

**Advanced Surface Engineering**  
**Room: 22 - Session SE+NS-MoM**

## **Nanostructured Thin Films and Coatings I: Interface Aspects**

**Moderator:** J. Patscheider, EMPA, Switzerland

**8:40am SE+NS-MoM2 Ion-guided Phase Separation of Carbon-Nickel Composite Films during Ion Beam Assisted Deposition: 3D Sculpting at the Nanoscale.** *G. Abrasonis*, Helmholtz-Zentrum Dresden-Rossendorf, Germany, *M. Krause*, Helmholtz-Zentrum Dresden-Rossendorf and Technische Universität Dresden, Germany, *T.W.H. Oates*, Leibniz-Institut für Analytische Wissenschaft, Germany, *A. Mücklich*, *S. Facsko*, Helmholtz-Zentrum Dresden-Rossendorf, Germany, *C. Baehtz*, *A. Shalimov*, Helmholtz-Zentrum Dresden-Rossendorf, Germany and European Synchrotron Radiation Facility, France, *S. Gemming*, Helmholtz-Zentrum Dresden-Rossendorf, Germany

Ion assistance during film growth provides unique opportunities to influence the microstructure due to energy transfer and imposed directionality. During nanocomposite film growth at low temperatures, phase separation occurs at the growing film surface. Ion-assistance is a key parameter to control the surface processes during multiphase film growth, and hence the resulting nanocomposite morphology. A systematic study of ion irradiation as a pure energy and momentum transfer agent in the context of surface diffusion assisted phase separations is, however, lacking. Here the influence of low energy (50-130 eV) assisting Ar<sup>+</sup> ion irradiation on the morphology of C-Ni thin films will be reported. Ion-beam assisted deposition (IBAD) promotes the columnar growth of carbon encapsulated metallic nano-columns at low deposition temperatures for Ar<sup>+</sup> ion energy ranges of 50-100 eV. Moreover, the momentum transfer results in a tilting of the columns relative to the film surface. The potential to grow complex matrix encapsulated metallic structures such as chevrons is demonstrated. Furthermore, a window of deposition conditions will be reported where the ion assistance leads to the formation of regular 3D nanopatterns with well-defined periodicity. The influence of such anisotropic film morphology on the optical properties is highlighted.

**Acknowledgements:** Funding by the European Union, ECEMP-Project D1, "Nanoskalige Funktionsschichten auf Kohlenstoffbasis", Projektnummer 13857 / 2379, is gratefully acknowledged.

**9:00am SE+NS-MoM3 Interface Phenomena in Nanostructured Thin Films and Coatings.** *D. Rafaja*, Freiberg University of Technology, Germany **INVITED**

The properties of nanostructured thin films and coatings are strongly influenced by the structure of internal interfaces. Thus, the understanding of the formation of the interfaces and the knowledge of the relationship between the microstructure and the materials properties are the first steps in designing nanostructured materials with tailored properties. This talk will focus on partially coherent interfaces between adjacent crystalline phases in nanostructured thin films and coatings, discussing the mechanisms of their formation, showing the capabilities of experimental methods for microstructure analysis to detect these interfaces and to describe their structure on the atomic scale, and recognizing the influence of the interfaces on the materials properties.

The interface phenomena and their impact on hardness and thermal stability of nanostructured thin films and coatings will be illustrated on physical vapor deposited transition metal nitrides containing aluminum and/or silicon, where the internal interfaces form as a consequence of the decomposition of metastable supersaturated solid solutions. It will be shown how the local fluctuations of the chemical composition arising during the deposition process and the local strain fields resulting from differences in the interatomic distances at partially coherent interfaces influence the decomposition process and the stability of the metastable phases.

The description and quantification of the interface phenomena on atomic scale would be impossible without a detailed microstructure analysis that is required to reveal the constitution of the nanostructured materials, to reproduce the structure of the internal interfaces and to assess the coherence of the interfaces. Hence, this talk will also recapitulate the recent developments in the microstructure analytics on the nanostructured thin films and coatings.

**9:40am SE+NS-MoM5 Mechanical Properties, Fracture Toughness, and Thermal Stability of CrN/AlN Superlattice and Multilayer Thin Films.** *M. Schlögl*, *B. Mayer*, *J. Paulitsch*, *J. Keckes*, *C. Kirchlechner*, *P.H. Mayrhofer*, Montanuniversität Leoben, Austria

Transition metal nitrides, such as CrN are highly attractive materials for a wide range of applications due to their outstanding properties like high hardness, excellent corrosion and oxidation resistance. Consequently, many research activities deal with their synthesis-structure-properties-relations. However, it has been reported that CrN/AlN superlattice coatings improve the mechanical properties compared to single CrN especially when keeping the AlN in its metastable cubic phase. Hence, we investigated the influence of the layer thickness of CrN on the stabilization of c-AlN and the critical layer thickness for AlN before transforming into the stable wurtzite phase. Furthermore, stress measurements and thermal stability were accomplished by the in-situ wafer curvature method during vacuum annealing to 700°C, differential scanning calorimetry to 1500°C and hardness measurements after annealing up to 1100°C.

The fracture toughness of the coatings is studied by means of in-situ scanning electron microscopy and transmission electron microscopy microbending and microcompression tests. The small test-specimens are prepared by focused ion beam milling of individual free-standing thin films. As generally monolithic coatings with their columnar structure provide low resistance against crack formation and propagation we perform our studies for CrN films, CrN/AlN multilayers and the CrN/AlN superlattice as mentioned above. Especially the multilayers and superlattices provide additional interfaces perpendicular to the major crack-propagation-direction. Adjusting the AlN layer-thicknesses to allow for cubic or wurtzite structure enables to study the influence of the extremely stress sensitive cubic-to-wurtzite AlN phase transformation on the crack propagation.

The microtests clearly demonstrate that the monolithic CrN as well as the CrN/AlN multilayer coating with the wurtzite AlN layers crack with the behavior and features for brittle fracture. Contrary, the CrN/AlN multilayer coatings composed of cubic stabilized AlN layers are able to provide resistance against fatal crack propagation. Hence, they allow for significantly higher loads during the microbending and microcompression tests. Detailed structural investigations, in-situ and after the tests, suggest that the cubic AlN layers, which are stabilized by coherency strains in the CrN/AlN multilayer coatings, phase transform with the connected nature expansion when experiencing additional strain fields and thereby hinder crack propagation.

**10:00am SE+NS-MoM6 High-temperature Nanoindentation of Hard Coatings.** *M. Rebelo de Figueiredo*, University of California Berkeley, *M. Tkadletz*, Materials Center Leoben, Austria, *M. Schlögl*, *R. Hollerweger*, *P.H. Mayrhofer*, *C. Mitterer*, Montanuniversität Leoben, Austria, *P. Hosemann*, University of California Berkeley

In the past decades, measurement techniques to probe the mechanical properties of hard coatings have been evolved dramatically and nowadays a wide variety of methods and devices are available. Within the field of evaluating the hardness of coating materials, nanoindentation has been established as a standard method utilizing the Oliver and Pharr approach. The measurements are commonly performed at room temperature. Industrial applications like metal cutting, however, demand resistance to wear also at temperature levels of up to 1000°C, which can easily be reached in the contact zone between a coated tool and the machined part. Therefore, knowledge about the mechanical properties of hard coatings at elevated temperatures is of vital importance. Nanoindentation devices allowing to go to temperatures as high as 750°C became available in recent years. While it appears simple to install heating devices in a nanoindenter, the minimization of the thermal drift, tip durability, and environmental control are a particular challenge to perform measurements at these temperatures. Therefore, significant efforts in monitoring all effects of a measurement performed at these conditions need to be spent in order to gain valid indentation data.

Within the present work, a series of different hard coatings were analyzed, utilizing nanoindentation experiments up to 750°C. The coatings evaluated cover selected samples representing the state-of-the-art employed in cutting operations like Al<sub>2</sub>O<sub>3</sub> and TiAlN as well as newly developed coating materials like TiAlTaN. Possibilities and experimental limitations of high-temperature nanoindentation are critically discussed. A sound knowledge of the dependence of hardness on microstructural changes occurring at elevated temperatures provides the basis for the further development of coating materials and design.

10:40am **SE+NS-MoM8 Improving the Phase Stability of Metastable Aluminum Oxide Thin Films**, *F. Nahif, H. Bolvardi, D. Music, S. Mráz, J.M. Schneider*, RWTH Aachen University, Germany

Charge state resolved ion energy distribution functions (IEDFs) of  $\text{Al}^+$ ,  $\text{Al}^{2+}$  and  $\text{Al}^{3+}$  were measured as a function of Ar

pressure in the range from  $5.7 \times 10^{-5}$  to 2.13 Pa (0.01 to 256 Pa cm). A close to monoenergetic beam of  $\text{Al}^+$  ions was obtained in an Ar/O<sub>2</sub> mixture at 128 Pa cm. Al<sub>2</sub>O<sub>3</sub> films are deposited employing this monoenergetic  $\text{Al}^+$  beam using a substrate bias potential to increase the ion energy. A critical  $\text{Al}^+$  ion energy of 40 eV for the formation of the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> 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 the well known surface diffusion the previously non considered diffusion in sub-surface regions is an important atomistic mechanism in the phase formation of Al<sub>2</sub>O<sub>3</sub>. Using density functional theory and cathodic arc deposition experiments the effect of Si and Y addition on the stability of  $\gamma$ - and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> has been investigated. Si additives clearly shift the relative stability towards the  $\gamma$ -phase which can be understood based on the electronic structure. As the additive concentration increases, strong silicon-oxygen bonds are formed giving rise to the observed stabilization of the  $\gamma$ -phase.

11:00am **SE+NS-MoM9 Thermal Stability of (Al<sub>x</sub>Cr<sub>1-x</sub>)<sub>2</sub>O<sub>3</sub> Solid Solution Coatings Grown by Cathodic Arc Evaporation**, *V. Edlmayr, M. Pohler*, University of Leoben, Austria, *I. Letofsky-Papst*, Graz University of Technology, Austria, *C. Mitterer*, University of Leoben, Austria

Corundum-type (Al<sub>x</sub>Cr<sub>1-x</sub>)<sub>2</sub>O<sub>3</sub> coatings were grown by reactive cathodic arc evaporation in an oxygen atmosphere using AlCr targets with an Al/Cr atomic ratio of 1. Since the (Al<sub>x</sub>Cr<sub>1-x</sub>)<sub>2</sub>O<sub>3</sub> solid solution shows a miscibility gap below 1300°C, where spinodal decomposition is predicted, the microstructural changes upon annealing were investigated by a combination of transmission electron microscopy, X-ray diffraction, Raman spectroscopy and differential scanning calorimetry. The as-deposited coating consists primarily of the corundum-type (Al<sub>x</sub>Cr<sub>1-x</sub>)<sub>2</sub>O<sub>3</sub> solid solution, with smaller fractions of cubic (Al<sub>x</sub>Cr<sub>1-x</sub>)<sub>2</sub>O<sub>3</sub>. An additional Al-rich amorphous phase and a Cr-rich crystalline phase stem from the droplets incorporated. The corundum-type (Al<sub>x</sub>Cr<sub>1-x</sub>)<sub>2</sub>O<sub>3</sub> was still present after vacuum annealing at 1050°C for 2 hours, whereas additional  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub> phases were formed due to decomposition of the cubic (Al<sub>x</sub>Cr<sub>1-x</sub>)<sub>2</sub>O<sub>3</sub> phase. Likewise, Cr and Cr<sub>2</sub>O<sub>3</sub> have been detected in the annealed coating, most probably originating from the partial oxidation of Cr-rich droplets. Upon crystallization of the amorphous phase fractions present,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> is formed, which partially transforms in  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. No evidence for decomposition of the corundum-type (Al<sub>x</sub>Cr<sub>1-x</sub>)<sub>2</sub>O<sub>3</sub> solid solution could be found within the temperature range up to 1400°C.

11:20am **SE+NS-MoM10 Protective Coatings Against Corrosion and Wear for 3D Components with Combined ALD and PVD Techniques**, *S. Ek*, Picosun, Finland

Corrosion-related problems have always been a major challenge in various industries because of the components' shortened lifetime. Huge efforts are being made to improve the current corrosion protection procedures and to develop new corrosion preventing techniques. The objective is to find more efficient, environmentally sustainable, and cost-effective solutions for advanced corrosion protection of materials. However, in some applications it is not only corrosion protection that is needed but also wear resistance is required.

Relatively thick PVD coatings are generally used in applications where wear resistance is required. However, achieving simultaneous corrosion protection with that kind of coatings is challenging because the coating doesn't grow conformally and uniformly enough on the nano/microscale details of the surface of the protected material. This is where ALD coatings are needed: they enable reliable, long-term corrosion resistance through dense, uniform and conformal layers and they block the possible cracks, pinholes and nano/microscale voids and irregularities of the PVD layer, thus improving and securing the performance of the PVD coatings. At the same time, ALD contributes to structural strengthening and better chemical stability.

