore-array surfaces contribute to an increase in the air/water interface. It leads to the enhanced hydrophobicity of PNIPAm films on rough substrates at high temperatures. It results in stimuli-responsive wettability switching by the combination of the change in surface chemistry and surface roughness.

HP-20 Thermal Conductivity and Morphology of Silver-Filled Multi-Walled Carbon Nanotubes and Polyimide Nanocomposite Films, ***M.-H. Tsai*** *(tsaimh@ncut.edu.tw), D.-S. Chen,* National Chin-Yi University of Technology, Taiwan, *C.-J. Chang,* Feng Chia University, China, *J.-M. Yeh,* Center for Nanotechnology at CYCU and R&D Center for Membrane Technology, Taiwan, *J.-W. Lee*, Mingchi University of Technology, Taiwan

Polyimide (PI)/Silver-filled multi-wall carbon nanotubes (Ag-MWNTs) hybrid film with high thermal conductance could be applied to electronic circuitry and flexible circuits and buried film capacitors. Silver-filled multi-wall carbon nanotubes (Ag-MWNTs) are successfully incorporated into a polyimide (PI) matrix using a highly efficient and simple methodology. The intercalation of Ag within MWNTs is performed using capillary action prior to adding Ag-MWNTs into PI matrix. In this study, MWNTs are considered as nano-module and also can facilitate the distribution of Ag particle within PI. The morphology and structure of Ag-MWNTs/PI hybrid film is analyzed with a field emission scanning electron microscope (FE-SEM), high-resolution transmission electron microscope (HR-TEM) and X-ray diffraction (XRD). The existence of Ag is also verified with the energy-dispersive X-ray (EDS) spectrum. Furthermore, the thermal conductivity of hybrid film is discussed in relation to the content of Ag-MWNTs incorporated.

HP-22 Corrosion Behaviour in Artificial Seawater of Thermal Sprayed WC-Co Based Coatings on Mild Steel, *S. Brioua, K. Belmokre,* LCTS, Université de Skikda, Algérie, France, *V. Debout,* Bodycote, CRDA, France, *P. Jacquot,* Bodycote, France, *E. Conforto,* ***J. Creus*** *(jcreus@univ-lr.fr)*, Université de la Rochelle, France

The corrosion behavior in artificial seawater of different HP-HVOF cermet coatings applied on low alloyed steel was studied. 5 conditions, associated to modifications of the composition of the powder or deposition parameters were evaluated. The degradation mechanisms were studied during extended immersion tests using conventional electrochemical measurement and electrochemical impedance spectroscopy.

The extended immersion tests reveal that these thermal sprayed coatings present a cathodic behavior compared to steel. During the first hours of immersion, the electrolyte infiltrates the defects of the coatings, which then result to the local degradation of the substrate accelerated by the galvanic coupling with the cermet coating. Optical observations and Raman and FTIR analyses reveal the formation of calcium carbonates like aragonite on the cermet surface, very close to the appearance of local anodic sites. The cross-sectioned view reveal the infiltration of the corrosive solution, and the depth penetration of the degradation of steel substrate probably due to the acidification of the anodic sites.

HP-23 A Study of the Influence of Pulse Length and Duty Factor on Hafnium Films Deposited with High Power Impulse Magnetron Sputtering, ***A.N. Reed*** *(amber.reed@wpafb.af.mil), M.A. Lange,* Air Force Research Laboratory / Universal Technology Corporation, *J. Jones,* Air Force Research Laboratory, *J.J. Hu,* UDRI / Air Force Research Laboratory, *A.A. Voevodin*, Air Force Research Laboratory

Different pulse widths at constant duty factors were examined to develop an understanding of the relationship between pulse width and deposition rate during high power impulse magnetron sputtering. Specifically, the effect of target heating at long (>100 ms) pulse durations was investigated. In one study, hafnium films were grown on silicon substrates at constant duty factors. The deposition rate was essentially constant for pulse durations of 50 and 100 µs, but doubled at a pulse width of 200 µs. The structure of these films was studied using x-ray diffraction. The XRD measurements of the hafnium films grown with shorter pulse lengths exhibited a preferential growth in the (002) plane, while films grown with longer pulse lengths had a random polycrystalline structure. SEM and TEM were used to examine the surface features, grains and density of the films. Unusual features throughout the cross-sections of films processed at higher pulse widths were observed. It is believed that thermal effects during deposition could be responsible for these differences in film structure, and was investigated by mass spectrometry measurements of ionized and neutral plasma species at different pulse widths.

HP-24 Self-Organized Nanodots of SiO_x Deposited by Atmospheric Pressure Plasma Enhanced Chemical Vapour Deposition, ***G. Arnoult****, T. Belmonte (thierry.belmonte@mines.inpl-nancy.fr), G. Henrion*, Ecole des Mines de Nancy, France

Deposition of patterned nanostructures by atmospheric pressure plasma enhanced chemical vapour deposition (PECVD) is today of fundamental importance in material science research. A breakthrough has recently been done by using micro-plasmas [1]. These results combine the benefits of a plasma environment together with the advantages of self-organization. Observation of self-organization phenomena under plasma conditions is still limited, and even less is known about self-organization promoted by atmospheric microplasmas.

Recently, we have developed a small-scale remote plasma at atmospheric pressure based on a resonant microwave cavity. By controlling the hydrodynamics of the gas, we have shown that it is possible to extract through a tinny hole in the cavity a straight beam of active species (~500 µm in radius) over a length of 10 cm . By mixing this beam of atoms with a flux of HDMSO, we could grow SiO_x coatings on stainless steel substrates. Deposition rate is about 80 nm/s.

Under specific conditions, self-organized nanodots are obtained. Their diameter is close to 200 nm. Depending on time, these particles get assembled into threads, separated one from another by an almost constant distance, and reminding a Volmer-Weber nucleation step followed by coarsening.

In this work, we describe the influence of the main experimental parameters on the synthesis of these patterned structures. Image analysis is essentially used to determine the distributions in size and distance of the nanostructures. A specific analysis of thermal fluxes is also carried out to try to determine the influence of the temperature gradients on the growth. Results are based on simulations of rotational spectra of the OH (306.4nm—$A^2\Sigma^+$; v = 0–$X^2\Pi$; v’ = 0) transition and infra-red camera measurements.

[1] D. Mariotti, V. Švrček and D.-G. Kim, Appl. Phys. Lett. 91, 183111 (2007)

HP-25 Effect of Interlayers on Field Emission Characteristics of Ink-Jet Printed CNT Emitter, ***D. Song***, Korea University, Korea, *K.-I. Lee, S.-H. Kim, J.-H. Han,* KETI, Korea, *H.-G. Yoon,* Korea University, Korea, *C.S. Lee (assong@keti.re.kr)*, Korea Electronics Technology Institute, Korea

Recently, field emission emitters made by carbon nanotubes (CNTs) and ink-jet method have been extensively studied due to their low cost, little limitation of size and a high resolution. In this process, an interlayer was inevitable which improved adhesion between CNTs and a substrate. In this study, the identity of the interlayer was investigated for field emission characteristic of the ink-jet printed CNT emission device. In order to discern the role of the interlayer, we prepared two series of samples. One was an Indium layer with thickness of 200nm deposited by thermal evaporator, the other was a Chromium layer with thickness of 200nm deposited by magnetron sputter system. The ITO coated glass substrate was printed by ink-jet using 0.5wt% and 5~6cps MWNTs ink. The patterned substrate was thermally annealed using the RTA system for the physical bonding between MWNTs and substrate. After annealing, we executed an activation using the rolling method. We observed the field emission characteristics using the field emission system and analyzed the samples by FE-SEM, AFM, AES. Although In interlayer had the lower turn-on electric field (1.5 V/um) than that of Cr layer, but Cr interlayer showed more stable and reproducible emission properties under repeated measurements. Furthermore, the life time of Cr interlayer was longer than that of In layer. We could conclude that the generated surface oxide layer of Cr interlayer played a role of regulating the destruction by an abnormal arcing phenomenon.

HP-27 Improved Adhesion of Polymethylsilsesquioxane Hard Coatings on Polymer Substrates, ***Y.-C. Kao***, *F.C.-N. Hong (wcyu75@hotmail.com)*, National Cheng Kung University, Taiwan

Polymethylsilsesquioxane (PMSQ) is well-known abrasion-resistant coating material as protective coatings for the relatively soft resin, which is particularly desirable in the hard coatings of optically transparent materials such as plastic window glazing, anti-abrasion coating of mobile phone or portable display screens, etc. as well as other applications like oxidation barrier of metal. However, PMSQ films exhibited poor adhesion to polymer substrates. In this study, PMSQ coatings on PMMA, PC, PC/ABS alloy substrates were studied by grafting the substrate with trimethyl ethoxysilane (TMES) after surface functional treatments with oxygen plasma or chromic acid. The polymer surfaces after various surface treatments were also characterized by contact angle measurements and ATR-FTIR in order to optimize the treatment time. The improvement of adhesion and hardness was examined respectively by cross cut test and pencil hardness test.

PMMA substrate treated with oxygen plasma followed by TMES grafting was found to show great improvement of adhesion between PMMA and PMSQ with the significant decrease of the peeling area percentage from ~100% to <1%. PC or PC/ABS substrate showed better adhesion after the chromic acid oxidation treatment than those after oxygen plasma treatment. The peeling area percentages for both PC and PC/ABS alloy with chromic acid oxidation treatment followed by TMES grafting were 50% and <1%, respectively. The hardness of PMSQ-coated polymer substrate was greatly affected by the original hardness of polymer substrate by pencil test. The same results were also observed for the diamond-like-carbon (DLC) coated polymer substrates. The hardness of polymer substrates coated with PMSQ film was significantly improved by two to three levels (e.g. <2B to 1H for PC, 4H to 7H for PMMA) whether surface treated or not.

