

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^{1,2}, as has direct raster milling with 5 nm machining precision in 100 nm thick gold films³. 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 μm x 1.5 μm square and 1 μm deep on a pitch of 2 μm . 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.

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

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

³ 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. Vandencastele, 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/CF₄ atmosphere. The influence of the bias voltage applied to the substrate (VBias) as well as of the gas mixture composition (%CF₄) 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 Fe₂O₃ 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 Fe₂O₃ 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 μm , 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*, 24th INVC, Wuppertal, (2011) 158.

4:20pm **SE+NS-MoA8 Cost Efficiency Trade Off in Nanostructured Thermoelectric Energy Conversion Systems**, *A. Shakouri, K. Yazawa*, Birck 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 SiO₂ 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, SrTiO₃-TiO₂ 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 SrTiO₃-TiO₂ nanocomposites. Sr_(1-x)Ti_(1+x)O_(3+2x) layers with 0 ≤ x ≤ 0.67 were grown on SrTiO₃ (001) substrates at 700°C in 1 × 10⁻⁶ Torr O₂ by high-vacuum pulsed laser deposition using a KrF excimer laser (λ = 248nm) operating at 10 Hz pulse rate and 1.7 J/cm² 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 SrTiO₃ with TiO₂ 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 SrTiO₃-TiO₂ interfaces), decreased thermal conductivities, and enhanced thermoelectric figure of merit, large enough to compete with current state-of-the-art high-temperature thermoelectric materials.

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