The choice and composition of the ALD coatings for corrosion protection depend on the substrate material and the kind of environmental conditions to which the protected components are exposed. Especially, certain metal oxides or their laminates or mixtures deposited by ALD form efficient and functional corrosion protection layers. Optimization of the protective thin film thickness and composition has been performed during the last three years in the European Union 7<sup>th</sup> Framework Program collaborative project CORRAL ("Corrosion protection with perfect atomic layers" [CPFP213996-1]).

In the present work, high-quality coatings with less than 0.001 % porosity were achieved. The coatings were able to seal 100Cr6 steel substrates for over 800 h in neutral salt spray tests (NSS). The lifetime of 3D test components was increased by a factor of 3-10 depending on the substrate material.

# Monday Afternoon, October 29, 2012

**Advanced Surface Engineering**  
**Room: 22 - Session SE+NS-MoA**

**Nanostructured Thin Films and Coatings II:  
Multifunctional Properties**  
**Moderator:** E. Broitman, Linköping University, Sweden

**2:00pm SE+NS-MoA1 Layered Binary Metal Oxide Solid Lubricants for High Temperature Moving Assemblies, S. Aouadi, D. Stone, Southern Illinois University Carbondale, A. Martini, University of California Merced, C. Muratore, A.A. Voevodin, Air Force Research Laboratory**

**INVITED**

Oxides exhibit an unparalleled variety of physical properties that give them great promise for many applications in optics, magnetism, and electronics. Oxides that possess layered crystal structure inherently display anisotropic properties as a result of their non-symmetrical crystal structure. This flexibility in their structural skeleton offers a great opportunity to create new materials with designed functionality. This paper provides an overview of the current research developments in understanding how a class of layered binary metal oxides is effective at reducing friction at moderate and high temperatures. Oxides, known to be abrasive at low temperatures, are particularly desirable lubricious materials at high temperatures considering that most materials will oxidize in air under these conditions. Four different, non-exclusive, mechanisms are reported to cause their enhanced lubricity: (1) oxide softening due to the working temperatures between 0.4-0.7 of the absolute melting temperature ( $T_m$ ), (2) melting of the oxide by exceeding  $T_m$ , (3) the creation of a material with a lamellar crystal structure with weak interplanar bonds, and, (4) shearing due to dislocations or grain boundary sliding. We will focus on understanding the fundamental mechanisms that impart their advantageous material properties at high temperatures using computational (density functional theory and molecular dynamics simulations) and experimental tools (in situ Raman spectroscopy, X-Ray diffraction, scanning electron microscopy, and transmission electron microscopy). The frictional and wear properties of these materials, tested in various controlled environmental conditions, will be discussed in detail.

**2:40pm SE+NS-MoA3 Free-standing Nanoscale Gold Pyramidal Films with Milled Nanopores, J.A. Grant-Jacob, W.S. Brocklesby, T. Melvin, Optoelectronics Research Centre**

Thin films of micro and nanostructured metals are important for the construction of plasmonic devices and microelectromechanical systems (MEMS). The fabrication of individual metallic, pyramidal shells as well as ultra-smooth metal films with grooves, bumps, pyramids and holes has previously been demonstrated<sup>1,2</sup>, as has direct raster milling with 5 nm machining precision in 100 nm thick gold films<sup>3</sup>. Routine fabrication of micro and nanostructured thin films is desirable. In this work, the fabrication of arrays of nanoscale pyramidal structures in free-standing gold films is demonstrated, and single nanopores are milled into the nanostructures for DNA translocation.

Silicon Klarite® pyramidal micro-structured substrates are an effective tool for surface enhanced Raman scattering (SERS) experiments, owing to the strong field enhancement within the pyramids. Here, the substrates are used as moulds for creating pyramidal structured gold as free-standing thin films. The silicon substrates contain an array of pyramids etched into a 4 mm x 4 mm square region on the substrate's surface. These pyramids are 1.5  $\mu\text{m}$  x 1.5  $\mu\text{m}$  square and 1  $\mu\text{m}$  deep on a pitch of 2  $\mu\text{m}$ . An Edwards E306A Thermal Evaporator is used to coat silicon samples in a 50 nm layer of Teflon® and then a 100 nm layer of gold. Epoxy is then deposited on top of the gold layer using a pipette. Once the epoxy has cured, the epoxy together with the gold is mechanically lifted from the Teflon® coated substrate. The gold-coated epoxy is then placed over a micron-sized aperture and the epoxy dissolved away using acetone. Initial imaging is performed using a Carl Zeiss SMT, Inc., Evo® scanning electron microscope (SEM), while the subsequent imaging and milling of 50 nm holes through the free-standing gold is carried out using an Carl Zeiss SMT, Inc., Orion® Plus helium ion microscope (HIM). These films are suspended over micron-sized apertures for integration into platforms already proven for DNA translocation, and to optically interrogate the structures using Raman based techniques.

<sup>1</sup> Q. Xu, I. Tonks, M.J. Fuerstman, J.C. Love, and G.M. Whitesides, *Nano Letters* **4**, 2509-2511 (2004).

<sup>2</sup> P. Nagpal, N.C. Lindquist, S.-H. Oh, and D.J. Norris, *Science* (New York, N.Y.) **325**, 594-7 (2009).

<sup>3</sup> L. Scipioni, D.C. Ferranti, V.S. Smentkowski, and R. a. Potyrailo, *Journal of Vacuum Science & Technology B: Microelectronics and Nanometer Structures* **28**, C6P18 (2010).

**3:00pm SE+NS-MoA4 Synthesis of Superhydrophobic PTFE-like Thin Films by Self-Nanostructuring in a Hybrid Plasma Process, F. Henry, University of Mons, Belgium, F. Renaux, S. Coppée, Materia Nova Research Center, Belgium, R. Lazzaroni, University of Mons, Belgium, N. Vandecasteele, F. Reniers, ULB, Belgium, R. Snyders, University of Mons, Belgium**

Superhydrophobic Poly(tetrafluoro-ethylene) (PTFE) like thin films were grown using a plasma-based hybrid process consisting on sputtering a carbon target in a Ar/CF<sub>4</sub> atmosphere. The influence of the bias voltage applied to the substrate (VBias) as well as of the gas mixture composition (%CF<sub>4</sub>) on the chemical composition, the wettability and the morphology of the deposited thin films were evaluated.

The chemical composition measured by X-Ray photoelectron spectroscopy (XPS) reveals that the fluorine content is lower than in conventional PTFE (50 at.% maximum > 66%) and that it decreases when VBias increases (from 50 at.% for VBias = -100 V to 30 at.% for VBias = -200 V). This behaviour is associated with the preferential etching of the fluorine atoms during the plasma-assisted growth of the films. Consecutively to this etching, a self-nanostructuring enhanced by increasing VBias, is observed. As a consequence, the water contact angle (WCA) measurements range from 70° up to 150° depending on (i) the fluorine content and (ii) on the magnitude of the nanostructuring. In addition, for the films presenting the highest WCA angles, a small hysteresis between the advancing and receding WCA is observed (< 10°) allowing these films to fulfil completely the requirements of superhydrophobicity.

In order to get more understanding on the wettability mechanisms of these surfaces, the topology of the films has been evaluated by atomic force microscopy (AFM). The data reveal, for all films, a dense and regular structure composed by conic objects for which the dimensions increase with VBias. We were able to correlate the ratio of the average height (AvH) of the objects and the average distance (AvD) between them with the WCA. Theoretical evaluations of the WCA using the Wenzel and Cassie equations with, as inputs, the features of the deposited thin films surfaces measured by AFM suggest that the wetting regime is intermediate between these two ideal situations.

**3:40pm SE+NS-MoA6 Creation of Highly Functionalized Polymer-Metal Oxide Nanomaterials Using A Novel Rotating Drum Plasma Reactor, J.C. Shearer, E.R. Fisher, Colorado State University**

The use of nanoparticles in biological applications has grown rapidly in recent years. Understanding the surface chemistry and protein-nanoparticle interactions is critical in the fabrication of biomedical devices. Some nanoparticle surfaces are not compatible with specific applications, and thus must be modified to make them viable. Plasma processing of nanomaterials is an effective method for functionalization and encapsulation of nanoparticles. Our lab has designed a rotating drum inductively coupled plasma reactor that has afforded the ability to create specifically tailored nanoparticle surfaces. The rotating drum apparatus was utilized to encapsulate Fe<sub>2</sub>O<sub>3</sub> and Au nanoparticles with various polymer films. Allyl alcohol, allylamine, and acrylic acid plasmas were used to incorporate alcohol, amine, and carboxylic acid functionality to nanoparticle surfaces, respectively. Tailoring of film composition was achieved by lowering the duty cycle (d.c.) of the plasma to facilitate less fragmentation of the monomer. This resulted in the deposited films being more stoichiometrically similar to the parent monomer gas and thus having a high concentration of functional groups present within the film. For example, the alcohol functionality of plasma polymerized allyl alcohol films on Fe<sub>2</sub>O<sub>3</sub> nanoparticles can be substantially increased by lowering the d.c. of the plasma from 100 % to 10 %. Specifically, x-ray photoelectron spectroscopy elemental analysis shows that films deposited under low d.c. conditions increase O/C ratios from 0.17 to 0.35, which is comparable to that of the parent monomer (0.33). FTIR data reveal complementary results, where increases in OH functionalities are observed for low d.c. plasmas. Electron microscopy confirms there is no appreciable change in size and shape of the nanoparticles upon plasma treatment. The solubility and stability of the encapsulating films were analyzed to measure the longevity of the particles in biological systems. Highly functionalized films were also deposited onto supported nanoparticle substrates to investigate how plasma processing affects surface roughness, as this can affect cell adhesion. We have demonstrated that plasma processing can change the RMS roughness of supported nanoparticles by 0.2  $\mu\text{m}$ , thereby affording the ability to tailor the roughness of a surface for specific cell interactions. A variety of gas-phase and surface analysis data will be presented to show how plasma processing

can tailor the composition of deposited films of as a function of plasma parameters and gas-phase species. Understanding how these films are produced will undoubtedly advance the fabrication of novel biomedical devices.

**4:00pm SE+NS-MoA7 Field Emission Dynamic Investigation of the Polymer-MWCNT Composite Films Depending from Vacuum Conditions, E.O. Popov, A.G. Kolosko, M.V. Ershov, S.V. Filippov, A.F. Ioffe** Physico-Technical Institute, Russian Federation

It is obvious that research I-V characteristics remains the basic criterion of an estimation of field emission process. However the techniques, allowing to do exhaustive conclusions about the physical processes occurring on nano dimensional emission sites by macroscopical values of a current and voltage does not exist yet. Especially it is expressed at research of dynamics of field emission, the phenomena accompanying functioning flat multityps cold cathodes (emitters).

Attempts to observe other phenomena that can accompany emission processes, except for observation of I-V characteristics, are being made. There are the registration of radiation of the emitter and the anode, heating of electrodes, change of vacuum conditions, mass spectrometer researches. Application of computer processing during record I-V characteristics opens additional possibilities of knowledge of evolution and emitter work, allows to approve models of physical processes is directly during emission experiment.

In our work was developed the technique of multichannel record and *in situ* data processing about evolution of field emitters. On-line processing of signals is performed on the basis of own program written on Labview 10. The technique includes multichannel system of gathering of signals of a current and voltage, record of vacuum values and temperature. As a part of mass spectrometer installation the given system collects the data about kinetics allocation of the volatile products accompanying emission process. Data for representation in a kind convenient for the analysis is in addition processed: beta values of field increasing, active resistance of inter-electrode gap, visualization of height of emitters and the estimation of a total emitting surface and number of the emission centers is made.

Some characteristic areas in dependence SK [1,2] which are treated as desorption gases from surface MWNT, area of growth of number of sites without change of the geometrical sizes (almost vertical growth SK), area of smooth change of geometry of the emitter (increase in intensity of a field and increase in the area of the emitter - intercept increasing) have been found out.

[1] M. Kawasaki, Z. He, Y. Gotoh, H. Tsuji, J. Ishikawa, *J. Vac. Sci. Technol. B* 28, (2010) C2A77.[2] E.O.Popov, M.V. Ershov, *IEEE*, 24<sup>th</sup> INVC, Wuppertal, (2011) 158.

**4:20pm SE+NS-MoA8 Cost Efficiency Trade Off in Nanostructured Thermoelectric Energy Conversion Systems, A. Shakouri, K. Yazawa, Birek Nanotechnology Center, Purdue University INVITED**

Energy consumption in our society is increasing rapidly. A significant fraction of the energy is lost in the form of heat. In this talk we introduce thermoelectric devices that allow direct conversion of heat into electricity. Some new physical concepts and nanostructures make it possible to modify the trade-offs between the bulk electrothermal material properties through the changes in the density of states, scattering rates and interface effects on the electron and phonon transport. We will review recent experimental and theoretical results on nanostructured materials as well as solid-state thermionic power generation devices. Theory and experiment are compared for several III-V and nitride nanocomposites and multilayers. Potential to increase the energy conversion efficiency and bring the cost down to \$0.1-0.2/W will be discussed.