SESSIONS TS1-TS4
Room: Golden Ballroom - Session TSP

TSP Poster Session

TSP-4 Anti-Bacterial TaN-Ag Coatings on Titanium Dental Implants, *Y.-Y. Chang (yinyu@mail2000.com.tw), M.-C. Lai,* ***Tsai-Jung Lin***, Mingdao University, Taiwan, *H.-L. Huang*, China Medical University, Taiwan

Titanium-based materials have been used for dental implants due to their excellent biological compatibility, superior mechanical strength and high corrosion resistance. The osseointegration rate of titanium dental implants is related to their composition and surface treatment. A better anti-bacterial performance of the abutment seated in the prosthetic crown is beneficial for the osseointegration rate. In this study, TaN-Ag coatings with different Ag contents were deposited on bio-grade pure Ti dental implant materials. A twin-gun magnetron sputtering system was used for the deposition of the TaN-Ag coating. The Ag content in the deposited coatings was controlled by the magnetron power ratio of Ag/(Ta+Ag) targets. The films were then annealed using rapid thermal annealing (RTA) at 350°C for 8 min to induce the nucleation and growth of Ag particles on the film surface. WDS was used to characterize the composition of the deposited TaN-Ag coatings. The crystalline structure and bonding states of the coatings were analyzed by XRD and XPS. The antibacterial behavior will vary, depending on the amount and size of the Ag particles on the coated Ti sample. In this study, Staphylococcus aureus, a major pathogen frequently found in the dental implant-associated infections, were cultured on the TaN-Ag coated samples. The antibacterial effects were determined using a standard Syto9 fluorescence staining method. The antibacterial activity was quantified as the fluorescence detected at 488 nm by an ELISA (enzyme-linked immunosorbent assay). It showed that the nanostructure and Ag content of the TaN-Ag coatings were correlated with the biocidal property.

TSP-5 Two-Functional DC Sputtered Cu-Containing TiO_2 Thin Films, ***M. Meissner*** *(michal14@kfy.zcu.cz), V. Ondok, J. Musil, R. Cerstvy,* University of West Bohemia, Czech republic, *K. Fajfrlik*, Charles University in Prague, Czech republic

The article reports on structure, optical properties, UV induced hydrophilicity and biocidal activity of DC sputtered Cu-containing TiO_2 thin films. The TiO_2/Cu films with low (≤10 at.%) Cu content were reactively sputtered from a composed Ti/Cu target in a mixture Ar+O_2 at different partial pressures of oxygen p_{O2} on glass substrate held on floating potential U_{fl}. This way TiO_2/Cu films with Cu homogeneously distributed in the whole volume of film were prepared. The main attention was concentrated on the effect of amount of Cu added to TiO_2 film on its crystallization, structure, optical properties and correlations between the structure and (i) the hydrophilicity of and (ii) the efficiency of killing of *E.coli* bacteria on the surface of TiO_2/Cu composite film under UV irradiation. It is shown that ~1000 nm thick TiO_2/Cu composite film with ~1.5 at.% Cu exhibits simultaneously two functions: (1) good hydrophilicity with water droplet contact angle (WDCA) $\alpha \leq 20°$ and (2) strong killing power for *Escherichia coli.*

TSP-6 Electrochemical Performance of Magnetron Sputter Deposited $LiFePO_4$-Ag Composite Thin Film Cathodes, *K.-F. Chiu,* ***C.-L. Chen*** *(jack231010@yahoo.com.tw)*, Feng Chia University, Taiwan

Carbon-free $LiFePO_4$ thin films have been mixed with Ag by sputtering from a pure $LiFePO_4$ target with silver sheets attached, or by depositing on Ag/stainless steel (SS) substrates. The deposited films were annealed at 700°C for 1 hr in H_2/Ar (5 %) atmosphere. The morphologies of the $LiFePO_4$ thin films fabricated using different methods were similar. Both showed a grain size of 200-50 nm. Energy dispersion spectra (EDX) and x-ray photoelectron spectra (XPS) revealed that Ag was mixed in the $LiFePO_4$ films. The film conductivity (5 x 10^{-3} Scm^{-1}) is therefore elevated by an order of six, compared with pure $LiFePO_4$ (10^{-9} Scm^{-1}). The electrochemical measurements of the $LiFePO_4$-Ag films showed a flat plateau at 3.4 V (v.s. Li/Li^+) and a reversible capacity of 80 mAh/g. Optimization of Ag contents may further improve the discharge capacity.

TSP-7 PTFE Coated Nafion Proton Conducting Membranes for Direct-Methanol Fuel Cells, *K.-F. Chiu,* Feng Chia University, Taiwan, ***Y.-R. Chen** (d98527015@ntu.edu.tw)*, National Taiwan University, Taiwan

The performances of direct methanol fuel cells (DMFC) are affected by the methanol cross-over, due to the concentration gradient and electrosmosis between the anodes and cathodes. In this study, Polyterafluorethylene (PTFE) has been sputter deposited on conventional proton conducting membranes, Nafion117. It was found that the problem of the methanol cross-over was eased by the PTFE coating. The properties of coated and uncoated Nafion117 were investigated by scanning electron microscopy, electron spectroscopy for chemical analysis, gas chromatography and AC impedance spectroscopy. The coated film can form a barrier layer between the methanol solution and the polymer membrane. The PTFE barrier layer can effectively retard the methanol molecules, whereas the proton conductivities were not significantly influenced. The conductivity/permeability ratio of ~10^4 at 80°C, which is one order higher than conventional Nafion117 membranes, has been achieved under an optimized coating time. This technique developed shows great potential for the applications in DMFCs.

TSP-8 Bioactivity and Biocompatibility of Carbon Based Nanocomposites/Nanolaminates Formed on Template Surfaces, ***C. Tsotsos** (tsotsos@ucy.ac.cy), P. Epaminonda, S. Gravani, K. Polychronopoulou, C. Doumanidis, C.G. Rebholz*, University of Cyprus

Carbon based nanocomposites and/or nanolaminate coatings display low friction coefficients of less than 0.06 and low wear rates when subjected in nano-triboscope tests. In this work we investigate the possibility of using such coatings not only as wear resistant films in biomedical implants, but also as a bioactive coating that promotes bone ingrowth for areas in medical implants that are in direct contact with bone. To confirm the tissue compatibility of the films carbon-based nanocomposites and nanolaminates were deposited on polished and anodic nanoporous template on CrMo and Ti6Al4V substrate coupons. Human osteoblasts and fibroblasts were then cultured on the treated surfaces in order to study cellular adhesion, proliferation and viability. To further assess the bone-bonding capabilities of the coatings, "in vitro" mineralisation studies were performed where human osteoblasts were grown on the treated samples, leading to the formation of mineralised structures. Samples were subjected to morphological analysis using standard and electron microscopy techniques. To assess their biochemical compatibility cultured surfaces were investigated using x-ray microanalysis.

TSP-12 Influence of Humidity on the Tribological Performance of Unmodified Soybean and Sunflower Oils, *M.T. Siniawski (msiniawski@lmu.edu), N. Saniei,* Loyola Marymount University, ***P. Stoyanov***, McGill University, Canada

In general, vegetable oils exhibit superior lubrication properties to, but lack the thermal stability of petroleum base stocks. However, vegetable oils could make an ideal candidate as a base stock for lubrication applications involving high humidity levels, such as marine and offshore applications. This study focuses on the friction and wear rate of unmodified soybean and sunflower oils in comparison to an unformulated mineral oil at various levels of relative humidity, ranging from 10-98% RH. It was observed that the vegetable oils retain their friction and wear reducing capabilities much better than the mineral oil at high humidity levels. This was attributed to their inherent ability to react with the metallic contacting surfaces and form multilayers of soap films. Furthermore, the soybean oil provided a superior level of wear resistance when compared to the sunflower oil at extremely high levels of relative humidity due to its lower viscosity and differences in chemical compositions.

TSP-13 YSZ-Ag Composites With Adaptive Thermal Conductivity, ***J. Gengler** (jamie.gengler.ctr@wpafb.af.mil), S. Roy,* Spectral Energies, LLC, *J. Gord, C. Muratore, J. Jones, A.A. Voevodin*, Air Force Research Laboratory

Nanocomposite coatings provide improved tribological characteristics compared to many homogenous material counterparts. The design of smart coatings, often termed "chameleon", allows changes in microstructure in response to environmental stimuli. The use of silver embedded within yttria stabilized zirconia (YSZ) is a thermal lubrication example in which high temperature induces Ag migration to the surface of the host, thereby creating a thermally conductive coating on an insulating film. We present a study of thermal conductivity of YSZ thin films as a function of initial Ag content. The YSZ-Ag composite films were grown on a substrate and then heated to stimulate Ag flow to the surface. The Ag was then removed leaving porous YSZ. The changes in thermal conductivity of porous YSZ has been speculated but never measured. Thermal conductivity experiments were performed utilizing time-domain thermoreflectance (TDTR), which is a conventional femtosecond laser pump-probe technique. All samples were coated with 74 nm of aluminum to enhance the TDTR signal. Surface reflectivity was monitored for 4 nanoseconds after modulated laser heating. The subsequent decay rates were modeled using Cahill's frequency domain solution. A control sample comprised of 25nm grains of pure YSZ (7% Y_2O_3) yielded results comparable to published values. For YSZ samples of various initial Ag content, changes in thermal conductivity by up to a factor of 4 were observed.

TSP-14 Thermodynamic Approach for DC Reactive Sputtering Process, ***S. Faddeeva**, J. Oseguera (joseguer@itesm.mx)*, ITESM, Mexico

A new approach to estimate the sputtering and deposition rates for steady reactive sputtering process is developed. Mass and energy balance principles are applied to a reactive ideal gas mixture as a system, and system interactions with surroundings are taken into account. The resulting system of algebraic equations is resolved for Al - O_2 reactive sputtering process in an argon atmosphere. Model's numerical predictions are evaluated and compared to the experimental results that are in reasonable agreement.

TSP-15 Molecular Dynamics Simulations of the Sputtering Process of Boron Nitride, ***A.-P. Prskalo** (alen-pilip.prskalo@mpa.uni-stuttgart.de), S. Schmauder,* University of Stuttgart, Germany, *S. Ulrich, C. Ziebert, J. Ye*, Karlsruhe Institute of Technology, Germany

Experimentally, thin c-BN films can be deposited by rf magnetron sputtering of a hexagonal boron nitride (h-BN) target in Ar/N_2 atmosphere. Variations of the ion rates and impact energies result in different sputter yields and are important for the formation of the c-BN films. All variables such as vacancy energy, migration and surface binding energy were analysed by the method of molecular dynamics simulations, using the ITAP Molecular Dynamics (IMD) software package. A Tersoff potential was used to simulate B-N-interactions within the bulk and on the surface while the interaction with Argon was described by the Ziegler-Biersack-Littmark (ZBL) potential. At first, the vacancy energy of h-BN and c-BN was analysed by comparing two equivalent specimens with and without vacancy inside. Secondly, the migration energy was defined as the energy barrier between two neighboring lattice sites, one occupied, other vacant. The knowledge of these energy values is important for the understanding of the penetration depths of argon ions and the forward sputtering of B and N atoms. For the process of their back sputtering, the surface binding energy with and without the recombination of the crystal surface was analyzed.

Using these energy values, the sputter yield of BN was determined as a function of ion impact energy, within the range of 20-1000 eV, the impact site on the surface and the crystal orientation. These simulation results have been compared with experimental values as determined by plasma diagnostics and by Ar ion etching of a thick BN film in a microwave plasma.

An analysis of the retrieved data such as back sputter yield with the distinction to atom type and cluster size was performed. Additionally, penetration depths of argon ions as well as the forward sputter yield were analysed.

Hard Coatings and Vapor Deposition Technology
Room: Town & Country - Session B3

CVD Coatings and Technologies
Moderator: F. Maury, CNRS-CIRIMAT, H. Holzschuh, SuCoTec AG

8:00am **B3-1 MOCVD Processed Metallic Alloy Coatings: Requirements, Achievements and Challenges**, ***D. Vahlas*** *(constantin.vahlas@ensiacet.fr)*, CIRIMAT, France **INVITED**

Chemical vapor deposition of coatings containing metallic alloys is expected to open for these materials the gate to numerous application fields. The design, validation and optimization of this white spot in processing science request an insight on different aspects, the stone corner of which is precursors' selection. The use of organometallic and molecular compounds widens the possibilities of CVD, provided they are appropriately designed and evaluated. Other important points are optimized reactor design, dedicated methodologies and on line, in situ and ex situ diagnostics for the gas phase and the growing surface.

In the presentation, the correlation among processing conditions, microstructure and properties of AlCu coatings is used as a paradigm to illustrate the above. AlCu coatings were processed in a vertical, cold wall, stagnant flow reactor. Dimethylethylamine alane and either copper cyclopentadienyl triethyl phosphine or copper N,N'-Di-isopropylacetamidinate were used as aluminium and copper precursors, respectively. Silicon and stainless steel were used as substrates. Deposition was performed either simultaneously or sequentially, followed by post deposition annealing. Gaseous by-products were identified by on line and in situ mass spectrometry and helped in modeling the process by considering fluid flow patterns, temperature profile and chemical kinetics. The microstructure, elemental composition and the nature of the phases (including complex metallic alloys such as the approximant phase Al4Cu9) present in the films were determined. They were correlated with the processing conditions and with the properties of the films, namely their wetting and tribological behavior. Based on these results, strategies for the processing of higher order alloys are discussed.

8:40am **B3-3 Upscaling of an a-C:H:Si Triplex Treatment Process in an Industrial DC PACVD System**, ***C. Forsich*** *(c.forsich@fh-wels.at)*, University of Applied Sciences, Austria, *D. Heim,* University of Appliced Science, Austria, *T. Mueller*, Rubig, Austria

a-C:H:Si coatings have attracted significant attention due to their properties of high hardness, chemical inertness, low friction coefficient and high wear resistance. However, when deposited on "soft" steels the substrate deforms plastically when the applied load is high. By pre-nitriding steels the support of the thin hard coating can be remarkable improved. The corrosion resistance can be significantly increased by an additionally post-oxidizing process before coating deposition. The deposition of a-C:H:Si coatings on pre-nitrided and post-oxidized heat treatable steels is a promising technique in many areas of mechanical engineering, where low friction coefficients and low wear rates are needed or the corrosion behaviour has to be enhanced.

In this work a triplex treatment process (plasma nitriding and postoxidation followed by plasma deposition of a-C:H:Si) was developed in a commercially available DC-PACVD system in one run and further scaled up. The process gases H_2, C_2H_2, Ar and HMDSO were fed into the vacuum chamber by mass flow controllers. An important point during upscaling is the assurance for a homogeneous distribution of plasma density and energy. The results show a decreasing deposition rate during upscaling while leaving the plasma density constant. It was also found that the shape and even the position of the charging have a great influence on the plasma process and the properties of the deposited coatings. Chemical analysis of the a-C:H:Si films exhibits a decreasing Si-content with increasing charging.

The determination of the composition of the a-C:H:Si films was carried out using GDOES (glow discharge optical emission spectroscopy) whereas the adhesion was evaluated by a scratch tester. The hardness measurements were conducted by a nano-indenter and the topography of the layers was characterized by means of SEM (scanning electron microscopy) whereas the tribological properties were assessed with a ball-on-disc test.

9:00am **B3-4 Epitaxial and Polycrystalline Growth of AlN by High Temperature CVD : Experimental Results and Simulation**, ***R. Boichot*** *(raphael.boichot@simap.grenoble-inp.fr), A. Claudel, N. BACCAR, E. Blanquet, M. Pons*, Grenoble Institute of Technology, France

The availability of a relevant computation of aluminum nitride CVD (Chemical Vapor Deposition) growth process is one of the steps toward the understanding of crystal quality dependence to experimental conditions. The objective of this study is a comprehensive modeling of this CVD process from aluminum trichloride ($AlCl_3$) and ammonia (NH_3) used as reactants, at high temperature (1200-1600°C). Recent studies of Dollet et al. (2002) and Swihart et al. (2003) provide sufficient kinetic data to build a reliable set of 94 homogeneous chemical reactions. At the same time, the thermodynamic data of 5 from the 28 involved chemical species were lacking. We propose here the ab-initio thermodynamic estimated properties for these species. The critical point of the simulation is surface reaction data. Nearly none is published on this subject. We take inspiration from the sticking coefficients of the main surface reactants evaluated by Dollet et al. (2002) to start our simulation, refining them with experimental data. We chose to adopt a 'simplified' 20 surface reactions set, not taking into account the adatoms diffusion and recombination on the surface, but only considering direct sticking through activation energies.

We have obtained two main results after the simulation. Firstly, the chemical reaction set could be greatly reduced by a wise analysis of the reaction activation barriers. First dehydrogenation of NH_3 and dechlorination of $AlCl_3$ are highly improbable even at the process temperature, ensuring that the main species flow nearly unchanged from the reactant inlet to the growing surface. The only noticeable reaction is the formation of the unstable, but non negligible, $AlCl_2NH_2$ intermediate. The second result is that the growth rate is easily fitted for low values (<20 µm/h), but a discrepancy between simulations and experiments provided by Claudel et al. (2009) appears for high growth rates. This difference cannot be reduced by optimizing the activation energies of the surface reactions. We think that the phenomenon involved is the change from a 2D to a 3D growth. Indeed the surface rugosity, so the total number of atomic site available for crystal growth, varies with growth rate. Despite the lack of numerous data on epitaxial growth, we foresee to have a better agreement with numerical results in this case.

A.Claudel, E.Blanquet, D.Chaussende, M.Audier, D.Pique, M.Pons. Journal of Crystal Growth, Vol. 311 (2009), Issue 13, 3371-3379.

A. Dollet, Y. Casaux, G. Chaix, C. Dupuy. Thin Solid Films 406 (2002), 1–16.

M. T. Swihart, L. Catoire, B. Legrand, I. Gökalp, C. Paillard. Combustion and Flame 132 (2003) 91-101.

9:20am **B3-5 High Temperature Chemical Vapour Deposition of AlN/W Coatings on Bulk SiC**, ***F.-Z. Roki***, *C. Bernard, M. Pons (michel.pons@simap.grenoble-inp.fr), E. Blanquet, M. Morais,* Grenoble Institute of Technology, France*, A. Claudel, G. Huot,* ACERDE, France*, S. Poissonnet*, CEA Saclay, France

Excellent high temperature properties, chemical stability and low radioactivity under neutron irradiation make silicon carbide (SiC) and SiC-base ceramics composite attractive materials for use in advanced nuclear energy systems. The objective of this work is the fundamental study of (i) the high temperature stability of tungsten (W) coatings on bulk SiC and (ii) the role and potential of an aluminium nitride (AlN) diffusion layer. The multilayered material, bulk SiC/AlN/W is produced by high temperature chemical vapour deposition (HTCVD).

AlN films were first grown on SiC-3C at 1000°C by HTCVD chlorinated process. The precursors used are ammonia NH3 and aluminium chlorides AlClx species formed *in situ* by reaction of Cl2 on high purity Al wire. W coating on AlN at 700°C was grown by HTCVD using WF_6 on H_2. The interfacial zones SiC/AlN/W were characterized using scanning electron microscope, X-Ray diffraction and electron microprobe microanalysis. No cracking zone has been observed and no interface reaction or parasitic phases have been revealed between the different layers at high temperature (1000°C). This is in agreement with thermodynamic computations. Simple thermomechanical calculations were performed to optimize the thickness of each layer to reduce stress and cracking. This new multilayered structure based on bulk SiC allows paving the way of the use of SiC composites in nuclear energy systems.

9:40am **B3-6 Scale-up Industry Application, and Up-Scale for Three-Dimensions: Process Design Study for Pulsed-Pressure MOCVD**, ***S. Krumdieck*** *(susan.krumdieck@canterbury.ac.nz), V. Siriwongrunson, C.W. Lim, M. Jermy, H. Cave, D. Pons, M. Alkaisi*, University of Canterbury, New Zealand **INVITED**

Scale-up for industry application, and up-scale for three-dimensions: process design study for Pulsed-Pressure MOCVD Susan Krumdiecka, Vilailuck Siriwongrunsona, Chin Wai Lima, Mark Jermya, Hadley Cavea, Dirk Ponsa, and Maan Alkaisib aDepartment of Mechanical Engineering, University of Canterbury, Private Bag 4800, Christchurch, New Zealand bDepartment of Electrical and Computer Engineering, University of Canterbury, Private Bag 4800, Christchurch, New Zealand Abstract There are a range of applications where a ceramic thin film or coating on a metal part would be of benefit. There are a limited number of cost-effective processes for producing such a coating, particularly on complex shaped parts. This paper reports deposition of TiO_2 from TTIP on 3-dimensional metal objects in a cold-walled reactor. The heating of the parts is a major issue in the process. However, the pulsed pressure processing method (PP-MOCVD) eliminates thermally driven flow effects and produces a uniform molecular arrival rate over the surface of the part. SEM images show the uniformity of the coating over the objects. A new type of flow modelling was used to describe the deposition process. The model was used to perform a hypothetical reactor design investigation for coating a batch of parts to a prescribed film thickness and uniformity at a required production throughput. The results indicate that the PP-MOCVD system could provide a higher quality ceramic coating in production with lower complexity and lower cost than plasma spray or sol-gel processes.