**5:00pm SE+NS-MoA10 The Effects of Interfacial Bond Stiffness on Heat Transport: An Experimental Study Using Self-Assembled Monolayers, M.D. Losego, M. Grady, N.R. Sottos, D.G. Cahill, P.V. Braun,** University of Illinois at Urbana Champaign

Compared with our ability to precisely control the flow of electrons or light within a material, our capacity to design the flow of heat, particularly at the nano-scale, is rather rudimentary. For example, billions of microscopic transistors with coordinated electronic transport are routinely fabricated for computers, cell phones, and iPods. In contrast, thermal management is largely limited to macroscopic solutions (e.g. fans, insulation). Examples of confining and controlling heat with precision at micro- or nanometer length scales are relatively rare

Crucial to nanoscale thermal management is an understanding of interfacial heat transport. Interfaces between two materials act as a barrier to heat flow. For nano-scale systems, interfacial heat conduction and not just bulk thermal conductivity is important and possibly dominant in controlling heat transfer. However, thermal transport across interfaces is still not well

understood. Historically, differences in bulk acoustic properties and/or phonon densities of states have been used to explain the interfacial thermal boundary resistance. However, more recently, atomic level structural features, such as interfacial roughness and interfacial bonding, have been proposed as contributors to the thermal boundary resistance.

This talk will describe experimental work that attempts to validate recent molecular dynamics (MD) simulations suggesting that interfacial thermal conductance can be strongly modulated by adjusting the strength of interfacial bonds. Our experimental system consists of self-assembled monolayers (SAMs) on SiO<sub>2</sub> substrates having either methyl or mercapto terminations. Gold films are transfer printed onto these surfaces forming either a van der Waals or covalent bond respectively. The interfacial thermal conductance across the Au/SAM interface is measured via time-domain thermoreflectance (TDTR) and found to increase by nearly 2x when the interface is switched between a van der Waals interaction and a covalent bond. The interfacial bond stiffness is independently measured using picosecond acoustics. Together these experiments represent the first clear demonstration of how changing the stiffness of a single atomic-scale interfacial bonding layer affects thermal conductance.

To further elucidate the mechanism for this change in interfacial thermal conductance, we will present temperature dependent thermal conductance measurements. This data reveals that high frequency phonon modes cannot traverse interfaces with lower stiffness. Finally, we will show proof-of-concept experimental results that outline a scheme for designing materials with specified values of interfacial thermal conductance.

**5:20pm SE+NS-MoA11 Growth, Nanostructure Formation, and Physical Properties of Single-Phase, Epitaxial, SrTiO<sub>3</sub>-TiO<sub>2</sub> Nanocomposites: A Topological Insulator Approach to High-T Thermoelectrics, B.M. Howe,** Air Force Research Laboratory, *E. Thomas,* University of Dayton Research Institute, *D. Dudis,* Air Force Research Laboratory

Here, we present a novel approach towards creating efficient thermoelectric materials for energy conversion and thermal management under high-temperature and oxidizing environments. Several transition-metal oxide systems have recently been investigated, however most studies involve the doping of single-phase compounds to enhance electrical conductivity; while very few address decreasing thermal conductivity (in the same direction as electron transport). Thus, we present an investigation into the growth, nanostructure formation, and physical properties of epitaxial, immiscible SrTiO<sub>3</sub>-TiO<sub>2</sub> nanocomposites. Sr<sub>(1-x)</sub>Ti<sub>(1+x)</sub>O<sub>(3+2x)</sub> layers with 0 ≤ x ≤ 0.67 were grown on SrTiO<sub>3</sub> (001) substrates at 700°C in 1 × 10<sup>-6</sup> Torr O<sub>2</sub> by high-vacuum pulsed laser deposition using a KrF excimer laser (λ = 248nm) operating at 10 Hz pulse rate and 1.7 J/cm<sup>2</sup> fluence. HRXRD and XTEM results show that perovskite-structure layers grow epitaxially with a cube-on-cube orientational relationship to the substrate. The lattice parameter increases linearly while crystalline quality decreases from x=0 to x=0.67. We find a remarkably broad metastable single-phase field given the immiscible nature and crystal structure mismatch of the two alloy components. Alloying SrTiO<sub>3</sub> with TiO<sub>2</sub> leads to the formation of nanostructured compositional modulations due to the onset of spinodal decomposition, resulting in increased in electrical conductivities (due to the formation of 2D electron gas layers at the SrTiO<sub>3</sub>-TiO<sub>2</sub> interfaces), decreased thermal conductivities, and enhanced thermoelectric figure of merit, large enough to compete with current state-of-the-art high-temperature thermoelectric materials.

# Tuesday Morning, October 30, 2012

**Advanced Surface Engineering**  
**Room: 22 - Session SE+PS-TuM**

## **Pulsed Plasmas in Surface Engineering**

**Moderator:** C. Mitterer, University of Leoben, Austria

**8:00am SE+PS-TuM1 Strong Localization of Ionization in High Power Impulse Magnetron Sputtering in Reactive and Non-Reactive Gas Environments, A. Anders, Lawrence Berkeley National Laboratory**  
**INVITED**

Self-organized structures of plasmas in high power impulse magnetron sputtering (HiPIMS) have recently been observed by several groups. The structures move along the racetrack in the ExB drift direction but only with about 10% of the electron drift velocity (E and B are the electric and magnetic field vectors). The bright structures are zones of concentrated ionization: they can be related to the amplification mechanism of self-sputtering and gas recycling. The ionization zones can readily be observed with fast cameras providing time resolution of 1 microsecond or better. The situation will be illustrated with images taken with a gated intensified frame image camera (Princeton Instruments) and with an intensified streak camera (Hamamatsu). Both end-on and side-on views to the magnetron are utilized. The side-on view reveals that each dense ionization zone is associated with an electron beam leaving the target region. Such beam maintains the quasi-neutrality of the plasma as ions are "evacuated" towards the target. The motion of the ionization zones is not a motion of plasma but a displacement of the region of greatest ionization. Its speed is mainly limited by the inertia of ions. The mechanism will be discussed and supported with images taken for various targets in noble and reactive gas atmospheres. Finally, the consequences of the localization of ionization for film formation will be considered in the greater context of energetic condensation.

**8:40am SE+PS-TuM3 The Magnetic Field Configuration's Effect on Plasma Parameters in High-Power Pulsed Magnetron Sputtering, H. Yu, L. Meng, P. Raman, T.S. Cho, D.N. Ruzic, University of Illinois at Urbana Champaign**

Magnetic field design is crucial in DC magnetron sputtering operation, but has been largely overlooked in high power pulsed magnetron sputtering (HPPMS). In a HPPMS discharge, plasma disperses after each short pulse, unlike in the DC operation which requires a good magnetic confinement to maintain the plasma. It is thus interesting to study the effect of magnetic field configuration on HPPMS discharge for further optimization. A special magnet pack was fabricated with the magnet positions fully adjustable. Different designs were made, with the corresponding magnetic field calculated by Comsol. For example, the magnetic field (B) strength in the racetrack was varied, as 200, 500, and 800 Gauss. Different racetrack shapes were used, such as ring-like and bean-like. Designs were also made to have incomplete racetrack, and weak racetrack in which piles of magnets were placed evenly across the whole pack and polarities of adjacent piles were opposite. These magnetic configurations were then tested in a large magnetron system with a 36 cm target using a conventional HPPMS plasma generator. The I-V discharge characteristics were measured. A time-resolved triple Langmuir probe was employed to study the temporal evolution of electron temperature ( $T_e$ ) and density ( $n_e$ ) across the substrate. Ionization fractions of sputtered metal were also measured using quartz crystal microbalance combined with electrostatic filters. The results showed that higher B field strength and longer racetrack produced higher pulse current. The 500 Gauss configuration however had higher  $n_e$  in the pulse than 800 Gauss did, likely because it allowed easier plasma diffusion. In all the designs with a racetrack, the distribution of  $n_e$  on the substrate was non-uniform that  $n_e$  was typically about 10 times higher right below the racetrack than at the center. The weak racetrack configuration was found to work and showed certain superiority over the normal DC magnet design. The plasma was generated from almost the entire target surface indicating an improvement in target utilization without the need for rotation. The discharge current was comparable with the racetrack designs. Furthermore, the plasma density distribution over the substrate was very uniform.

**9:00am SE+PS-TuM4 Plasma Generation and Transport in High-Power Pulsed Magnetron Sputtering, L. Meng, H. Yu, T.S. Cho, D.N. Ruzic, University of Illinois at Urbana Champaign**

High power pulsed magnetron sputtering (HPPMS) processes, including its potential application in interconnect metallization during microfabrication, require a precise control of fluxes and energies of various plasma species. A more fundamental understanding of the pulsed discharge mechanisms and the underlying physics thus becomes necessary. In a 36 cm planar

magnetron system, a triple Langmuir probe was used to study the time-resolved behaviors of the HPPMS plasma under various discharge and pulsing parameters, as well as at different positions extending from the target surface. The pulsed plasma was shown to be established through multiple stages. And the 3-dimensional probe characterization depicted a scenario of plasma expansion from the plasma-confined racetrack, producing high density peaks up to  $10^{19} \text{ m}^{-3}$  into the pulse-off period. The delay time of these peaks from the pulse-off edge varied from several to several hundred  $\mu\text{s}$  with different probe positions, and was found to depend on the plasma density in the racetrack which affects the diffusion constant, and the temporal location of the peak plasma density in the racetrack as well. In addition to the probe measurements in the vicinity of the racetrack, a special setup with quartz crystal microbalance and current collecting plate behind orifices drilled in the target was designed. Ion fluxes to the cathode were directly measured, while the metal ion and argon ion fluxes were distinguished time-averagely. The self-sputtering theory of HPPMS is supported by a higher metal ion fraction measured at a higher pulse peak current. Based on the above experiments, a 1-dimensional time-dependent HPPMS discharge model was developed incorporating the surface reactions, ionization process in the plasma, and plasma diffusion. It was able to describe the essential processes of plasma buildup and dispersion, and to predict some important plasma properties such as density and ionization fraction from the basic inputs of magnetic field, discharge and pulsing parameters, etc.

**9:20am SE+PS-TuM5 Metallic Film Modification through the Use of Non-standard HiPIMS Waveforms, P.M. Barker, E. Lewin, J. Patscheider, EMPA, Switzerland**

High power impulse magnetron sputtering, HiPIMS, has been the source of significant scientific interest in recent years. HiPIMS consists of a high voltage / high current pulse, followed by a long off-period resulting in low duty cycles. In the present study additional control parameters are explored by using non-standard HiPIMS waveforms, consisting of pulse sequences. These pulse sequences consist of a number of micro-pulses, which can be varied in length. In a further novel approach to HiPIMS, the pulses were also applied in a bi-polar manner, with a positive voltage supplied to the same target between negative voltage pulses. Films have been grown using varied pulse sequences, in both uni- and bi-polar mode, and compared to materials grown both by traditional, single pulse, HiPIMS and dcMS. The deposition of Ti metal was chosen as a model system, and the attained coatings were analysed using X-ray diffraction, XRD, scanning electron microscopy, SEM, and X-ray photoelectron spectroscopy, XPS. An increased deposition rate, relative to a comparable standard HiPIMS pulse, was observed. The coating microstructures show increased smoothening of the coating surface and shallower surface oxidation for samples deposited using micro-pulsed HiPIMS.

**10:40am SE+PS-TuM9 Reactive Modulated Pulse Power Magnetron Sputtering of Molybdenum Oxides: Optical Behavior as a Function of Process Parameters, N.R. Murphy, Air Force Research Laboratory, L. Sun, General Dynamics Information Technology, J.T. Grant, University of Dayton Research Institute, J.G. Jones, R. Jakubiak, Air Force Research Laboratory**

Molybdenum oxide, a material prized for its ability to facilitate thermochromism and electrochromism, has displayed considerable sensitivity to oxygen concentrations present during reactive DC magnetron sputtering. Typical depositions performed using continuous reactive DC magnetron sputtering have demonstrated low deposition rates and limited control over stoichiometry as a result of oxygen induced target poisoning. In the following study, molybdenum oxide films were deposited using reactive modulated pulse power magnetron sputtering (MPPMS) using a 99.999% pure molybdenum sputtering target within an argon-oxygen atmosphere. At a pressure of 10 mTorr, the oxygen concentration was varied between 1 and 20%. The resulting films were characterized by way of in-situ spectroscopic ellipsometry, x-ray photoelectron spectroscopy, x-ray diffraction and UV-visible spectroscopy. The as-deposited films were determined to be amorphous by way of x-ray diffraction analysis and were analyzed without any prior heat treatment. *In-situ* spectroscopic ellipsometry was conducted throughout the deposition process, monitoring real time changes in the refractive index, extinction coefficient and thickness of the film.