10:20am **B3-8 Aluminium-Rich TiAlCN Coatings by LPCVD**, ***I. Endler*** *(ingolf.endler@ikts.fraunhofer.de), M. Höhn, M. Herrmann,* Fraunhofer IKTS Dresden, Germany, *H. Holzschuh,* Walter AG, Germany, *R. Pitonak,* Boehlerit GmbH & Co.KG, Austria, *S. Ruppi,* Seco Tools AB, Sweden, *H. van den Berg, H. Westphal,* Kennametal Technologies GmbH, Germany, *L. Wilde*, Fraunhofer CNT Dresden, Germany

$Ti_{1-x}Al_xN$ is a well established material for cutting tool applications exhibiting a high hardness and an excellent oxidation resistance. A main route for improving the performance of $Ti_{1-x}Al_xN$ is the incorporation of further elements. Now a new LPCVD process allows the deposition of a very aluminium-rich TiAlCN. The process works with a gas mixture of $TiCl_4$, $AlCl_3$, NH_3, H_2, N_2, Ar and ethylene or acetonitrile as carbon source. At deposition temperatures between 800°C and 900°C hard TiAlCN layers can be prepared. In this work structure, composition, properties and cutting performance of CVD-TiAlCN coatings were investigated.

Aluminium-rich TiAlCN was obtained at 800°C and 850°C consisting of a major fcc-$Ti_{1-x}Al_xC_yN_z$ phase. Lattice constants and WDX analysis indicate only a low carbon content < 1 at.-%. At 900°C the metastable fcc-TiAlCN disappears and co-deposition of Ti(C,N) and h-AlN occurs. From TEM analysis it is evident that in the TiAlCN layer deposited at 850°C the carbon is mainly located at the grain boundaries and not in the crystals of the fcc-$Ti_{1-x}Al_xC_yN_z$ phase. The layers deposited at 800°C and 850°C possess a high hardness around 3000 HV. A strong adherence on hardmetal inserts is achieved by a bonding layer system consisting of an initial TiN layer followed by a TiAlN gradient layer. Scratch test measurements showed high critical loads of about 100 N. TiAlCN prepared at 850°C showed also an amazing thermal stability under vacuum conditions up to 1350°C. The wear behavior was investigated by different milling tests. For milling steels 42CrMo4V and C45 as well as cast iron GGG70 coatings containing aluminium-rich fcc-$Ti_{1-x}Al_xC_yN_z$ with $x > 0.8$ exceed the performance of different state-of-the-art CVD and PVD coatings.

10:40am **B3-10 TiO_xN_y Coatings Grown by Atmospheric Pressure MOCVD**, ***F. Maury*** *(francis.maury@ensiacet.fr),* CNRS-CIRIMAT, France, *F.D. Duminica*, CIRIMAT, France

Titanium oxynitride coatings were deposited by atmospheric pressure MOCVD using titanium tetra-isopropoxide and N_2H_4 as reactive gas. The films composition was controlled by variation of the N_2H_4 mole fraction. The variation of the N content in the films results in changes in structural, electrical and optical properties. When a large excess of the nitrogen source is used the resulting film contains around 20 at. % of nitrogen and forms dense and amorphous ternary solid solution. Relatively high growth rate of these amorphous TiO_xN_y coatings was obtained. Correlations between the structure, the morphology, the composition and the growth rate of the films are presented and discussed in relation with deposition conditions and preliminary properties.

11:00am **B3-11 Thermal Stability of Doped CVD κ-Al_2O_3 Coatings**, *D. Hochauer,* Materials Center Leoben, ***C. Mitterer*** *(christian.mitterer@unileoben.ac.at),* Montanuniversität Leoben, Austria, *M. Penoy, C. Michotte,* CERATIZIT Luxembourg S.a.r.l., Luxembourg, *H.-P. Martinz,* Plansee Se, Austria, *M. Kathrein*, CERATIZIT Austria GmbH, Austria

The application of wear resistant alumina-containing coating systems is a common approach to improve cutting performance of cemented carbide cutting inserts. This work focuses on the influence of B- and Ti-B-doping on the thermal stability of κ-Al_2O_3 deposited at high temperature and low pressure by chemical vapor deposition. The investigated coating architecture includes a κ-Al_2O_3 bilayer, separated by a TiN/TiCN interlayer, and a TiCN base-layer grown on cemented carbide substrates. The transformation from κ-Al_2O_3 to α-Al_2O_3 was examined with high temperature X-ray diffraction at 1030 and 1000°C as well as glancing angle X-ray diffraction after different heat treatment times at 1000°C. Chemical composition and coating morphology were determined with glow discharge optical emission spectrometry and scanning electron microscopy, respectively. In general, doping retarded the κ-α-transformation. Ti-B- and, to a lower degree, B-doping entailed a slower diffusion of base-layer and substrate species through the κ-Al_2O_3 bilayer, thus retarding the formation of segregated species on the coating surface. In addition, the heat treatment atmosphere decisively affected the κ-α-transformation.

11:20am **B3-12 Deposition of Chromium-Containing Al_2O_3-CVD-Coatings**, *M. Höhn (mandy.hoehn@ikts.fraunhofer.de), I. Endler,* Fraunhofer IKTS Dresden, Germany, ***H. van den Berg***, *H. Westphal*, Kennametal Technologies GmbH, Germany

CVD-alumina is one of the most important components in modern coating systems for cutting tools. There were many activities in the last years to improve the properties of these coatings like hardness and wear resistance using different dopants.

The aim of this work is to examine the influence of chromium addition on the structure and properties of alumina CVD coatings. There is a lack on suitable chromium-containing precursors for thermal CVD processes. In this work a new chromium precursor based on a ternary aluminium chromium chloride is applied.

For determining the temperature range where the ternary aluminium chromium chloride is formed investigations using the chemical transport of chromium(II)chloride with aluminium(III)chloride are performed. Gaseous $AlCl_3$ reacts at a minimum temperature of 270°C with $CrCl_2$ and the ternary Al_2CrCl_8 is formed.

Deposition of chromium-containing layers is carried out in a LPCVD process using the new precursor, CO_2 and H_2. Composite coatings consisting of alumina, aluminium chromium oxide and chromium carbides are prepared at deposition temperatures between 920°C and 1030°C. Depending on deposition temperature and CO_2 concentration different types of layers were obtained. A first coating system consists of $Al_{2-x}Cr_xO_3$ and chromium carbides Cr_7C_3 and $Cr_{23}C_6$ showing a hardness of 2600 HV[0.01]. A total chromium content of 13 at.-% in the layer is analyzed by WDX. In $Al_{2-x}Cr_xO_3$ an x-value of 0.015 is calculated from the lattice constants. Additionally the existence of $Al_{2-x}Cr_xO_3$ is verified by ruby luminescence. A second coating type exhibit a composite structure consisting of $Al_{2-x}Cr_xO_3$ and Cr_7C_3 with a low total chromium content about 1 at.-%. This layer possesses a high hardness up to 2800 HV[0.01].

Thermodynamic calculations show a good agreement between theoretical and experimental phase compositions in the coatings. The wear behavior of the prepared coating types was investigated by milling tests.

11:40am **B3-13 Synthesis and Properties of $(Al,Cr)_2O_3$**, ***K. Tomita*** *(kohei@mmc.co.jp), M. Igarashi, E. Nakamura, A. Osada*, Mitsubishi Materials Corporation, Japan

Al_2O_3 coatings have been one of the most important coatings for the cutting tool and are mostly produced by CVD (Chemical Vapor Deposition) process. PVD Al_2O_3 coatings had been developed for a long time and introduced to the market a few years ago. Recently there are some reports about properties of $(Al,Cr)_2O_3$, Cr_2O_3 coatings by cathodic arc evaporation, however no reports in case using CVD process. In this work $(Al,Cr)_2O_3$ and Cr_2O_3 coatings were deposited using a hot wall CVD equipment, with AlC_3 – Cr-chloride – CO_2 – HCl – H_2 gas mixture. The growth textures and morphologies of coatings were analyzed by XRD, SEM and TEM. The effects of the Cr content on these properties will be discussed.

Carbon and Nitride Materials: Synthesis-Structure-Property Relationships
Room: Pacific Salon 3 - Session D3

Carbon and Nitrogen-Containing Nanostructured Composite and Nanolaminated Films
Moderator: J.-M. Ting, National Cheng Kung University

8:00am **D3-1 Optical and Electronic Properties of Carbon- and Nitrogen-Based Nanostructured Inorganic Thin Films**, ***A. Schuler*** *(andreas.schueler@epfl.ch)*, Ecole Polytechnique Federal de Lausanne (EPFL), Switzerland **INVITED**

Nanostructuring carbon- and nitrogen based inorganic films result in novel fascinating optical and electronic properties. Such films are deposited by vacuum processes such as reactive magnetron cosputtering or combined physical vapor deposition (PVD) and plasma assisted chemical vapor deposition (PECVD). Already during film preparation, useful information on the optical properties can instantaneously be obtained by in-situ measurements such as laser reflectometry during film preparation. Complementary ex-situ techniques such as spectrophotometry or spectroscopic ellipsometry allow a precise optical characterisation in a wide spectral range. While nanolaminated films can be treated as multilayered interference stack, the dielectric function of nanocomposite films can be described within the framework of effective medium theories taking into account finite grain size effects. The superiority of the Ping Sheng theory with respect to the theories of Maxwell Garnett and Bruggeman can clearly be demonstrated. The optical properties of nanostructured films are closely related to their electronic properties. A powerful tool for the characterization of the latter is in-situ photoelectron spectroscopy. Due to the high surface sensitivity of the technique it is preferable to work with in-situ sample transfer between the preparation chamber and the UHV photoelectron spectrometer, thus avoiding any exposure of the sample surface to air. X-ray photoelectron spectroscopy (XPS) allows quantifying atom concentrations, identifying compounds by comparing chemical shifts of the involved core levels, and studies of characteristic electron energy losses and final state screening effects. Ultraviolet photoelectron spectroscopy (UPS) allows characterizing experimentally the valence band, yields spectra which can be compared to band structure calculations, and provides important information on the density of states of conduction electrons at the Fermi edge. The small dimensions occurring in nanostructured films give rise to one-electron charging effects which are a typical feature of embedded metallic nanocrystals. Examples for carbon- and nitrogen- based nanostructured inorganic materials include thin films based on a-C:H/Ti, a Si:C:H/Ti, and Ti Al N. Potential optical applications include selective absorber coatings for solar collectors and architectural solar control glazing.