11:00am SE+PS-TuM10 Cathodic Arc Plasma of AlCr Composite Cathodes in Inert and Reactive Atmospheres, R. Franz, J. Wallig, Lawrence Berkeley National Laboratory, P. Polcik, PLANSEE Composite Materials GmbH, Germany, A. Anders, Lawrence Berkeley National Laboratory

In the past, the distributions of ion charge states of vacuum arcs have been studied in great detail under various conditions, including their dependence on arc current level, strength of a magnetic field (if present), pressure and kind of background gases, and the distance from the plasma-producing cathode spots. Most of the work was done using pure elementary cathodes since the presence of two or more elements in the cathodes would most likely further complicate the situation when studying the physics of cathodic vacuum arcs. However, in many practical applications ternary or quaternary thin films are used. For their synthesis it is common to employ composite cathodes consisting of the elements of interest.

In the field of hard and wear-resistant coatings, thin films based on the system aluminium and chromium represent the state of the art. With the addition of nitrogen and/or oxygen ceramic coatings covering a wide compositional range can be synthesised. In the present study, a time-of-flight spectrometer was used to investigate the arc plasma composition in terms of elemental and ion charge state composition when using  $Al_xCr_{1-x}$  ( $0 \leq x \leq 1$ ) composite cathodes in different gaseous environments, i.e. in vacuum as well as argon, nitrogen and oxygen atmosphere. The observed ion distributions were interpreted in the established framework of plasma generation at cathode spots and ion-gas interactions.

# Tuesday Afternoon, October 30, 2012

**Advanced Surface Engineering**  
**Room: 22 - Session SE+PS-TuA**

## Atmospheric Pressure Plasmas

**Moderator:** H. Barankova, Uppsala University, Sweden,  
P.H. Mayrhofer, Montanuniversität Leoben, Austria

2:00pm **SE+PS-TuA1 Plasma Medicine: The Journey of a New Field of Research, from Killing of Bacteria to Killing of Cancer Cells.** *M. Laroussi*, Old Dominion University **INVITED**

Research on the biomedical applications of low temperature plasmas started with few limited experiments mainly concerned with the ability of plasma to kill harmful microorganisms, especially bacteria as it relates to sterilization of abiotic and/or biotic surfaces (such as tissues). Low temperature plasmas produce a potent cocktail of highly reactive chemical species including reactive oxygen species (ROS) such as O, O<sub>2</sub>, and OH and reactive nitrogen species (RNS) such as NO and NO<sub>2</sub>. These species are known to exhibit strong oxidative properties and can trigger signaling pathways in biological cells. For example oxidation of the lipids and proteins that constitute the membrane of biological cells leads to the loss of their functions. In such environment bacterial cells were found to die in minutes or even seconds, depending on the strain. Plasmas were also found to be an effective method to control the proliferation of biofilms. Biofilms are very resistant to chemicals found in detergents and even to antibiotics. Therefore, if not controlled, biofilms (including dental plaque, for example) could represent serious health hazards.

Experiments on eukaryotic cells demonstrated that under some conditions, low temperature plasmas appear to cause little damage to living animal and plant tissues. For example, skin fibroblast cells are found to remain viable under plasma conditions that can be lethal to bacterial cells. The proliferation of fibroblasts is an important step in the wound healing process. The ability of plasma to kill bacteria and to accelerate the proliferation of specific tissue cells opened up the possibility to use plasma for the healing of chronic wounds such as diabetic ulcers. Tens of thousands of amputations occur every year in the US alone because of the inability of present medical methods to heal chronic wounds.

Low temperature plasmas have been found to be able to trigger apoptosis in cancer cells. Apoptosis is a natural process of "programmed" cell death. Cancerous cells lose the ability to initiate such a killing process. However, mediated through its specific chemical species, plasmas can trigger the signaling pathway that can start the cascade of events that result in apoptosis. This unique plasma capability opened up the possibility to use plasma for cancer treatment.

Low temperature plasmas therefore constitute a new transformational approach to healthcare referred to as Plasma Medicine [1]. In this paper background work as well as new results both in fundamental understanding and applications will be discussed.

### References

[1] M. Laroussi, "Low Temperature Plasmas for Medicine?", *IEEE Trans. Plasma Sci.* **37**, 714 (2009).

2:40pm **SE+PS-TuA3 VHF Atmospheric Glow Discharge: Electrical and Optical Characterization for Multiple Gases.** *B. Byrns, A. Lindsay, S. Shannon, A. McWilliams, S. Hudak, J. Cuomo*, North Carolina State University

Atmospheric plasmas have the potential to increase the efficiency of many processes involving interactions between materials and plasma due to the increased reactive species densities in the plasma. One challenge in the integration of these sources into high volume applications is the difficulty of producing large area, high density atmospheric plasmas without reaching thermal equilibrium or relying on the formation of arcs; a secondary challenge is the formation of these discharges without helium or other rare gas species that are typically used to sustain atmospheric glows. In this work a large area atmospheric pressure glow discharge operating at 162MHz has been created utilizing a VHF ballasting effect [1]. An electrical model paired with a simple global plasma model is used to characterize the electrical properties of the plasma. Several different feed gases including air, CO<sub>2</sub>, nitrogen, and argon are used to validate the model and study the production of reactive species in the plasma volume; both of these endeavors also enable intelligent process setpoint design to achieve the necessary operating conditions for various gases. These measurements are made using various electrical and optical diagnostics including OES, B-loop probe measurements, and in-line RF metrology. The effects of increasing the pressure, through the use of nozzles, are examined and used

to further refine and validate the system model. This greater understanding of the plasma allows for the potential to increase the size of the plasma, allowing for an increase in the number of reactive species and thus an increase in the efficiency for the treatment of surfaces. Currently the plasma is being studied for use in the removal of HDPE from surfaces as well as for the treatment of water. Preliminary results for both of these applications will be presented.

[1] Brandon Byrns et al 2012 J. Phys. D: Appl. Phys. 45 195204

\* Work supported by the State of North Carolina, SERDP contract 1762, and by a generous gift donation from Advanced Energy Incorporated, Verity Instruments, and Bird Technologies.

3:00pm **SE+PS-TuA4 Atmospheric Pressure Glow Discharge for Point-of-Use Water Treatment.** *A. Lindsay, B. Byrns, S. Shannon, D. Knappe*, North Carolina State University

Treatment of biological and chemical contaminants is an area of growing global interest where atmospheric pressure plasmas can make a significant contribution. Atmospheric plasmas have demonstrated the potential to reform aqueous chemistry<sup>1</sup> and mitigate water contamination<sup>2</sup>. One of the key challenges is scaling of these systems for volume processing. A large volume VHF coaxial plasma source has been developed that enables scale up of these systems under ambient air conditions, addressing volume processing and operating cost due to the absence of a noble gas carrier to sustain a volume glow.<sup>3</sup> The 162 MHz atmospheric glow discharge presented here offers several features uniquely applicable for disinfection. Because of ballasting effects, attributable to the very high drive frequency, the electric discharge is maintained at a steady glow, allowing formation of critical non-equilibrium chemistry. High densities,  $n_e = 10^{11}$ - $10^{12}$ , have been recorded. The atmospheric nature of the device permits straightforward and efficient treatment of material samples. Using air as a process gas, [H] concentrations in 150 milliliter tap water samples have been shown to drop five orders of magnitude after five minutes of discharge exposure. Recent literature has demonstrated that increasing acidity is strongly correlated with a solution's ability to deactivate microbial contaminants.<sup>1</sup> The work presented here will explore the impact of treatment gas, system configuration, and power density on water treatment including disinfection and PFC abatement. An array of plasma diagnostics including optical emission spectroscopy and electrical measurement of plasma discharge condition are combined with post-process water chemistry analysis including Quanti-Tray analysis of coliform and E.coli bacteria, gas chromatography, and mass spectrometry. Continued development of volume processing atmospheric plasma disinfection technology offers promise for point-of-use treatments in developing areas of the world, potentially supplementing or replacing supply-dependent chemical and weather-dependent solar disinfection methods.

1. Traylor (2011) J. Phys. D: Appl. Phys. 44 (2011) 472001

2. Takeuchi (2011) IEEE Trans. On Plasma Sci. 39(12) 3358-3363

3. Byrns (2012) J. Phys. D: Appl. Phys. 45 (2012) 195204

\* Work supported by generous gift donations from Bird Technologies, Advanced Energy, and Verity Instruments

4:00pm **SE+PS-TuA7 Cold Atmospheric Plasma in Liquids.** *H. Barankova, L. Bardos*, Uppsala University, Sweden

Atmospheric pressure plasmas and their applications, especially those based on non-thermal processes, have been extensively studied in the last decade, with focus on surface treatment, coatings and gas conversion. Individual applications depend on the current status of development in atmospheric pressure plasma sources. The plasma source based on the Fused Hollow Cathode (FHC) geometry was developed for generation of plasma in liquids. Effect of various generation regimes on the performance of plasma and on plasma distribution in water is studied without and with different auxiliary gases. The paper also discusses importance of the plasma source/reactor design for control of plasma chemical kinetics and comments on advantages and limitations of atmospheric plasma.

4:20pm **SE+PS-TuA8 Characterization of Amorphous and Microcrystalline Si Films Grown in Atmospheric-Pressure Very High-Frequency Plasma.** *H. Kakiuchi, H. Ohmi, T. Yamada, A. Hirano, T. Tsushima, K. Yasutake*, Osaka University, Japan

Hydrogenated amorphous silicon (*a*-Si) and microcrystalline silicon (*μ*c-Si) prepared at low temperatures are promising thin film materials for use in large-area electronic devices. The goal of our study is to develop a highly efficient deposition process of good-quality *a*-Si and *μ*c-Si films on polymer substrates using an atmospheric-pressure (AP) plasma technology in which

stable reactive plasma excited by a 150-MHz very high-frequency (VHF) power under AP is effectively used.

The experiments were conducted in an AP plasma CVD system that had a parallel-plate-type electrode ( $2 \times 8 \text{ cm}^2$ ), whose surface was coated by alumina of  $\sim 0.1 \text{ mm}$  thickness. By supplying a VHF power through an impedance matching unit, AP  $\text{He}/\text{H}_2/\text{SiH}_4$  plasma was stably confined in the narrow gap region ( $0.3\text{--}0.7 \text{ mm}$ ) between the electrode and a substrate. Under a constant process pressure of  $1 \times 10^5 \text{ Pa}$ , VHF power density ( $P_{\text{VHF}}$ ),  $\text{H}_2$  and  $\text{SiH}_4$  flow rates, plasma gap and substrate heating temperature ( $T_{\text{sub}}$ ) were varied as principal parameters. Si dusty particles formed by gas-phase condensation in the outside of the plasma region were completely removed by sucking the gas flow before their adhering to the substrate surface.

By examining the influence of gas residence time in the plasma on the film growth behavior, it was shown that the source  $\text{SiH}_4$  gas was immediately decomposed after being introduced into the plasma region and contributed to the film growth. Under the condition of  $P_{\text{VHF}} = 14 \text{ W/cm}^2$ ,  $\text{H}_2$  and  $\text{SiH}_4$  flow rates of 500 and 50 SCCM, respectively ( $\text{H}_2/\text{SiH}_4 = 10$ ), and  $T_{\text{sub}} = 220 \text{ }^\circ\text{C}$ , the film started to crystallize in only 0.3 msec. Both increasing  $P_{\text{VHF}}$  and  $\text{H}_2/\text{SiH}_4$  ratio caused the decrease in gas residence time necessary for the phase transition of the resultant Si films. On the other hand, an excessively long gas residence time ( $> 1 \text{ msec}$ ) led to the formation of highly crystallized  $\mu\text{c-Si}$  films even if  $\text{H}_2$  was not added to the process gas mixture. However, such  $\mu\text{c-Si}$  films showed poor electrical properties, which resulted from the sparse film structure without enough passivation of the grain boundaries with amorphous Si tissues. These suggest that the precise control of gas residence time is primarily important for the formation of good-quality *a-Si* and  $\mu\text{c-Si}$  films using AP-VHF plasma, together with the optimization of  $P_{\text{VHF}}$  and  $\text{H}_2/\text{SiH}_4$  ratio.

The *a-Si* and  $\mu\text{c-Si}$  films deposited with high rates ( $> 10 \text{ nm/s}$ ) in AP  $\text{He}/\text{H}_2/\text{SiH}_4$  plasma were used as the channel layers of bottom-gate thin film transistors (TFTs). The performance of the TFTs will be presented in the conference.

**4:40pm SE+PS-TuA9 Atmospheric Plasma Polymerization of Esters: Tuning the Coating Chemistry by Tuning the Precursor Chemistry.** *B. Nisol, A. Batan, Université Libre de Bruxelles, Belgium, A. Kakaroglou, M. Wadkar, G. Scheltjens, G. Van Assche, B. Van Mele, I. De Graeve, H. Terryn, Vrije Universiteit Brussel, Belgium, F. Reniers, Université Libre de Bruxelles, Belgium*

The influence of the chemical environment of an ester function on the plasma polymerization process and on the chemical structure of the deposited coating is investigated, and the consequences on the coatings properties (barrier and adhesion) are discussed. Allyl methacrylate (AMA), n-propyl methacrylate (nPMA) and propyl isobutyrate (PIB) containing respectively two, one and no double bonds were injected in a home made dielectric barrier discharge reactor. Argon was used as the main plasma gas, and the power of the discharge was varied from 30 to 80 W. The thickness of the deposited coating was determined by visible spectroscopic ellipsometry and allowed to calculate the deposition rate. The surface chemistry was investigated by X-ray photoelectron spectroscopy (XPS) and the bulk structure was analyzed by reflection – absorption infrared spectrometry (IRRAS). Differential scanning calorimetry was used to probe the remaining unreacted groups in the coating. The results evidence a great change in the polymerization rate that depends on the presence of the double bonds. Moreover, the concentration of ester groups at the surface of the coatings also depends on the surrounding double bonds present in the precursor. Indeed, whereas the relative amount of ester groups in poly-AMA remains stable when increasing the plasma power, it drops drastically for poly-PIB. A stabilization of the ester groups by the double bonds is suggested.

Acknowledgements: this work is part of the GREENCOAT project, financed by the Brussels Region, and by the IAP project “physical chemistry of plasma surface interactions”, funded by the Federal Government, Belgium.



# Tuesday Afternoon Poster Sessions

## Advanced Surface Engineering Room: Central Hall - Session SE-TuP

### Advanced Surface Engineering Poster Session

**SE-TuP1 Analysis of the Physical Damage during HBr/O<sub>2</sub>/Ar Gate Etching using Various Pulsed Plasmas, K.Y. Jeon, J.Y. Lee, G.J. Min, Samsung Electronics Co. Ltd., Republic of Korea**

Recent device has been rapidly scaled. The plasma oxidation and lattice damage by energetic ions cause the silicon oxidation in the channel and source/drain regions of the transistors. In addition, they generate the defects such as the Si/SiO<sub>2</sub> interface trap sites, contaminations, Si bond breaking and interstitial atoms. Those damaged regions by energetic ions can no longer be neglected. The continuous wave plasma is widely used in the conventional etch process, but it has some limitations to control the ion energy. It is difficult to reduce the damage layer in the atomic scaled device. This various plasma conditions in Gate etch process affect the physical damage on the substrate Si lattice and the gate oxide. In this work, the Si damage has been compared after etching by various plasma generation methods. Si etches has been performed in ICP chamber by using continuous wave HBr/O<sub>2</sub>/Ar plasmas, bias pulsed HBr/O<sub>2</sub>/Ar plasmas, synchronous pulsed HBr/O<sub>2</sub>/Ar plasmas, and especially DC pulsed plasma. Ellipsometry and TEM were used to analyze the Si lattice damage. Plus some electrical tests such as time zero dielectric breakdown (TZDB), charge pumping current, C-V measurement respectively. As a result, the pulsed plasma etching method is promising alternatives in respect of the physical Si damage, including the charge build-up and etch uniformity, and the mask selectivity

**SE-TuP2 Deposition of Hard SiOC(-H) Films by Atmospheric Pressure Plasma Enhanced CVD Method, M. Noborisaka, R. Horikoshi, A. Shirakura, T. Suzuki, Keio University, Japan**

Atmospheric pressure-plasma enhanced CVD method is a cost-effective process which has been widely developed because we do not have to vacuum during the deposition of thin films. In this study, SiOC(-H) films were synthesized by atmospheric pressure-plasma enhanced CVD method from tetramethoxysilane (TMOS) and O<sub>2</sub> diluted with N<sub>2</sub>. The deposited films were characterized by Fourier-transform infrared spectroscopy, nano-indentation technique, transmission electron microscopy and ellipsometry. The partially crystalline phase of silica was found in the deposited films. The nano-hardness of the films increased from 4.0 GPa to 6.9 GPa as the substrate temperature increased from 80°C to 300°C. The hardness slightly increased up to 4.5 GPa from 4.0 GPa by decreasing the TMOS flow rate at the substrate temperature of 80°C. The results suggested that increase in the relative ratio of Si-O-Si bonding in the network structure to Si-O-Si bonding in the cage structure led to increase in hardness.

**SE-TuP3 Thermal Transport at Metal-Carbon Interfaces, J.J. Gengler, Spectral Enegies LLC/Air Force Research Laboratory, S.V. Shenogin, UES Inc./Air Force Research Laboratory, A.A. Voevodin, A.K. Roy, C. Muratore, Air Force Research Laboratory**

Carbon nanotubes are appealing for diverse thermal management applications due to their high thermal conductivity (as high as 3,000 W m<sup>-1</sup> K<sup>-1</sup>) coupled with interesting mechanical properties (stiff and strong, but also exhibiting foam-like deformation in arrays). Unfortunately, CNT surfaces are generally non-reactive and demonstrate weak bonding to other materials, limiting thermal interfacial conductance. Functionalization with "linker molecules" has been shown to enhance interfacial conductance, but reduces thermal conductivity of the nanotubes themselves by altering carbon bond hybridization within the nanotube. Metal coatings provide a way to increase thermal interface conductance associated with carbon nanostructures, while maintaining their high thermal conductivity. We used Molecular Dynamics and vibrational modes analysis to study heat transfer through carbon nanotube - metal interfaces in highly nonequilibrium conditions (NEMD). The simulation results were compared to experimental measurements of conductance for metallized highly oriented pyrolytic graphite (HOPG) substrates. HOPG was selected as a practical 2-dimensional analog for nanotube sidewalls to facilitate experimentation by analysis of the two-color time domain thermoreflectance (TDTR) data from the samples. The TDTR analysis of the different metals on HOPG was made possible by employing an optical parametric oscillator on the probe beam which allows for tuning the probe beam wavelength to match absorption bands for each metal studied. Metal films were selected to identify effects of atomic mass (inversely proportional to Debye temperature), chemical interactions (i.e., interfacial carbide formation) and electron configuration. Measurements of chemically inert metals at the

carbon interface, including Al, Cu and Au demonstrated a strong dependence on Debye temperature, with conductance values differing by a factor of 3. The effects of interfacial carbide layers with varied areal densities on HOPG surfaces on thermal conductance were also examined, in addition to the presence of molecular interlayers. These results were applied to 3D assemblages of carbon nanotubes, such as dry spun CNT yarn, where metallization yielded significant enhancements of thermal conductivity in addition to increased tensile strength.

**SE-TuP4 Multilayer on a Staircase Substrate for Hard X-ray Gratings, C. Liu, Argonne National Laboratory, S. Lynch, E. Bennett, A. Gomella, National Institutes of Health, L. Assoufid, Argonne National Laboratory, H. Wen, National Institutes of Health**

Traditional hard x-ray transmission gratings are fabricated using lithography processes. They are constrained by the maximal attainable aspect ratio of the vertical walls, which limits the smallest attainable grating periods. Advanced X-ray phase contrast imaging techniques require large-area, high-density transmission gratings with smaller periods and higher aspect ratio to cover larger energy range for thicker samples. A new type of grating using multilayers grown on staircase substrates may meet this requirement. A thin Si substrate can be anisotropically etched to a staircase. With each stair surface supporting a multilayer as a micro grating and an X-ray beam shining through the layers at an oblique angle to the substrate and parallel to the layer surfaces, one has a large-area transmission grating with small grating periods. This method represents a new way to make gratings for hard x-rays. A [93 nm W / 93 nm Si] x 81 multilayer was grown on a 20 mm x 20 mm, 26°-blaze-angle Si staircase substrate using dc magnetron sputtering deposition. The multilayer thickness matches the stair height. A nitride layer was coated before multilayer deposition so that the Si substrate can be etched away to reduce x-ray absorption. Efforts have been made to grow the multilayer so that a major portion of layers is parallel to the stair surface with minimal amount on the sidewall. The sample was tilted during multilayer deposition to face the target. Deposition collimators were used to direct the coating flux. Uniform coatings were achieved using the profile-coating technique with specific masks made for each sputter gun. SEM images of sample cross sections and preliminary results of synchrotron x-ray diffraction and contact radiography at 25 keV are presented.

## Thin Film

Room: 11 - Session TF+SE+NS-WeM

### Glancing Angle Deposition (GLAD)

**Moderator:** T. Karabacak, University of Arkansas at Little Rock

8:00am **TF+SE+NS-WeM1 Tunable-Refractive-Index Materials – A New Class of Optical Thin-Film Materials with Applications in Solid-State Lighting and Solar Photovoltaics**, *E.F. Schubert*, Rensselaer Polytechnic Institute **INVITED**

Among the properties of optical materials, the refractive index is a most fundamental one. It determines many optical characteristics such as Fresnel reflection, Bragg reflection, Snell refraction, diffraction, and the phase and group velocity of light. The refractive index was introduced centuries ago by Isaac Newton who correlated the refractive index with the relative strength of refraction at the liquid-to-air interface. He realized that the degree of refraction is proportional to the mass density of the liquid, and therefore called the new optical quantity the “optical density.” Nowadays, this key quantity is known as the “refractive index.”

Among transparent dense materials, MgF<sub>2</sub> has the lowest refractive index:  $n = 1.39$ . Air and other gases have a refractive index very close to 1.0 but these materials are not viable for thin-film optoelectronic applications. Therefore, there are no dense materials with a refractive index in the range  $1.0 < n < 1.39$ . That is, this range has remained unavailable and unexplored.

Over the last few years, a new class of materials, tunable-refractive-index materials, has been developed. Optical thin-film materials, with a refractive index as low as 1.05, have been demonstrated. The tunable-index materials are based on nano-porous materials, such as, for example, nano-porous SiO<sub>2</sub>, nano-porous indium-tin oxide (ITO), and nano-porous TiO<sub>2</sub>. The porosity can be precisely controlled by using oblique-angle deposition, a technique in which the substrate is at non-normal angle with respect to the deposition source. Whereas dense films form for normal-incidence deposition, porous films with a self-organizing nano-structure form for oblique-angle deposition.

In this presentation, we will present examples of novel structures and devices that exploit the newly gained controllability of the refractive index. Devices to be discussed include distributed Bragg reflectors, light-emitting diodes, and solar cells, along with the performance enhancements enabled by the control of the refractive-index.

8:40am **TF+SE+NS-WeM3 Nanostructured Homogenous CdSe/TiO<sub>2</sub> Composite Visible Light Photoanodes Fabricated by Oblique Angle Codeposition**, *G.K. Larsen*, University of Georgia, *B.C. Fitzmorris*, University of California Santa Cruz, *C. Longo*, University of Campinas, Brazil, *J.Z. Zhang*, University of California Santa Cruz, *Y.-P. Zhao*, University of Georgia

A unique fabrication method, oblique angle codeposition, is used to deposit well-aligned nanorod arrays and thick films of homogeneously mixed CdSe/TiO<sub>2</sub> composites. The structural, optical, and photoelectrochemical properties of the films are investigated using a variety of experimental techniques. Ultrafast exciton dynamics are studied using femtosecond transient absorption (TA) spectroscopy. The CdSe/TiO<sub>2</sub> composites are compared with pure CdSe and TiO<sub>2</sub> films in order to determine their utility for photoelectrochemical (PEC) applications and to understand the mechanisms underlying the observed behaviors. The morphology of the deposited nanorods changes with film composition due to atomic collisions occurring in the vapor column, which can be modeled using a simplified Keller-Simmons expression. Furthermore, the two phase evaporation process of CdSe creates three different cluster types within the TiO<sub>2</sub> film structures: isolated Se, Se-deficient CdSe, and Se-rich CdSe. The prevalence of each cluster type is dependent on predicted film composition, and each is affected differently by open-air annealing. Isolated Se can be incorporated into the TiO<sub>2</sub> lattice, resulting in low energy rutile phase. Se-deficient CdSe clusters crystallize preferentially into cubic CdSe and are easily oxidized into CdO, while Se-rich CdSe clusters crystallize into hexagonal CdSe and are more stable. Furthermore, each of these cluster types interacts differently with the surrounding TiO<sub>2</sub> matrix, resulting in diverse optical and PEC behaviors. Interestingly, the stoichiometry of the CdSe domains is more important than overall CdSe content within the film in determining the structural, optical, and PEC properties of the films. The composite nanorod structure is a more efficient photoanode under visible light illumination than both the pure CdSe and TiO<sub>2</sub> nanorod array films. The higher efficiency of the composite films is attributed to efficient charge

transfer and separation in the homogeneously mixed composite. This is confirmed by the extremely high electron injection rate from CdSe into TiO<sub>2</sub> observed in the ultrafast TA studies.