8:40am **D3-3 Development of TiVCr-Based High Entropy Alloy Coatings**, ***F.-S. Shieu*** *(fsshieu@dragon.nchu.edu.tw), R.-S. Yu, D.-C. Tsai*, National Chung Hsing University, Taiwan **INVITED**

High entropy alloys have emerged as a new class of multifunctional materials over the years. Unlike conventional alloys with only one or two major components, high entropy alloys usually contain more than three principal elements of approximately equal fraction. One of the distinct characteristics of the high entropy alloys is that thermodynamiclly the Gibbs free energy decreases with increasing temperature due to maximal mixing entropy. Mechanical properties, e. g., tensile strength, of the alloys tend to increase or remain stable at high temperature. The crystal structure of the alloys also exhibits a simple form, such as body-centered cubic, face-centered cubic, and hexagonal closed-packed. Research on the properties and microstructure of TiVCr-based high entropy alloy films prepared by magnetron sputtering was carried out in this study. Attempt is made to correlate among deposition parameters, microstructure, and mechanical properties of the TiVCr-based high entropy alloy films.

9:20am **D3-5 Non-Uniform Elastic Deformation of MAX Phases**, ***C. Humphrey*** *(ch479@cam.ac.uk), H.J. Stone, W.J. Clegg*, University of Cambridge, United Kingdom, *M.G. Tucker*, Rutherford Appleton Laboratory, United Kingdom

In many layered structures, such as MAX phases, elastic deformation normal to the plane of the layers occurs more easily than deformation parallel to the layers due to the M-A bonds being much weaker than the M-X bonds in these structures. Such ideas are consistent with simulations and it has been suggested that this might explain why basal slip in MAX phases is very easy. However, there are no experimental measurements of the relative deformation of the individual atom layers when the material is compressed in the direction perpendicular to the layers. To examine this, the relative movement of the individual layers in 211 MAX phases (Ti_2AlC, Ta_2AlC and Cr_2AlC) under hydrostatic compression to 20 GPa was measured. Time-of-flight neutron diffraction data was collected from samples hydrostatically compressed using a Paris-Edinburgh cell with a deuterated methanol-ethanol mixture acting as a pressure medium and a lead pellet as the pressure marker. Full-profile Rietveld refinement of the patterns was carried out to obtain the changes in the lattice parameters and the change in position of the layers of the M atoms within the unit cell. It has been found that in Ti_2AlC that the Ti-Al layers do not appear substantially more compliant than the Ti-C layers so that the deformation of the unit cell, in Ti_2AlC at least, appears almost uniform.

9:40am **D3-6 Properties of Thin MAX Phase Films Produced by Ion-Beam-Assisted Deposition**, *R. Valizadeh (r.valizadeh@mmu.ac.uk),* ***V. Vishnyakov****, J. Colligon*, Manchester Metropolitan University, United Kingdom

Thin films of MAX phase alloys, which are multilayer materials with chemical composition $M_{n+1}AX_n$, where M is a transition metal, A is an element from the A group in the periodic table and X is either C or N. These materials were first reported by Nowotny et al (1,2) and are stable at high temperatures but are relatively easy to machine. A remaining problem is to produce thin films of these materials at temperatures low enough to preserve the properties of the substrates. Hence, in the present study thin films of around 1µm thickness of $Cr_{n+1}AlC_n$, MAX phases have been produced using a dual ion beam system at substrate temperatures ranging from 300 to 750 K and ion beam assistance was used to mediate the film growth. Substrates used were silicon, silica, sapphire and steel. The areas of the component species were adjusted to maintain film composition under various deposition conditions. Some films were later annealed in vacuum at temperatures up to 1150 K. Material chemical composition was determined by Energy- and Wave-Dispersive X-Ray Spectroscopy (EDX and WDX). Chemical bonding was probed by X-Ray Photoelectron Spectroscopy (XPS) and micro-Raman. Structural analysis was conducted by X-Ray Diffraction (XRD) and cross- sectional Transmission Electron Microscopy (TEM). Mechanical properties have been determined by nano-indentation and tribological properties have been measured by nano-scratch testing.

The fully developed MAX phase is known to have a precisely layered atomic structure (3,4,5). As-grown films already exhibit some ordering which increases with the substrate temperature and is influenced by ion assistance at low bombarding ion energies which leads to more uniform local chemical bonding. Sample annealing reinforces this trend. Most films show good crack resistance during nano-scratch testing. The mechanical properties depend on deposition and annealing conditions and possibly can be explained on the basis of nanostructural hardening associated with the transition from the disordered state to a layered atomic arrangement.

10:00am **D3-7 Tilting of Self-Organized Layered Arrays of Encapsulated Metal Nanoparticles in C:Ni Nanocomposite Films by Means of Hyerpthermal Ion Deposition**, ***G. Abrasonis*** *(g.abrasonis@fzd.de),* Forschungszentrum Dresden-Rossendorf, Germany & University of Sydney, Ausralia, *T.W.H. Oates,* Linköping University, Sweden, *G.J. Kovacs, J. Grenzer,* Forschungszentrum Dresden-Rossendorf, Germany, *P. Persson,* Linköping University, Sweden, *K.H. Heinig, A. Martinavicius, N. Jeutter, C. Baethz,* Forschungszentrum Dresden-Rossendorf, Germany, *M. Tucker, M.M.M. Bilek,* University of Sydney, Australia, *W. Moller*, Forschungszentrum Dresden-Rossendorf, Germany

Self-organization at the nanoscale is a key issue in modern material science as it promises a potential route to commercially scalable production of functional nanomaterials. Here we present the growth-structure study of self-organized layered arrays of carbon encapsulated Ni nanoparticles grown by means of pulsed filtered cathodic vacuum arc deposition. Influence of the oblique ion incidence and Ni content on the film morphology is investigated. The film morphology has been determined by transmission electron microscopy (TEM) and grazing incidence small angle x-ray scattering (GISAXS) while C/Ni ratio was determined by means of nuclear reaction analysis. The C:Ni films with the Ni content in the range of ~6-50 at.% are considered. The results show that for the perpendicular incoming depositing ion incidence the C:Ni film structure consists of alternating self-organized nickel carbide and carbon layer oriented parallel to the film surface. However, for the oblique ion incidence the layered structure tilts in relation to the surface. The tilting angle and periodicity strongly depends on the deposition angle as well as on the Ni content. Combined TEM and GISAXS analysis shows that the film cross-section can be described by two density modulation waves advancing with the growing film surface – one towards the incoming ions, another one with the weaker amplitude moving in roughly perpendicular direction. The results are discussed on the basis of the interplay between thermodynamically driven phase separation and energetic ion induced ballistic effects. Such structures show significant anisotropy which can be considered for tribological, optical, magnetic or magnetotransport applications.

10:20am **D3-8 Nano Composite TiNiC-Coatings for Low Friction and Low Contact Resistance**, ***B. André*** *(benny.andre@angstrom.uu.se), E. Lewin, U. Jansson, U. Wiklund*, Uppsala University, Sweden

Materials in electrical connectors should have low inherent resistivity and should be able to give a low contact resistance. It is also good if the friction against its mating surface is low for easy connection, and in case the contact is a sliding contact. Today, many electrical contacts have a surface made of noble metals such as gold or silver and in most of these cases both mating surfaces are made of the same material. The choice of noble metals is based on their ability to provide low contact resistance through a combination of softness that gives a large contact area, a low resistivity and a good oxidation resistance. The drawbacks with connectors coated with noble metal are their low wear resistance, high friction and the cost. In many cases there is also problem with cold welding of the surfaces giving low contact resistance but extreme forces for separation.

In this work carbon based nanocomposite coatings in the Ti-Ni-C system are considered as alternative coatings for electrical contacts. These have previously shown promising tribological performance, due to an ability to provide free carbon in the contact, but so far their combined tribological and electrical properties have not been studied in detail.

Nine different nanocomposite coatings with different compositions were deposited on copper cylinders with 20 µm nickel as an interlayer using sputtering. The tests where performed by having two cylinders, 10mm in diameter, sliding reciprocally in a crossed cylinder geometry. One cylinder was coated with nanocomposite coating and the other one by a thick silver layer. Since only one of the mating surfaces has a nanocomposite on top the contact area, determined by the hardness of the softest material and the load, will stay virtually the same as in the case of a silver-silver contact. This eliminates influences from contact area differences on the results. A load of 40N was applied and a current of 3A was fed through the contact to simulate a high current connector. The frequency of the sliding was 1 Hz and the amplidude was 1 mm. During the test the evolution of contact resistance and the coefficient of friction was measured and after the test the surfaces where closely investigated in SEM. The results show that the coatings give low contact resistance and coefficient of friction. The tests also show how the different amounts of carbon, dictated by the Ti to Ni ratio, influences the contact resistance, coefficient of friction and wear. Contact resistances as low as 100 micro Ohm was measured for the best coatings.

10:40am **D3-9 Nanometer-Thick Protective Films for Miniature Applications Deposited Using Reactive Magnetron Sputtering**, ***C. Tsotsos*** *(tsotsos@ucy.ac.cy), K. Polychronopoulou,* University of Cyprus, *N.G. Demas, R. Meschewski,* University of Illinois at Urbana-Champaign, *C.G. Rebholz,* University of Cyprus, *A.A. Polycarpou*, University of Illinois at Urbana-Champaign

TiN, TiC and TiCN thin films with thicknesses below <100 nm were deposited using reactive magnetron sputtering on Si-wafer substrates. A PCS300 magnetron sputtering deposition unit developed by the Assembly Systems and Special Machinery department of Robert Bosch GmbH in Stuttgart Germany was used for the coating experiments. Different analytical techniques were used, such as X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM) for crystalline phases, exact thin film thickness/surface topography and roughness evaluation, respectively. The XRD spectra demonstrated the formation of TiN, TiC and TiCN phases at the different films investigated with different preferred orientations. Cross sectional SEM images showed a thickness of about 85 nm. Laser acoustic waves (LAWAVE) technique was used to confirm the elastic modulus of the films, which was found to be between 100 and 240 GPa. Since miniature devices, such as MEMS and storage disks is the ultimate application of this work, nanomechanical properties of the thin films were also explored. Nanotribological performance was investigated using nanoscratch technique. Coefficient of friction in the nanoscale was found to be in the 0.08-0.1 range.

11:00am **D3-10 Magnetron Sputtered Ti_3SiC_2 as Ohmic Contact to SiC**, ***K. Buchholt*** *(kribu@ifm.liu.se),* Linköping University, Sweden, *R. Ghandi,* KTH – Royal Institute of Technology, Sweden, *P. Eklund,* Linköping University, Sweden, *M. Domeij, C.M. Zetterling,* KTH – Royal Institute of Technology, Sweden, *L. Hultman, A. Lloyd Spetz*, Linköping University, Sweden

SiC is a promising semiconductor material for power and sensor applications and for high temperature operation in harsh and corrosive environments due to its large bandgap, thermal conductivity, and chemical inertness. The formation of high quality ohmic contacts to SiC is very important to device performance and is an issue remaining to be satisfactorily solved. Ti_3SiC_2, which is a member of the MAX-phase family, form at the interface between SiC and Ti-containing contacts when annealed at high temperature [1] . Ti_3SiC_2 is thermally and electrically conductive like a metal, while simultaneously displaying ceramic properties such as high decomposition temperature and low thermal expansion [2, 3] . We propose that epitaxially grown Ti_3SiC_2 layers may give low resistance ohmic contacts to SiC.

We have grown Ti_3SiC_2 films on n-type and p-type 4H-SiC through magnetron co-sputtering from three separate targets at a temperature of 850 °C and investigated the ohmic contact properties of these films. The films have been characterized with X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), and Atomic Force Microscopy (AFM), confirming the successful growth of Ti_3SiC_2 with a stacked plate-like structure, which follows the structure of the 8° off axis cut SiC substrates closely. The sheet resistance of the Ti_3SiC_2 films is $\sim 1\ \Omega/cm^2$. Since patterning methods are essential for processing ohmic contacts, different methods for patterning the Ti_3SiC_2 were investigated, including wet chemical etching as well as dry etching methods, where Inductively Coupled Plasma (ICP) show the most promising results and was employed to pattern TLM structures for measuring the specific contact resistivity of the material.

[1] Pécz, B., et al., /Ti_3 SiC_2 formed in annealed Al/Ti contacts to p-type SiC./ Applied Surface Science, 2003. *206*(1-4): p. 8-11.

[2] Barsoum, M.W. and T. El-Raghy, /The Max Phases: Unique New Carbide and Nitride Materials./ American Scientist, 2001. *89*: p. 334-343.

[3] Eklund, P., et al., /The Mn + 1AXn phases: Materials science and thin-film processing./ Thin Solid Films. *Published online, Corrected Proof*.

Tribology and Mechanical Behavior of Coatings and Thin Films
Room: Pacific Salon 1 - Session E1-2

Friction and Wear of Coatings: Lubrication, Surface Effects and Modeling

Moderator: E. Broitman, Carnegie Mellon University, J.C. Sanchez-Lopez, Instituto de Ciencia de Materiales de Sevilla (CSIC-US), O.L. Eryilmaz, Argonne National Laboratory

8:00am **E1-2-1 Microstructure and Properties Evolution of AlSi Coated Surfaces**, ***O. Rashwan***, *M. Stoilov (vstoilov@uwindsor.ca)*, University of Windsor, Canada

Aluminum-Silicon alloys are extensively used in automotive applications due to their excellent physical and triobological properties. In this paper, the aluminum silicon alloys, with DLC, CrN and Al_2O_3 are investigated to determine the threshold fracture load of the whole system under monotonic loading condition. As it is known, the fracture and deboning of the silicon particles under monotonic loading might lead to nucleation, growth, and coalescence of voids, hence, failure of the cast aluminum silicon alloys occurs. Yet, there are a limited number of studies that have been done to study the combined effects of the coating materials, the coating thickness, and the shape of the Si particles, on the threshold fracture load of the aluminum silicon alloys. In this study, finite element analysis has been performed to study the combined effects of the above mentioned parameters on the critical fracture load of the coated aluminum silicon alloys. A cohesive layer has been assumed between the Si particles and Al matrix and the coating layer and the matrix. It was found out that there is no single parameter which affects the fracture and deboning of Si particles, yet it is the combination of different parameters. For example, the Si particle shape plays a major role in determining the critical fracture stress with a circular shape outperforms the elliptical shape. The combination the circular Si particle and the CrN as coating material gives highest critical fracture stress while Al_2O_3 exhibits very poor performance with elliptical Si particle and outstanding performance circular Si particle. Finally DLC does not perform well with the circular Si particles and it shows the highest possible fracture stress with elliptical Si particles.

8:20am **E1-2-2 Tribological Properties of CrN/AlN Thin Films Deposited on H13 Steel by Reactive Unbalanced Magnetron Sputtering**, *A. Rojo,* ITESM-TOL, Mexico, ***J. Solis-Romero*** *(josesolis@infinitum.com.mx),* DGEST-ITTLA/ITESM-CEM, Mexico, *J. Oseguera-Pena, O. Salis-Martinez*, ITESM-CEM, Mexico

This paper is related to the development of CrN/AlN thin films on H13 tool steel produced with the physical vapor deposition (PVD) process, where the objective was to determine the friction and wear of the layers on this tool steel used for hot work. The films were produced by reactive magnetron sputtering of aluminum under s everal modes of injection of nitrogen to find the optimum deposition conditions to form a satisfactory structure such that it provided a good adhesion to the substrate. The injection methods used were: convectional injection of Ar + N_2 mixture away from the substrate varying the amount of nitrogen, Ar + N_2 mixture away of the substrate with extra nitrogen near the substrate and direct injection of N_2 near the substrate. The injection method that results in a richer nitrogen atmosphere seems to produce better outcomes. The resulting coatings were characterized by X-ray diffraction (XRD), scanning electron microscopy equipped with energy dispersive X-ray micro analysis (SEM-EDS) and their tribological characterization was carried out by using a pin-on disk tribometer.

8:40am **E1-2-3 Influence of the Nitriding and TiAlN/TiN Coating Thickness on the Sliding Wear Behavior of Duplex Treated AISI H13 Steel**, ***R. Torres*** *(ricardo.torres@pucpr.br), P. Soares,* Pontifícia Universidade Católica do Paraná, Brazil*, C. Schmitz, C. Siqueira*, Universidade Federal do Paraná, Brazil

AISI H13 die steel substrates were low pressure gas nitrided in three different nitriding cases, named case A, B and C. The nitrided cases hardness was assessed by instrumented indentation. In the nitriding case A, the surface hardness was around 12 GPa and the nitriding thickness was around 40 µm. In the nitriding case B, the surface hardness was the same as in case A, but the nitriding thickness was around 70 µm. Finally, in the nitriding case C, the nitriding thickness was the same as in case B, but the surface hardness was around 14 GPa. XRD analyses and optical microscopy results showed that the nitriding cases microstructure was composed mainly by the diffusion layer with small amount of Cr2N precipitates. Nitrided and non nitrided samples were subsequently coated with TiAlN/TiN system in two total thicknesses: 3 and 7 µm. The deposition process was carried out in a cathodic arc evaporation facility. Finally, sliding experiments were conducted in a linearly reciprocating ball-on-flat tribometer. The sliding tests were performed using a 16Cr6 steel ball, the tests speed was 3.14 cm/s and the tests load was 1N. All the wear tracks produced during the sliding tests showed iron adhesion. Moreover, the friction coefficient of the duplex treated surface is highly influenced by the characteristics of the nitrided surface. The TiAlN/TiN over nitrided case A showed the lowest friction coefficient. TiAlN/TiN thickness does not play a major role in the friction coefficient of TiAlN/TiN over the nitrided cases. On the other hand, TiAlN/TiN thickness does change the friction coefficient of the non nitrided H13 specimens. It was observed that the friction coefficient of a 7 µm TiAlN/TiN is lower than a 3 µm TiAlN/TiN over non nitrided specimens.

9:00am **E1-2-4 Polymer Monolayers as Lubricious Coatings**, ***N.D. Spencer*** *(nspencer@eth.ch)*, ETH Zurich, Switzerland **INVITED**

Nature lubricates with polymer monolayers: The substrates are soft, the base lubricant is water, and the polymers are glycoproteins. Glycoproteins consist of a proteinaceous backbone with oligosaccharide side chains, and it is these latter structures that appear to lead to the lubricious behavior of the glycoprotein-covered surface.

Lubricating man-made devices with glycoproteins is not very practicable. They are expensive to obtain in quantity, and susceptible to bacterial attack. They are also not suited to the lubrication of many surfaces, especially those of hard materials. Nevertheless, some of the natural principles can be utilized for the design of lubricating polymer systems that can work in a variety of environments on a variety of substrates.

The majority of studies carried out in our laboratory have concerned aqueous lubricant systems. Water is rarely used at present as a lubricant in an industrial environment, but the combination of novel polymer additives with corrosion resistant sliding surfaces, such as engineering polymers or ceramics (e.g. Si_3N_4), could lead to the introduction of a new generation of oil-free bearing systems. The common factor in the polymer monolayers appled to date is that they have been surface tethered, like the oligosaccharides in nature, often leading to the formation of brush-like structures upon exposure to a "good" solvent. Polymer brushes have a variety of interesting applications in many different technologies, and their fabrication is either carried out by attaching ready-made polymers to the surface by one end ("grafting to"), or by immobilizing initiators on the substrate and then growing polymer chains out of the surface ("grafting from"). Both approaches have been utilized in our laboratories and have been shown to lead to substantial friction reduction under aqueous lubrication.