9:00am **TF+SE+NS-WeM4 Control the Biaxial Texture of Vertically Aligned Nanostructures using Oblique Angle Sputtering Deposition with Substrate Flipping Rotation**, *G.-C. Wang*, *L. Chen*, *T.-M. Lu*, Rensselaer Polytechnic Institute

It is known that oblique angle deposition can be used to grow 3D nanostructures with a variety of morphology such as nanorods and nanospirals. For a selective set of materials, the technique can also produce a preferred crystal orientation, particularly a biaxial texture where the texture selection occurs in both the out-of-plane and in-plane directions. Most frequently biaxial texture created using the oblique angle deposition is in the form of slanted nanorods. It is desirable to produce a biaxial structure in the form of vertically aligned nanostructures which may be useful as a buffer layer to grow functional films on top of it. In this talk we will discuss several strategies to grow vertically aligned nanostructures including nanorods with a biaxial texture by dynamically varying the incident flux angle with respect to the surface normal during deposition. A particularly robust technique to achieve this goal is a flipping rotation scheme where the substrate is rotated continuously at a fixed speed around an axis lying within and parallel to the substrate [1]. This is very different from the conventional substrate rotation mode where the rotational axis is perpendicular to the substrate surface. In the flipping rotational mode the incident flux is perpendicular to the rotational axis, and the incident flux angle changes continuously. Mo vertical nanorod films, grown on amorphous substrates under three orders of magnitude different rotation speeds, different flipping directions, and different ending deposition angles, were characterized using scanning electron microscopy. For texture characterization of these Mo nanostructures we used our newly developed reflection high energy electron diffraction surface pole figure technique [2]. Despite very different morphologies, such as 'C'-shaped, 'S'-shaped, and vertically aligned nanorods grown by the flipping rotation, the same (110)[1-10] biaxial texture with an average out-of-plane dispersion of ~15° was observed. In contrast, we showed that only a fiber-textured Mo film was obtained by using the conventional rotation mode with a fixed incident flux angle. These biaxial Mo vertical nanorod films have potential applications as buffer layers to grow near-single crystal semiconductor films through nanoheteroepitaxy. These films may find important applications in energy conversion and light emitting devices.

Work was supported by the NSF DMR-1104786.

[1] L. Chen, T.-M. Lu, and G.-C. Wang, *Nanotechnology* 22, 505701 (2011).

[2] F. Tang, T. Parker, G.-C. Wang, and T.-M. Lu, *J. of Physics D: Applied Physics* 40, R427 (2007).

9:20am **TF+SE+NS-WeM5 Flux Engineering to Control In-Plane Crystal and Morphological Orientation**, *J.M. LaForge*, *G. Ingram*, *M.T. Tashchuk*, *M.J. Brett*, University of Alberta, Canada

Texture evolution during oblique angle deposition (OAD) and glancing angle deposition (GLAD) is of fundamental interest and important applications. As the distribution of size, shape and orientation of crystal grains impacts film electrical, optical, magnetic and mechanical properties control over texture evolution is important to optimizing performance. Morphology and crystal texture of OAD or GLAD nanostructured films is influenced by the orientation of the substrate relative to the collimated vapor flux, namely angle of incidence and the azimuthal angle, during deposition. Previous work has demonstrated control over the out-of-plane orientation through changes in the angle of incidence or azimuthal motion of substrate (e.g. stationary or continuous rotation).<sup>[1][2]</sup> However, work on the development of in-plane orientation has focused on material kinetic effects, such as deposition temperature, residual gas concentration, and deposition rate rather than substrate motion.<sup>[3][4]</sup>

We have deposited iron nanocolumns that have a tetrahedral apex and an out-of-plane texture (fiber texture) at a deposition angle of 88° under continuous substrate rotation. It is possible to induce in-plane crystal texture and morphological orientation by engineering the azimuthal distribution of the flux to match the symmetry of the nanocolumns (i.e. 3-fold rotational symmetry). Thus, biaxially textured nanocolumns with an in-plane alignment that is predominantly controlled by substrate motions (or flux configuration) can be created using this technique. In principle, this method could be generalized to nanocolumns with 4-fold and 6-fold azimuthal symmetry and therefore provides a mechanism to form biaxially textured, nanostructured films from a variety of materials deposited on amorphous or crystalline substrates.

[1] P. Morrow, F. Tang, T. Karabacak, P.-I. Wang, D.-X. Ye, G.-C. Wang, T.-M.T.-M. Lu, *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films* **2006**, *24*, 235.

[2] R. Krishnan, T. Parker, S. Lee, T.-M. Lu, *Nanotechnology* **2009**, *20*, 465609.

[3] K. Okamoto, T. Hashimoto, K. Hara, M. Kamiya, H. Fujiwara, *Thin Solid Films* **1985**, *129*, 299-307.

[4] K. Okamoto, T. Hashimoto, K. Hara, M. Kamiya, H. Fujiwara, *Thin Solid Films* **1987**, *147*, 299-311.

9:40am **TF+SE+NS-WeM6 Bi-axial Texture Development in AlN Layers during Off-axis Sputter Deposition**, R. Deng, D. Gall, Rensselaer Polytechnic Institute

Polycrystalline AlN layers were deposited by pulsed-DC reactive magnetron sputtering from a variable deposition angle  $\alpha = 0-84^\circ$  in 5 mTorr pure N<sub>2</sub> at room temperature. X-ray diffraction pole figure analyses show that layers deposited from a normal angle ( $\alpha = 0^\circ$ ) exhibit fiber texture, with a random in-plane grain orientation and the c-axis tilted by  $42 \pm 2^\circ$  off the substrate normal, yielding wurtzite AlN grains with the {10-12} plane approximately parallel ( $\pm 2^\circ$ ) to the substrate surface. However, as  $\alpha$  is increased to  $45^\circ$ , two preferred in-plane grain orientations emerge, with populations I and II having the c-axis tilted towards and away from the deposition flux, by  $53 \pm 2^\circ$  and  $47 \pm 1^\circ$  off the substrate normal, respectively. Increasing  $\alpha$  further to  $65$  and  $84^\circ$ , results in the development of a single population II with a  $43 \pm 1^\circ$  tilt. This developing bi-axial texture is attributed to a competitive growth mode under conditions where the adatom mobility is sufficient to cause inter-grain mass transport but insufficient for the thermodynamically favored low energy {0001} planes to align parallel to the layer surface. Consequently, AlN nuclei are initially randomly oriented and form a kinetically determined crystal habit exposing {0001} and {11-20} facets. The expected direction of its highest growth rate is  $49 \pm 5^\circ$  tilted relative to the c-axis, in good agreement with the  $42-53^\circ$  measured tilt. The in-plane preferred orientation for  $\alpha > 0^\circ$  is well explained by the orientation dependence in the cross-section of the asymmetric pyramidal nuclei to capture off-normal directional diffusion flux. The observed tilt is ideal for shear mode electromechanical coupling, which is maximized at  $48^\circ$ .

10:40am **TF+SE+NS-WeM9 Engineered Indium Tin Oxide Nanowhiskers via Vapour Liquid Solid Glancing Angle Deposition**, A.L. Beaudry, R.T. Tucker, J.M. LaForge, M.T. Taschuk, University of Alberta, Canada, M.J. Brett, University of Alberta, Canada and The National Institute for Nanotechnology

The vapour liquid solid (VLS) nanowire growth technique has been recently modified with spatially modulated vapour flux through glancing angle deposition (GLAD).<sup>1,2</sup> Using this new technique, named VLS-GLAD, our group has demonstrated improved morphological control over indium tin oxide (ITO) nanowhiskers.<sup>1</sup> Single crystal ITO nanowhiskers are grown via a self-catalyzed VLS growth mechanism, resulting in branched structures.<sup>3</sup> VLS-GLAD exhibits improved control over the diameter, spacing, branching density and branching orientation of ITO nanowhiskers. As the angle of deposition is increased to glancing angles, there is a transition from a dense interconnected network to a porous film of individual ITO nanowhisker structures. In addition, branching was found to increase significantly with increasing deposition angle. This result is attributed to an increase in the proportion of vapour flux incident on the sides of the structures, resulting in an increase in self-catalytic VLS growth of branches. This effect has been used to engineer branch morphology and orientation. Vapour flux rate modulation at glancing angles results in further in-situ control over ITO nanowhisker features. HRTEM imaging revealed a continuation of crystal planes from the trunk into the branch. XRD results indicated single crystal cubic bixbyite structures with a  $\langle 400 \rangle$  growth direction. Haacke's figure of merit was used to assess the suitability of ITO nanowhisker films as transparent electrodes.<sup>4</sup>

<sup>1</sup> Beaudry, A.L. et al. *Nanotechnology* **23**, 105608 (2012).

<sup>2</sup> Alagoz, A.S. and Karabacak, T. *MRS Proceedings* **1350**, (2011).

<sup>3</sup> Castañeda, S.I. et al. *Journal of Applied Physics* **83**, 1995 (1998).

<sup>4</sup> Haacke, G. *Journal of Applied Physics* **47**, 4086 (1976).

11:00am **TF+SE+NS-WeM10 CoPt Nanopillars for Advanced Media by Glancing Angle Deposition**, H. Su, A. Natarajathinam, S. Gupta, The University of Alabama

We report for the first time the fabrication of CoPt+AlN "granular nanorods" utilizing glancing angle deposition (GLAD) on a multi-gun, planetary sputtering system. Initially, AlN was deposited by reactive sputtering from an Al target while CoPt multilayers were simultaneously sputtered using cobalt and platinum targets. Various ratios of Co and Pt, ranging from Co80Pt20 to Co50 Pt50, were used to deposit CoPt-AlN

nanorods with different AlN volume percentages. X-ray diffraction (XRD), electron dispersive X-rays (EDX), scanning electron microscopy (SEM), and alternating gradient magnetometry (AGM) were employed to characterize the structural and magnetic properties, respectively. SEM micrographs indicated that the nanorods were approximately 16 nm in diameter, the angle between the substrate plane and the growth direction was about 78 degrees, while the lengths of the nanorods ranged from 30 to 50 nm, depending on deposition time. The angles between the substrate plane and incident flux ranged from 47 degrees to 82 degrees as the substrate presented itself at different angles to the target during the planetary deposition. The composition of CoPt-AlN has been studied by EDX for different ratios of AlN. M-H loops showed that the planetary GLAD sample had twice the coercivity of the flat sample.

We have also compared stationary vs. planetary GLAD, and sequential deposition of AlN/CoPt multilayers with true co-deposition, using an annular CoPt target with an Al insert. Simulations of the deposition have been carried out to gain a better understanding of where the AlN segregates with respect to the CoPt grains. These preliminary results indicate a novel and promising approach to nanopatterned graded media that is the subject of intense research in the data storage industry.

11:20am **TF+SE+NS-WeM11 Through-post Electrical Characterization of GLAD Thin Films**, A. Lalany, R.T. Tucker, M.T. Taschuk, University of Alberta, Canada, M.D. Fleischauer, University of Alberta and The National Institute for Nanotechnology, Canada, M.J. Brett, University of Alberta, Canada

Glancing Angle Deposition (GLAD) [1] thin films are increasingly used in optoelectronic applications that benefit from their unique optical properties or ultra-high surface area. GLAD produces porous nanostructured thin films which have found applications as high surface area electrodes. Potential performance benefits of these nanostructured thin-films for optoelectronic devices include, but are not limited to, increased charge extraction [2]. Suitable electrical conductivity along the length of GLAD structures (normal to substrate plane) is necessary to exploit a GLAD film's high surface area for electronic devices. However, optimization of GLAD films for these devices has proven difficult without direct measurements of post resistivity.

In-plane resistivity measurements of metals and conductive oxide GLAD films have been performed [3-5], showing increasing in-plane resistivity with increasing oblique deposition angle (due to decreased film density resulting in fewer conductive pathways). Electrical anisotropy has also been observed, with differing in-plane resistivity for different nanocolumn orientations [3-5]. Through post conductivity measurements present additional challenges - it has been shown that as crystallite grain size approaches the range of bulk electron mean free path, column-boundary scattering effects begin to dominate standard bulk-scattering mechanisms [6]. As such, the extensive boundaries present in GLAD structures can result in complex electrical behavior. While several attempts have been made to access through-post electrical properties, results have been limited to relative measures or are extremely low yield processes [7, 8].

We require a measurement technique that is both time and cost effective, statistically robust, and has high yield. This has been achieved with a Kelvin Cross-Bridge Resistor architecture specifically designed to measure through-post resistivity. Our devices can measure resistivities between  $100 \mu\Omega \text{ cm} < \rho < 11 \text{ G}\Omega \text{ cm}$ , and we have successfully measured through-post conductivities for Indium-tin-oxide (ITO) and Cr GLAD films. Here, we will present device fabrication, validation and current experimental results.

[1] M.M. Hawkeye et al., *J. Vac. Sci. Technol. A* **25** (2007) 1317.

[2] D.A. Rider et al., *Nanotech.* **22** (2007) 0857060.

[3] J. Lintymer et al., *Surf. & Coat. Tech.* **174-175** (2003) 316.

[4] K.D. Harris et al., *Adv. Funct. Mater.* **18** (2008) 2147.

[5] D. Vick et al., *J. Vac. Sci. Technol. A* **24** (2006) 156.

[6] A. Besnard et al., *J. Phys. D: Appl. Phys.* **44** (2001) 215301.

[7] M.F. Cansizoglu et al., *ACS Nano.* **4** (2010) 733.

[8] S.P. Chiu et al., *Nanotech.* **20** (2009) 105203.