Water has a major drawback as a lubricant, in that its viscosity is essentially pressure independent. This results in poor performance under classical EHL conditions, as encountered in traditional ball bearings, for example. Two approaches can mitigate this situation: the use of elastomeric contacting surfaces, such that the soft EHL regime is encountered, and the addition of a viscosity-enhancing fluid, such as glycerol, to the water. The latter approach has the advantage that the transition to mixed and hydrodynamic lubrication happens at a lower speed, leading to a lower friction coefficient over a wider range of conditions. The pressure coefficient of viscosity of glycerol, being greater than that of water, also brings with it additional benefits.

9:40am **E1-2-6 On the Relationships Between the Fretting and Ball Cratering Behaviors of Solid Lubricant Coatings**, ***V. Fridrici*** *(vincent.fridrici@ec-lyon.fr),* Ecole Centrale de Lyon - LTDS, France*, D.B. Luo,* Ecole Centrale de Lyon - LTDS & Southwest Jiaotong University, France*, Ph. Kapsa*, Ecole Centrale de Lyon - LTDS, France

Employing solid lubricant coatings to reduce friction is one of the most effective methods to mitigate fretting damage. However, facing numerous available coatings, users often feel confounded, and the selection of the optimum coating for a specific application is still a tough task. Some simple methods are expected to help the selection. Ball cratering as a promising technique is becoming popular in the developing process of new coatings to assess their abrasion resistance. The objective of this paper is to identify the relationships between the fretting behavior and the ball cratering resistance of coatings, and attempt to use ball cratering to pre-select coatings for fretting conditions in order to cut down the number of candidate coatings and shorten the fretting tests. In this study, several bonded solid lubricant coatings, principally based on PTFE or MoS_2, were investigated by ball cratering and fretting tests. The results showed that the coatings in ball cratering presented similar tribological performance as in fretting tests in terms of endurance and wear resistance, i.e., the coatings with good ball cratering resistance also exhibited long lifetime in fretting tests, so ball cratering can be considered as a simple test to pre-select solid lubricant coatings for fretting applications.

10:00am **E1-2-7 Temperature Effects on the Wear Behavior of Molybdenum Disulfide Solid Lubricant Films**, ***R.S. Colbert****, J.H. Keith, W.G. Sawyer (wgsawyer@ufl.edu)*, University of Florida

The space environment, with high vacuum conditions ($1x10^{-6}$ Torr) and a wide thermal range (T>200ºC or T<0ºC), is one of the most difficult tribological environments in which to operate. These environmental conditions have led to the use of thin solid films to prevent seizure of many joints which include highly loaded restraints and hinges. The solid lubricant thin films primarily used are molybdenum disulfide (MoS_2) based, but the tribological performance of these MoS_2 films under space relevant conditions remains largely unquantified. This study examines the effects of temperature on the wear rate and debris size of MoS_2 films in high-vacuum environments. We find that the debris size increases by a factor of 5 over a temperature range from -100°C to 100°C.

10:20am **E1-2-8 Tribological Properties in Different Test Conditions of Thin Films TiTaBN Deposited by CFUBMS**, ***O. Baran*** *(obaran@erzincan.edu.tr),* Erzincan University, Turkey*, I. Efeoglu,* Atatürk University, Turkey*, B. Prakash*, Luleå University of Technology, Turkey

TiBN films are used as wear protective coatings for various industrial applications. The mechanical and tribological properties of this coatings varies depend on boron, nitrogen and alloying elements contents. In this study, we investigated machenical and tribological properties of TiTaBN co-sputtered with Ta at the different nitrogen gas flux.TiTaBN films were deposited on D2 steel substrates and silicon wafers by Closed-Field Unbalanced Magnetron Sputtering (CFUBMS). Composition, morphology and structure were analyzed by EDS, SEM, XRD, microhardness tester. Friction and wear properties of this films were determined using a pin-on disc tribo-tester in different test conditions (air,dry nitrogen,distillated water,oil and elevated temperature).

10:40am **E1-2-9 Comparison of Abrasive Wear Resistance of Low Carbon Steels Subjected to Carburizing, Nitriding, Nitrocarburizing, and Boriding Treatments**, ***V. Sista****,* Argonne National Laboratory*, G. Kartal,* Istanbul Technical University, Turkey*, A. Erdemir (erdemir@anl.gov), O.L. Eryilmaz, G. Krumdick,* Argonne National Laboratory*, S. Timur*, Istanbul Technical University, Turkey

A Calotest micro-abrasion machine (which is used widely to determine the thickness of hard coatings) was used to

perform abrasive wear tests on AISI 1018 steel substrates after a variety of surface treatments such as carburizing, nitro-carburizing, electrochemical boriding and pack boriding. Using a variety of abrasive slurries (containing alumina, SiC, and diamond particles), the effects of test duration on the wear resistance of untreated and surface treated substrates were evaluated and the results were compared in terms of wear crater depths and the weight losses. Using the present technique, wear resistance of single phase boride layers (Fe_2B) for pack boriding, electrochemical boriding, and double phase boride layers (FeB + Fe_2B) formed during electrochemical boriding have been calculated. We found that borided surfaces are much more resistant to abrasive wear than the surfaces that were treated by other methods.

11:00am **E1-2-12 The Effect of Rhenium on The Tribological Properties of Al-Ti-Re-N and Cr-Re-N Coatings**, ***Z. Kahraman***, *K. Kazmanli,* Istanbul Technical University, Turkey, *A. Erdemir,* Argonne National Laboratory, *M. Urgen (urgen@itu.edu.tr)*, Istanbul Technical University, Turkey

In this study, the effects of rhenium on the tribological properties of Al-Ti-N and Cr-N coatings were investigated. The coatings were produced by cathodic arc + magnetron sputtering hybrid physical vapor deposition technique. Al-Ti-N and Cr-N coatings were deposited by using cathodic arc. The arc current and N_2 pressure were 80 Amps and 1 Pa, respectively. In order to incorporate rhenium into Al-Ti-N and Cr-N coatings, a rhenium target was simultaneously sputtered with 200 W. The rhenium content of Al-Ti-Re-N and Cr-Re-N were 2.52 at.% and 1.58 at.%, respectively. In order to characterize the coatings, Calotest, X-Ray Diffraction, Scanning Electron Microscopy, EDS and micro hardness techniques were used.

The tribological properties of the coatings were investigated by using ball-on-disc and reciprocating tests against Al_2O_3 balls at different temperatures starting from room temperature up to 200 °C. The wear of the coatings and the counter body surfaces were observed with 3D optical profilometer and SEM. The wear debris in the wear tracks were analyzed with Micro Raman Spectroscopy. The wear behavior of the coatings were correlated with the chemistry of the compounds formed in the wear track. The interdependent role of temperature and rhenium content on the tribological behavior of the coatings were presented.

Applications, Manufacturing, and Equipment Room: Royal Palm 4-6 - Session G3

Atmospheric and Hybrid Plasma Technologies

Moderator: V.H. Baggio-Scheid, Institute of Advanced Studies, D. Pappas, U.S. Army Research Laboratory

8:00am **G3-1 Scaling Down Atmospheric Pressure PECVD Processes**, ***T. Belmonte*** *(thierry.belmonte@mines.inpl-nancy.fr), G. Arnoult, G. Henrion*, Ecole des Mines de Nancy, France **INVITED**

Resorting to atmospheric pressure plasmas (APP) in the field of PECVD offers several interests. Because of their versatility, APP have pratical application in surface cleaning, deposition of thin films or coating of nanoparticles, etc. They could also be used to create metamaterials. This quality is mainly due to the large availability of sources operating at atmospheric pressure. Various plasma sources have been proposed, including DC arc, corona discharges, Dielectric Barrier Discharges, or microwaves excited plasmas.

The recent development of small-scale plasmas, including micro-plasmas, offers new capabilities. The APP may be used to localize the surface treatment on very small areas. Several new applications emerged from this capability. For example, one can pattern a surface with stripes of different wettabilities for lab-on-chip application and micro-chemical analysis systems. Bio-MEM sterilization, displays and micropropulsion are also possible fields of application. About PECVD, localized treatments could be useful to structure surfaces or to process small-scale materials. This idea was first proposed by Babayan *et al.*[1] . They used an atmospheric-pressure plasma jet that was produced by flowing oxygen and helium between two coaxial metal electrodes driven by 13.56 MHz radio frequency power. The remote plasma exiting from between the electrodes was mixed with tetraethoxysilane. Since these pioneer works, other developments were proposed. The “Torche à Injection Axiale”, also called the TIA was used to perform such localised PECVD treatments at atmospheric pressure but at much higher temperatures than those encountered in DBDs. Another interesting approach deals with microstrip split-ring resonator microplasma sources. With such a device, self-ignition in atmospheric air could be accomplished with a device that has a gap size of only 25µm.

Recently, we have developed a small-scale remote plasma at atmospheric pressure based on a resonant microwave cavity. By controlling the hydrodynamics of the gas, we have shown that it is possible to extract through a tinny hole in the cavity a straight beam of active species over a length of 10 cm [2]. We will describe a way to solve the scaling-down of the sources to reach the nanoscale.

[1] S E Babayan, J Y Jeong, A Schütze1, V J Tu, M. Moravej, G S Selwyn and R F Hicks, Plasma Sources Sci. Technol. **10** (2001) 573–578

[2] G Arnoult, R P Cardoso, T Belmonte and G Henrion, Appl. Phys. Lett., **93** (2008) 191507

8:40am **G3-4 High Density Large Area Hydrogen Plasma by Hollow Cathode Plasma Array**, *J. Cho, J. Yang,* PSK Inc., Korea, *H. Park, D. Park,* ***S. Park*** *(sgpark@inha.ac.kr)*, Inha University, Korea

Hollow cathode plasma (HCP) has been used for sputtering apparatus because of its localized high density characteristics. An array of HCP’s has once been used to generate large area plasma for chemical vapor deposition of amorphous silicon in TFT-LCD manufacturing, where applied RF power is usually small.

In this work, array of HCP’s has been designed to have high density hydrogen plasma for photoresist etching process, where high RF power is needed. Twenty hollow cavities of cylindrical shape were formed in an aluminum cathode plate of 200mm diameter. After engraving hollow cavities, the cathode plate was anodized. In general, plasma generation from the hollow cavity depended on cavity size, chamber pressure, process gas used and applied RF power.