11:40am **TF+SE+NS-WeM12 Direct Label-Free Detection of microRNA Using a Multi-well SERS Chip Fabricated By Oblique Angle Deposition**, J.L. Abell, University of Georgia, J.M. Garren, Georgia Health Science University, J.D. Driskell, Illinois State University, R.A. Tripp, Y.-P. Zhao, University of Georgia

Direct label-free nucleic acid detection is a desirable yet challenging task. The current mainstay detection and screening technologies, namely polymerase chain reaction (PCR) and DNA microarrays (i.e. DNA chips), rely heavily upon the use of extrinsic reporter molecules to detect the

hybridization of a probe sequence to a target sequence. Removing the need for external labels reduces the cost and complexity of DNA detection assays. This, however, requires a sensing platform capable of highly sensitive, specific, direct chemical analysis. Surface-enhanced Raman spectroscopy (SERS) is an analytical technique capable of detecting highly resolved chemical signatures with superior sensitivity, and can be used to determine the relative quantities of a compound adsorbed on a nanostructured metal surface. The challenge for SERS detection is to produce a large area, uniform and highly sensitive substrate. Here, we report the use of Ag nanorod (AgNR) SERS substrates fabricated by oblique angle deposition (OAD) for microRNA (miRNA) detection. With such a large area (wafer size) and uniform response (signal intensity variation  $\leq 10\%$ ) of the AgNR substrates, we have developed a simple molding technique to pattern the substrates into multi-well arrays. We demonstrate a 40-well 1" x 3" glass slide allowing for parallel screening of multiple specimens with uniform response. This multiwell substrate has been used in conjunction with a linear least squares (LS) analysis method by assuming that the SERS spectrum of miRNA is a convolution of the individual signals of each of the four A, C, G, and T components, where the contribution of each source signal to the total DNA signal is weighted by the relative quantities of A, C, G, and T present within the sequence. Experimentally we have demonstrated this method for detection and differentiation of four different DNA sequences. In addition, we show for the first time the subtle spectral changes observed after label-free hybridization can be quantified with LS to confirm the capture of the target sequence. This study reveals that the use of OAD SERS substrate could be a potential technique to replace to current microarray technique for DNA/RNA detection.

## Tribology Focus Topic

Room: 19 - Session TR+SE-WeM

### Tribology and Wear of Low-Friction Coatings and Materials

Moderator: D.L. Burris, University of Delaware

8:00am **TR+SE-WeM1 Seeing Things as They Really are: *In Situ* Studies of Materials in Application Environments and the Development of Temperature-Adaptive Nanocomposites.** C. Muratore, Air Force Research Laboratory, J.J. Hu, J.E. Bultman, UDRI/Air Force Research Laboratory, A.A. Voevodin, Air Force Research Laboratory **INVITED**

In the early 1940s, military pilots and those who serviced their planes were surprised by serious problems with ignition systems and diverse electrical troubles in their state of the art aircraft. Further study revealed that the graphite commutator brushes used in the electrical generator on the airplane (similar to the alternator in our automobiles) were the source of these technical difficulties, because they wore out 100 to 1000 times faster than expected. Over 70 years later, sensitivity of materials at contact interfaces to the extreme ambient environments aircraft are subjected to is still limiting aerospace capability. One of the reasons materials scientists haven't overcome these problems sooner is because it is difficult to do materials science, at least the part where you correlate performance to structure and composition, when there is such a big difference between the operating environment and the environment in which analysis is conducted. All the materials tribologist can really do is *post mortem* forensics work on materials designed to get hot after they have cooled down to a convenient handling temperature. During that cooling down time, phase changes and grain growth occur, perhaps misleading the researcher on the compounds or phases yielding high or low friction at interfaces in relative motion. In this talk we will review innovative characterization techniques designed to provide the insight necessary to produce environmentally adaptive tribological coatings, especially materials designed to operate over broad ranges of humidity (i.e., earth to space) and temperature (i.e., ignition to supersonic flight). Characterization of temperature adaptive nanocomposite lubricant materials, such as MoN/Ag and VN/Ag via Raman spectroscopy will be reviewed in depth.

8:40am **TR+SE-WeM3 Tribological Surface Chemistry of Model Lubricant Additives Measured in Ultrahigh Vacuum.** W.T. Tysoe, University of Wisconsin Milwaukee

Additives are generally added to lubricants, which react with the surfaces to form a boundary lubricating film that can lower friction and/or prevent wear. At the high interfacial temperatures that occur under so-called extreme-pressure conditions, the surface reaction and film growth kinetics are dominated by thermal processes. In contrast, it is postulated that, under mild conditions, where the surface temperature rise is low, a surface film can be formed by a shear-induced, surface-to-bulk transport mechanism. This effect is investigated by studying the tribologically induced surface

reactions of model sulfur- and boron-containing additives on copper surfaces in ultrahigh vacuum (UHV) where the background pressure is  $\sim 1 \times 10^{-10}$  Torr. The nature of the initial surface species that are formed by exposure of the copper surface to the model lubricant additive is investigated using a range of surface analytical techniques such as temperature-programmed desorption (TPD), reflection absorption infrared spectroscopy (RAIRS) and X-ray photoelectron spectroscopy (XPS). This enables the nature of the initial surface species to be identified, and their thermal stability to be measured in some detail. The effect of rubbing these adsorbate-covered surfaces is investigated, also in UHV, by measuring the friction coefficient and contact resistance during rubbing. The chemical composition of the wear track is followed using high-spatial-resolution Auger spectroscopy to follow the fate of the surface species caused by rubbing and to test the above postulate.

In addition, the effect of low-coordination sites formed on the surface by rubbing on the reactivity of gas phase lubricants is explored and finally, this strategy is used to understand the tribochemistry of borate esters on copper under mild rubbing conditions.

9:00am **TR+SE-WeM4 Nanomechanical and Nanotribological Properties of ZnO Thin Films.** E. Broitman, L. Martinez de Olcoz Sainz, Linköping University, Sweden, C. Bojorge, Cinso, Citedef-Conicet, Argentina, J.B. Miller, Carnegie Mellon University, H. Canepa, Cinso, Citedef-Conicet, Argentina, L. Hultman, Linköping University, Sweden

During the last years, with the advances in nanotechnology, zinc oxide (ZnO) thin films have attracted an increased attention for applications as sensor devices in microelectromechanical systems. In these applications, where high mechanical stress could be imparted on the film in contact situations, the knowledge of the coating nanomechanical and nanotribological properties is critical since they will affect the functions and durability of the films. Sol-gel method is a simple and low cost process for the fabrication of ZnO thin films; interestingly, there are only two publications partially dealing with their mechanical and tribological properties.

In this work, we studied ZnO thin films grown on glass substrates by sol-gel process. Single and multilayered films were deposited by spin-coating technique onto glass substrates, and subsequently transformed into nanocrystalline films using different thermal treatments Tt.

The microstructural properties and morphology of the films have been studied by X-ray diffraction (XRD), scanning electron microscopy, and surface probe microscopy. XRD patterns of films dried at room temperature show features characteristic of layered basic zinc acetate, a lamellar ZnO precursor, consisting of zinc hydroxide hydrate sheets separated by intercalated acetate groups. At higher Tt, ZnO diffraction patterns are dominated by features corresponding to the (100), (002) and (101) reflections of the crystalline zinc oxide "wurtzite" structure. The higher relative (002) intensity in some films is evidence of preferential growth of the structure along the c-axis, the axis of symmetry in the wurtzite structure.

The nanomechanical and nanotribological properties were measured by a Triboindenter TI-950 from Hysitron. The hardness H and reduced Young's modulus Er of the ZnO thin films were investigated by nanoindentation measurements with a Berkovich indenter at peak loads of 150  $\mu$ N. The films with the lower Tt exhibit a wide dispersion in the values due to the inhomogeneities on the degree of coating crystallinity. At the higher temperatures, the dispersion vanishes and we obtained H = 5.6 GPa and Er = 99 GPa. We also observed at low temperatures the presence of pop-in events that can be associated to the presence of the multilayers. The friction coefficient was measured at ambient conditions using a conical diamond tip in a reciprocal test, applying a normal force of 10  $\mu$ N and a stroke distance of 10  $\mu$ m. The friction coefficient decreases from 0.37 to 0.30 when Tt is increased. The different mechanical and tribological properties can be correlated to the changes in the microstructure upon different heat treatments.

9:20am **TR+SE-WeM5 Tribological and Compositional Properties of Electroless Nickel-Boron Coatings Annealed at Various Temperatures.** K. Gilley, University of Florida, Y. Riddle, UCT Coatings Inc., S.S. Perry, University of Florida

In this study, the tribological and compositional properties of annealing temperatures on electrolessly deposited nickel boride coatings were investigated. All samples were coated in the same bath and had approximately the same starting composition: 31 atomic % Ni, 19 atomic % B, 42 atomic % O, and 8 atomic % C. Samples were annealed at temperatures of 250°C, 400°C, 550°C, and 700°C under a constant flow of oxygen. The tribological properties of the samples were tested using a novel pin-on-disc tribometer. The pin-on-disc tribometry was performed in air

under ambient RH conditions, keeping conditions the same throughout all tests that were performed. The influence of the annealing temperature on surface composition was studied by X-ray photoelectron spectroscopy (XPS), used to identify and relatively quantify the elements present. Raman spectroscopy was used to differentiate between chemical species that were indistinguishable in XPS. Increasing annealing temperatures were seen to influence the tribological properties of the coatings to a large degree; with the samples with higher annealing temperatures having a significantly lower coefficient of friction,  $\mu \approx 0.16$  for the sample annealed at 550°C and  $\mu \approx 0.06$  for the sample annealed at 700°C, than the lower temperature annealed samples,  $\mu \approx 0.5$  for samples annealed at 250°C and 400°C. Similarly, the chemical nature of the coatings were strongly affected by the differing annealing temperatures; with the higher annealing temperature samples showing heavy oxidation and migration of boron to the surface, while the lower annealed samples remained largely unchanged. The lowering of the friction coefficient in the samples annealed at 550°C and 700°C was attributed to the migration and subsequent oxidation of boron forming low friction  $B_2O_3$  at the surface.

10:40am **TR+SE-WeM9 First Contact: SPR and SERS Studies of the Initial Transfer Behavior of PTFE**, *K.L. Harris, B.A. Krick, D.W. Hahn, W.G. Sawyer*, University of Florida

Traditionally the tribological behavior of PTFE (polytetrafluoroethylene) has been studied in the steady state after many sliding cycles. Steady state studies neglect events that occur during the first contact and sliding cycles, as well as the early transient behavior of PTFE. In-situ surface plasmon resonance (SPR) tribology experiments allow for the observation of initial transfer after the first contact and first sliding cycle of PTFE. SPR showed transfer of PTFE after the first cycle of sliding, contrary to previous models of films formed by delamination wear debris. Surface enhanced raman spectroscopy (SERS) verified the chemical identity of the transfer film. Friction behavior of PTFE was shown to differ in the first cycle from the behavior seen after a transfer film was created and to depend on contact pressure and sliding speed.

11:00am **TR+SE-WeM10 Tribological Investigations of Octadecylphosphonic Acid (ODP) and Octadecyltrichlorosilane (OTS) Self-Assembled Monolayers: A Comparative Study of MEMS-type Interfaces**, *N. Ansari, Auburn University, S. Barkley, C. Bouxsein, M. Deram, N. Eigenfeld, St. Olaf College, O. Matthews, Luther College, A. Poda, W.R. Ashurst, Auburn University, B.P. Borovsky, St. Olaf College, E. Linn-Molin, E.E. Flater*, Luther College

Since microelectromechanical systems (MEMS) are critically-limited by interfacial phenomena such as friction and adhesion, strategies have been developed to reduce friction in these systems. One common strategy is to coat MEMS surfaces with molecularly-thin self-assembled monolayer (SAM) coatings. Silicon MEMS are most commonly coated with silane-based SAMs, such as octadecyltrichlorosilane (OTS). Continued development of MEMS technology may require new material systems to be employed. Therefore, in this study, we investigate the frictional properties of octadecylphosphonic acid (ODP) monolayers deposited on aluminum oxide surfaces. Measurements using an atomic force microscope (AFM) and separately using a nanoindenter-quartz crystal microbalance system were performed each with a microsphere-terminated probe, allowing for a comparative study between different velocity regimes using contacts with similar sizes, surface roughnesses, and interfacial chemistries. AFM colloidal probe friction measurements indicate that while the frictional properties of aluminum oxide can be reduced with the use of an ODP monolayer, a more dramatic rubbing-induced modification is clearly evident for both bare and SAM-coated aluminum oxide substrates. These modification effects depend on scanning duration and environmental conditions such as humidity. We hypothesize that a tribochemical reaction occurs between aluminum oxide and ambient water, which has also been observed in macroscopic tribological studies of aluminum oxide published in the literature.

11:20am **TR+SE-WeM11 Diffusion of Gold Islands on Graphene**, *B. Dawson, M. Lodge, M. Ishigami*, University of Central Florida

Recent theoretical work has suggested that gold nanoclusters on graphite can exhibit both diffusional friction and a novel ballistic friction behavior [1]. This ability to tune friction at nanoscale interfaces can be useful for developing nanoscale motors and machines in general. Furthermore, understanding this nanotribological behavior can be utilized for various nanomechanical devices fabricated from graphene, which is chemically identical to graphite.