After diameter and depth of the cavity were varied, we found cavity with 6 mm in diameter and 10 mm in depth showed the highest density in the pressure of 2 Torr with 2.5 KW of RF power in case of hydrogen. Arc discharge could occur at the inside and outside corners of the cavities and sputtering phenomena in the cavity was observed after a long time operation. Redistribution of injection holes of process gas in the cathode plate and insertion of ceramic tub with rounded shape into the cavities could successfully solve these problems.

For photoresist stripping a baffle with holes was placed between the cathode and the wafer stage in order to have hydrogen radicals for the stripping reaction. Stripping rate of 200 nm/min and uniformity of 7 % could be obtained over 300 mm wafers. This high density hydrogen plasma can be a very effective method of photoresist stripping in dual damascene process of copper metal and low-k dielectrics where oxygen plasma cannot be used.

9:00am **G3-5 Thin Film Deposition and Surface Modification with Atmospheric Pressure Dielectric Barrier Discharges**, ***F. Fanelli*** *(fiorenzafanelli@chimica.uniba.it), F. Fracassi, R. d'Agostino*, University of Bari, Italy **INVITED**

Nowadays atmospheric pressure cold plasmas, in particular in Dielectric Barrier Discharge (DBD) configuration, attract significant interest in the field of surface processing of materials. This interest is mainly dictated by the potential practical and economic benefit resulting from the dismissal of vacuum systems; the advantage of atmospheric operation coupled with non-equilibrium plasma conditions makes these approaches a promising alternative to the low pressure counterpart for a wide field of applications. DBDs for surface processing are still characterized by several open questions, for instance, some of the most debated topics are the different discharge regimes (i.e. filamentary and glow regime), the effect on plasma processes of gas feed contaminants (i.e. air and water vapour), the influence of substrate composition, electrical characteristics and shape, and the possibility of tuning the chemistry and morphology of the treated surfaces and hence their final properties.

These and other aspects of DBDs will be examined in this presentation along with our recent results obtained with fluorocarbon- and organosilicon-containing feeds. The utilization of a multidiagnostic approach, which couples both plasma and surface investigation, allows to enhance hypotheses on the atmospheric pressure plasma chemistry and to gain insights into plasma-surface interactions.

The etching-deposition competition and the influence of contaminants (i.e. O_2, N_2 and H_2O) during fluoropolymer deposition in atmospheric pressure DBDs will be discussed. This will allow to highlight important fundamental aspects of the fluorocarbon plasma chemistry at atmospheric pressure and to assess the highest level of contamination compatible with an acceptable process performance, and consequently, to evaluate the possibility of depositing fluorocarbon films in contaminated environments.

Recent results on SiO_x deposition with atmospheric pressure DBDs fed by argon in mixture with oxygen and different methyldisiloxanes (i.e. hexamethyldisiloxane, pentamethyldisiloxane and tetramethyldisiloxane) will be also presented. The influence of the chemical structure of the organosilicon precursor and of the oxygen-to-monomer feed ratio, on the properties of the deposited films will be discussed. The quali-quantitative determination of stable by-products contained in the exhaust gas of the plasma, performed by gas chromatography coupled with mass spectrometry, will contribute to the identification of the thin film precursors and main reaction steps and to the correlation of the plasma chemistry with the coatings properties.

9:40am **G3-7 Nanoparticles of Polypyrrole Obtained by Atmospheric Pressure Plasma**, *M. Vasquez-Ortega,* CINVESTAV-IPN, Mexico, ***J. Morales-Corona***, Universidad Autonoma Metropolitana, Mexico, *M. Ortega,* CINVESTAV-IPN, Mexico, *G. Cruz-Cruz, G. Olayo,* ININ, Mexico, *R. Olayo (oagr@xanum.uam.mx)*, Universidad Autonoma Metropolitana, Mexico

This work presents the synthesis of polypyrrole nanoparticles by radiofrequency capacitive atmospheric pressure plasmas. The polymerization was done in a tubular glass reactor with stainless steel caps and square electrodes with a gap of 2 mm . Each electrode was covered with glass to form a dielectric barrier which homogenizes the plasma discharges. The characterization of the polypyrrole particles was done by thermal analysis; IR and fluorescence spectroscopy; and by scanning, transmission, and atomic force electronic microscopy.

The results showed that the polymers were formed in spherical conformation with core-shell morphology. Some of the particles joined to form thin films and others grew as separated spheres with external diameters from 130 to 280 nm. The wall thickness in the bigger particles reached up to 100 nm. The core of these particles is filled with agglomerates of several much smaller particles with individual diameter in the order of 40 nm. These polypyrrole nanoparticles have similar chemical structure as other films prepared with plasmas of pyrrole. Both, films and nanoparticles, can be combined to increase and enhance the applications of this polymer in the area of medicine and semiconductors.

10:00am **G3-8 Atmospheric Pressure Non-Thermal Plasma for Surface Modification of UHMW-PE Fibers**, ***J. Yim***, Drexel University, *D. Pappas,* U.S. Army Research Laboratory, *A. Fridman, G. Palmese (grp27@drexel.edu)*, Drexel University

High performance synthetic fibers, such as ultra-high molecular weight polyethylene (UHMW-PE), are key components in achieving energy absorption and/or toughening properties in fiber-reinforced polymer composites. However, these fibers exhibit poor wettability and adhesion when incorporated into common resin matrix systems, thus resulting in poor mechanical performance. To evade this problem, many have utilized various modes of surface modification techniques, the more common ones being the use of chemical coupling agents, acid treatments, and plasma treatments. The advantages of atmospheric pressure plasma surface treatments such as quick processing times, ability to treat large areas, and the effectiveness in creating chemical species outweigh those of other treatments.

We report the use of atmospheric pressure dielectric barrier discharge (DBD) plasma surface treatments to functionalize the surfaces of ultra-high molecular weight polyethylene (UHMW-PE) fibers and its effect on the chemical composition at the surface of these fibers and bulk material properties. Different plasma treatment conditions consisting of various exposure time and gas flow-rates were implemented to determine observable trends in the formation of specific chemical groups. X-ray photoelectron spectroscopy (XPS) coupled with conventional titration techniques were used to quantify the surface concentration of reactive groups, whereas the surface roughness before and after plasma treatment was determined by atomic force microscopy (AFM). To characterize the plasma and to elucidate plasma-surface interactions that occur within the plasma optical emission spectroscopy (OES) studies were employed. The correlation between surface group concentrations and surface morphology/roughness will be discussed.

10:20am **G3-9 Atmospheric Pressure Plasma-Enhanced Chemical Vapor Deposition of Thin Films**, ***R.F. Hicks*** *(Robert Hicks [hicks@surfxtechnologies.com])*, Surfx Technologies LLC **INVITED**

Our recent work will be presented on the science and technology of thin film deposition using chamberless, atmospheric pressure, radio frequency capacitive discharge plasmas. This plasma source is unique in that the metalorganic precursors are fed downstream of the plasma, where reactions occur exclusively between neutral molecules, radicals and the substrate surface. Films produced by this process are different from those obtained in low-pressure gas discharges (<1 Torr). For example, glass may be deposited on plastic that are highly flexible, but at the same time maintain outstanding chemical inertness and abrasion resistance. Other films deposited by atmospheric pressure plasma-enhanced chemical vapor deposition include silicon nitride, amorphous hydrogenated silicon, zinc oxide, and diamond-like carbon. These material processes further illustrate the unique advantages of this deposition technology.

New Horizons in Coatings and Thin Films
Room: Royal Palm 1-3 - Session H6

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

8:00am **H6-1 Processes Controlling Delamination and Buckling in Thin Hard Film-Compliant Substrate Systems**, ***N. Moody*** *(nrmoody@sandia.gov), E.D. Reedy, Jr., E. Corona, D. Adams,* Sandia National Laboratories, *J. Yeager, D. Bahr,* Washington State University, *D. Huber, H. Fraser*, Ohio State University

Performance and reliability are important factors governing the use of emerging thin film compliant substrate devices where compressive stresses can lead to delamination and buckling. We are therefore studying these effects combining compressively stressed thin hard tungsten films on compliant PMMA substrates with simulations employing cohesive zone elements to describe interface fracture. Following film deposition, high compressive film stresses triggered spontaneous buckling on all samples creating networks of small telephone cord buckles interspersed with regions of larger rosette-like and isolated straight walled buckles. Cohesive zone simulations showed that fracture energies varied strongly with buckle size and differed significantly with rigid elastic substrate models. Although all buckles formed by delamination along the film-substrate interface, FIB cross-sections showed that two crack tip deformation processes led to the two distributions of buckles. Sharp cracks led to large delamination-driven buckles while crack tip blunting led to small deformation-limited buckles. In this presentation we will use the observations and simulations to show how substrate deformation processes control delamination of thin hard films on compliant substrates.

This work was supported by Sandia National Laboratories under USDOE Contract DE-AC04 94AL85000.

8:20am **H6-4 Mechanical Integrity of Thin Inorganic Coatings on Polymer Substrates Under Quasi-Static, Thermal and Fatigue Loadings**, ***Y. Leterrier*** *(yves.leterrier@epfl.ch), A. Mottet, N. Bouquet, D. Gilliéron, P. Dumont, A. Pinyol, L. Lalande, J.H. Waller, J.-A.E. Manson*, Ecole Polytechnique Fédérale de lausanne (EPFL), Switzerland **INVITED**

The interplay between residual stress state, cohesive and adhesive properties of coatings on substrates is reviewed. Attention is paid to thin inorganic coatings on polymers, characterized by a very high hygro-thermo-mechanical contrast between the brittle and stiff coating and the compliant and soft substrate. An approach to determine the intrinsic, thermal and hygroscopic contributions to the coating residual stress is detailed. The critical strain for coating failure, coating toughness and coating/substrate interface shear strength are derived from the analysis of progressive coating cracking under strain. Electro-fragmentation and electro-fatigue tests in situ in a microscope are described. These methods enable reproducing the thermo-mechanical loads present during processing and service life, hence identifying and modeling the critical conditions for failure. Several case studies relevant to food and pharmaceutical packaging, flexible electronics and thin film photovoltaic devices are discussed to illustrate the benefits and limits of the present methods and models.

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We invite all attendees to participate in our Exhibition by visiting each booth of the firms that are listed below. They will be offering a wide variety of unique equipment and services in the application, testing and characterization of metallurgical coatings, thin films, and surface modification. Challenge them to meet your specific needs with the quality products and services that are associated with this world-renowned event.

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