We have measured the frictional energy dissipation of gold nanoclusters on graphene as a function of temperature and cluster size using the quartz crystal microbalance (QCM) ring-down technique. By measuring this

dissipation, it is possible to quantitatively measure the island diffusion coefficient and precisely monitor how the diffusion and slip time change with temperature, and directly compare these results with the recent theoretical studies. In addition, our measurements give insight into the nanotribological properties of a two dimensional material studied at higher sliding speeds than typically accessible using atomic force microscopy.

[1] R. Guerra *et al.* Nature Materials **9**, 634 (2010).

11:40am **TR+SE-WeM12 Synthesis and Tribology of  $MoS_3$  Nanoparticles**, *J.R. Lince*, The Aerospace Corporation, *A.M. Pluntze*, Colorado State University, *S.A. Jackson*, The Aerospace Corporation

There has been recent interest in the use of solid lubricant nanoparticles in coatings and as boundary additives in liquid lubricants. Examples include nanoparticles of  $MoS_2$  and  $WS_2$ . The formation of these nanoparticles is nontrivial, requiring techniques such as gas phase syntheses and electric discharges. We are exploring simpler syntheses using wet chemical techniques. In particular, the synthesis of  $MoS_3$  nanoparticles involves hydrothermal reaction between molybdate salts and sodium sulfide under controlled pH conditions.<sup>1</sup>

The use of  $MoS_3$  as a tribological material has not been explored beyond its use as an oil additive.<sup>2</sup> We are investigating its potential for use in solid lubricant coatings. Bonded  $MoS_2$  coatings experience widespread usage for lubricating mechanisms on virtually every spacecraft (i.e., using micron-sized  $MoS_2$  particles). We formulated resin-bonded coatings using  $MoS_3$  nanoparticles as the lubricating pigment, and compared their tribological performance to commercial bonded  $MoS_2$  coatings. Surprisingly, the  $MoS_3$ -formulated coatings performed similarly to the  $MoS_2$ -based coatings. Specifically, they showed similar coefficients of friction (i.e., 0.04 to 0.06) and durabilities in dry nitrogen (<0.1% RH). We will present results of surface analyses on worn coatings to reveal changes in composition and chemical state of the  $MoS_3$  that might explain the measured low friction. In addition, results of tribological performance in humid air atmospheres will be presented.

We have also explored syntheses of  $MoS_2$  nanoparticles using nanosize  $MoS_3$  as a starting material. A recent study purported to create  $MoS_2$  nanoparticles with the addition of an aqueous reducing agent during hydrothermal synthesis of  $MoS_3$ .<sup>3</sup> However, X-ray fluorescence analysis of the product of our synthesis showed that the S:Mo remained at 3.0 after using the reducing agent. Other conversion methods including vacuum reduction of the  $MoS_3$  nanoparticles will be discussed.

References:

1. P. Afanasiev, "Synthetic approaches to the molybdenum sulfide materials," *Comptes Rendus Chimie*, 11(1-2) (2008) 159-182.
2. O.P. Parenago, V.N. Bakunin, G.N. Kuz'mina, A.Yu. Suslov, and L.M. Vedeneva, "Molybdenum Sulfide Nanoparticles as New-Type Additives to Hydrocarbon Lubricants," *Doklady Chemistry*, 383(1-3) (2002) 86-88.
3. Y. Tian, X. Zhao, L. Shen, F. Meng, L. Tang, Y. Deng, Synthesis of amorphous  $MoS_2$  nanospheres by hydrothermal reaction," *Materials Letters* 60 (2006) 527-529.

This work was funded in part by The Aerospace Corporation's Sustained Experimentation and Research for Program Applications program.

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# Thursday Morning, November 1, 2012

## Thin Film

Room: 10 - Session TF+EM+SE+NS-ThM

## Nanostructuring Thin Films

Moderator: R.C. Davis, Brigham Young University

8:00am **TF+EM+SE+NS-ThM1 Plasma Effects in Nanostructuring Thin Films**, *K. Ostrikov*, CSIRO Materials Science and Engineering, Australia **INVITED**

In this presentation, several examples of uniquely plasma-enabled nanostructuring of thin film materials for applications in energy conversion and storage, environmental monitoring, and bio-sensing. Strong emphasis is made on atom-, energy-efficiency, and environment-friendliness of plasma-based nanotechnologies.

**1. Introduction:** Atom- and energy-efficient nanotechnology is the ultimate Grand Challenge for basic energy sciences as has recently been road-mapped by the US Department of Energy. This ability will lead to the energy- and matter-efficient production of functional nanomaterials and devices for a vast range of applications in energy, environmental and health sectors that are critical for a sustainable future. Here we present examples related to atom- and energy-efficient nanoscale synthesis of advanced nanomaterials for energy conversion and storage, environmental sensing, and also discuss effective cancer cell treatment using low-temperature plasmas.

**2. Atom- and energy-efficient nanostructure production for energy storage:** Here we show an example of a recent achievement of a very low amount of energy per atom (~100 eV/atom) in the synthesis of MoO<sub>3</sub> nanostructures for energy storage (e.g., Li-ion battery) applications. This was achieved by using time-programmed nanosecond repetitive spark in open air between Mo electrodes. Highly-controlled dosing of Mo and O atoms was achieved through the controlled evaporation and dissociation reactions and maintaining reactive chemistry in air. These nanomaterials show excellent electrochemical and energy storage performance.

**3. Environment-friendly, single-step solar cell production:** Highly-efficient (conversion efficiency 11.9%, fill factor 70 %) solar cells based on the vertically-aligned single-crystalline nanostructures have been produced without any pre-fabricated p-n junctions in a very simple, single-step process of Si nanoarray formation by etching p-type Si wafers in low-temperature environment-friendly plasmas of argon and hydrogen mixtures. The details of this process and the role of the plasma are discussed.

**4. Metal-nanotube/graphene environmental and bio-sensors:** Plasma processing was successfully applied for the fabrication of hybrid nanomaterials based on metal-decorated carbon nanotubes and vertically aligned graphenes. The applications of these structures in environmental (gas) and bio-sensing (SERC/plasmonic) platforms are presented. The vertically-aligned graphene structures have been grown without catalyst and any external substrate heating, owing to the unique plasma properties.

8:40am **TF+EM+SE+NS-ThM3 Directed, Liquid Phase Assembly of Patterned Metallic Films by Pulsed Laser Dewetting**, *Y. Wu*, University of Tennessee, *J.D. Fowlkes, M. Fuentes-Cabrera*, Oak Ridge National Laboratory, *N.A. Roberts, P.D. Rack*, University of Tennessee

Self-assembly of materials offer the potential to synthesize complex systems by defining the *initial and bounding* conditions if the fundamental scientific principles guiding the assembly are known. Much work has been performed studying the assembly of continuous thin polymer and metal films which reveal interesting dewetting phenomenon. Less work has been devoted to the directed assembly and pattern formation of confined or patterned metallic thin films. Meanwhile, the synthesis of functional metallic nanomaterials via self-assembly has been an effective and low-cost approach to realize many critical applications of nanoscience and nanotechnology. In this study, the dewetting and nanopattern formation of nanolithographically pre-patterned thin films of various shapes via pulsed nanosecond laser melting were investigated to understand how initial boundary conditions facilitate precise assembly. Specifically we will show experimental and computational results (continuum and molecular dynamics) illustrating how so-called synthetic perturbations can vary the dispersion of the resultant nanoparticle size and shape distribution of pseudo-one-dimensional liquid metal wires. Furthermore, we will show how controlling the shape and size of bi-metallic nanostructures, the assembly of multifunctional nanoparticles can be assembled.

9:00am **TF+EM+SE+NS-ThM4 Nanosphere Lithography for Bit Patterned Media**, *A.G. Owen, H. Su, A.M. Montgomery, S.M. Kornegay, S. Gupta*, University of Alabama

Nanosphere lithography<sup>1-4</sup> has been used to pattern perpendicular magnetic anisotropy Co/Pd multilayers into nanopillars for the first time for bit-patterned media applications. A multilayer stack of Pd<sub>10</sub>[(Co<sub>0.3</sub>Pd<sub>1</sub>)<sub>9</sub>Pt<sub>5</sub> nm nanolayers was deposited onto a bare silicon wafer. The nanospheres were spin-coated into a uniform monolayer and then reduced in size by plasma ashing in oxygen. The Co/Pd multilayer films were subsequently ion milled into nanopillars using the reduced nanospheres as masks. We tested two ranges of nanosphere sizes, one at about 100 nm, and the other at about 1000 nm. In order to optimize the ashing of the nanospheres, response surface methodology (RSM) was performed to optimize the ashing power and time. It was seen that ashing at low powers of less than 100 W for longer times was more effective than higher powers for short times in shrinking the nanosphere masks without damage. The subsequent ion milling of the Co/Pd films was performed at a near-perpendicular angle to minimize shadowing by the nanospheres. We will discuss some of the complex shapes the nanospheres were patterned into after ashing, and how they translated into variously sized and shaped nanopillars of Co/Pd multilayers after ion milling. Magnetometry was used to characterize the films before and after patterning, showing an improvement in the coercivity and squareness of the media after patterning with nanospheres that were shrunk, but not damaged, by ashing. Micromagnetic simulations using Object Oriented Micromagnetic Framework (OOMF) have been carried out to produce a simulated hysteresis loop which is then compared with the experimental results.

### Acknowledgements

The NSF ECCS 0901858 grant, entitled "GOALI: Nanopatterned graded media" is acknowledged for support. Alton Highsmith is acknowledged for support in the UA Microfabrication Facility.

### References

1. Xiao Li, T. R. Tadisina, S. Gupta, *J. Vac. Sci. Technol. A* **27**, Jul/Aug 2009, 1062
2. Kosmas Ellinis, A. Smyrnakis, A. Malainou, A. Tserepi, E. Gogolides, *Microelectronic Engineering*, **88**, 2011, 2547-2551
3. C. L. Haynes, R. P. Van Duyne, *J. Phys. Chem. B* **105**, 5599, 2001
4. S. M. Weekes, F. Y. Ogrin, W. A. Murray, *Langmuir* **20**, 11208, 2004

9:20am **TF+EM+SE+NS-ThM5 Effects of Nanometer Scale Periodicity on the Self-Propagating Reaction Behaviors of Sputter-Deposited Multilayers**, *D. Adams, R. Reeves*, Sandia National Laboratories

Nanometer-scale, vapor-deposited multilayers are an ideal class of materials for systematic, detailed investigations of reactive properties. Created in a pristine vacuum environment by sputter deposition, these high-purity materials have well-defined reactant layer thicknesses between 1 and 1000 nm, minimal void density and intimate contact between layers. If designed appropriately, these energetic materials can be ignited at a single point and exhibit a subsequent, high-temperature, self-propagating formation reaction. The nanometer-scale periodicity set through design tailors the effective diffusion length of the subsequent self-propagating reaction.

With this presentation, we describe effects of the nanometer-scale, multilayer periodicity on i) the reactivity of multilayers in different surrounding gaseous environments and ii) the reaction front morphology as viewed in the plane of the multilayer. We show that nickel/titanium and titanium/boron multilayers are affected by the surrounding gaseous environment, and describe how the magnitude of average propagation speed depends on multilayer periodicity. Fine multilayer designs are characterized by fast reaction waves, and there is no difference in average propagation speed when reacted in air (atm. pressure) versus vacuum (1 mTorr). Coarse multilayer designs are generally slower and are affected by secondary oxidation reactions when conducted in air. These thick multilayer designs are affected by the pressure of the surrounding gaseous environment with enhanced propagation speeds owing to the highly exothermic reaction of Ti with O. Regarding the effects of nanometer-scale multilayer periodicity on reaction front morphology, we show that reactive multilayers often have a smooth reaction front when layer periodicity is small. However, multilayers having larger periodicity (and hence larger effective diffusion lengths) exhibit reaction front instabilities and complex reaction front morphologies.

In this talk, we also stress how the propensity to oxidize and the propensity to form reaction front instabilities (as affected through nanometer-scale design) impact final properties of the multilayers for applications such as localized joining.

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9:40am **TF+EM+SE+NS-ThM6 Ag Nanoparticles Supported by (111) Facets on Biaxial CaF<sub>2</sub> Nanoblades**, *M. Auer, D. Ye*, Virginia Commonwealth University

Silver nanoparticles of different diameters were grown in an effort to study methods of preferentially orienting the geometry of metal nanoparticles. Arrays of calcium fluoride nanorods were grown on silicon substrates using oblique angle deposition at 75° incident angle. A method was then developed to grow silver nanoparticles exclusively on the (111) facet of the calcium fluoride tips. Cross sectional scanning electron microscopy and transmission electron microscopy imaging was used to verify that the nanoparticles adhered exclusively to the desired facet of the tip. Using selected area diffraction and dark field in the TEM, it was shown that the nanoparticles did grow at a [111] orientation at the interface between them and the calcium fluoride rods. Different thicknesses and diameters of nanoparticles were then grown to determine what an ideal size was to achieve the most [111] orientation of the nanoparticles.

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