Friday Morning, November 1, 2013

Accelerating Materials Discovery for Global Competitiveness Focus Topic
Room: 202 B - Session MG+AS+EM+NS+SA+SE+SP+SS+TF-FrM

Novel Synthesis Approaches and Innovative Characterization Techniques Coupled with Theory & Computations
Moderator: E.B. Svedberg, The National Academies, M.B. Holcomb, West Virginia University

8:20am **MG+AS+EM+NS+SA+SE+SP+SS+TF-FrM1 MWCT and Piezoelectric Thick Film Composites that Incorporate Graphene Electrodes**, *K. Cook-Chennault, S. Banerjee, R. Kappera, M. Chhowalla*, Rutgers University
Three-phase, PZT-Epoxy- Multi-walled Carbon-Nanotube (MWCNT) flexible thick films prepared by a combination of solvent and spin coating technique were prepared, where materials were spin coated onto flexible substrates. The substrates investigated included; stainless steel, graphene and graphene with PMMA. Graphene and graphene/PMMA films which were grown by a chemical vapor deposition process, and the film thicknesses were ~ 200 μm. The volume fraction of the MWCNTs was varied from 1% to 6%, while the PZT volume fraction was held constant at 30% . The strain coefficient and capacitance were measured as a function of the MWCNT volume fraction and used to determine the effective dielectric constant. Samples that incorporated graphene electrodes rendered higher dielectric properties in comparison to samples with graphene-PMMA. The maximum values of dielectric constant were ~ 4353, ~1945 and ~ 61, for samples with graphene, graphene/PMMA and no electrode respectively. Sample surface morphology and sample composition were observed using SEM and measured using Raman Spectroscopy respectively. Improved dielectric properties observed for samples with graphene coatings are due to graphene's high carrier mobility and its ability to readily conform to the surface of the sample.

8:40am **MG+AS+EM+NS+SA+SE+SP+SS+TF-FrM2 Morphological and Structural Characterization of Size-Selected Pt NPs Supported on TiO$_2$(110) and SiO$_2$/Si(111) via Polarized Total Reflection Fluorescence XAS in UHV**, *F. Behafarid, L.R. Merte,* University of Central Florida*, R. Gordon,* Argonne National Laboratory*, B. Roldan Cuenya*, University of Central Florida
A combination of polarized total reflection x-ray absorption spectroscopy (XAS) and atomic force microscopy (AFM) data have been used to determine the morphological properties of the size-selected micelle-prepared Pt nanoparticles (NPs) supported on TiO$_2$(110) and SiO$_2$/Si(111) in an ultrahigh vacuum (UHV) environment. The Pt NPs were cleaned in UHV using an O$_2$-plasma followed by annealing in O$_2$ (1x10^{-6} mbar) at 600°C after the *ex situ* sample transfer. Extended X-ray absorption fine-structure (EXAFS) measurements were carried out at Argonne National Laboratory in fluorescence mode. Measurements along different orientations, namely one perpendicular and two parallel to the sample surface were carried out on the Pt NPs supported on TiO$_2$(110). Our analysis revealed that while the Pt NPs on SiO$_2$ remained spherical, the NPs on TiO$_2$ wetted the substrate and adopted an epitaxial relationship with the support. It will be shown that the first shell EXAFS analysis of the data acquired along different directions provides valuable information regarding the size and aspect ratio of the NPs as well as the degree of disorder and strain in their structure. FEFF simulations were carried out on model NP shapes and the theoretical data compared with experimental EXFAS data.

9:00am **MG+AS+EM+NS+SA+SE+SP+SS+TF-FrM3 Materials Control on a Nanoscale: Artificial Oxide Structures**, *D.H.A. Blank*, MESA+Institute for Nanotechnology, University of Twente **INVITED**
In general, nanotechnology provides the tools for controlling key parameters for thin films performance: chemical composition (and crystalline structure at nano-sized domains), thickness and topography (including nano-scale patterning of thin films' surface) and controlled interfaces at the nanoscale.

As research in nanotechnology develops, new characterization and production tools, new materials and process models as well as more computational power will become available. Nanotechnology is giving a new boost to thin films' application development.

Pulsed Laser Deposition (PLD) is one of the attractive research tools for complex materials because it is fast and one can easily investigate a wide range of different materials and compositions. Currently, a major issue in the growth of oxide materials with PLD is the control of the surface morphology. For most materials it is necessary to control the thickness and roughness of the thin films down to an atomic scale. Such well-controlled growth can also be used to manufacture artificially layered structures. In this way it is possible to create a whole new class of materials.

Much effort is put in the deposition of excellent textured layers without grain boundaries. In general the properties of highly oriented films approximate the properties of single crystals. Single or multi-layer structures require a well-conditioned process technique. The deposited layers must have a large homogeneity with well-defined material properties, smooth surfaces, and, in the case of oxides, the correct oxygen stoichiometry. Important is the possibility to combine PLD with standard *in-situ* diagnostic techniques, like *high pressure* Reflecting High Energy Electron Diffraction (RHEED).

With our development of pulsed laser deposition with control at atomic level we are able to control the growth of complex materials and to introduce new growth manipulations, like pulsed laser interval deposition. At present, new superlattices can be synthesized that exhibit rare properties, like multiferroics. Extremely sharp and homogeneous interfaces can be realized and this is, for example, yet utilized in SrTiO$_3$-LaAlO$_3$ interfaces and artificial ferroelectric structures. In this presentation I like to show this unique technique and their use in obtaining complex materials systems 'on demand'.

9:40am **MG+AS+EM+NS+SA+SE+SP+SS+TF-FrM5 Catalytic Micro-/Nano- Motors Propelled by Bubbles**, *M.T. Manjare*, University of Georgia, Athens, *B. Yang,* University of Texas, Arlington, *Y.P. Zhao,* University of Georgia, Athens
Catalytic Micromotors are micro- or nano- objects that use catalytic reaction, most commonly H$_2$O$_2$ --> H$_2$O + 1/2 O$_2$, to propel themselves in fluid environment. The motion of the motors can be controlled by designing different motor geometries and functionalizations and to perform variety of tasks such as cargo towing and biosensing. One of the mechanisms by which the motors move is bubble propulsion, i.e., the O$_2$ generated in the reaction forms bubbles and propel the motors by ejecting or bursting the bubbles. Bubble propulsion is proven to be the most efficient and fastest way to drive the motors. Here we report our new discoveries on bubble propelled catalytic motors. For spherical particles, electron beam evaporation method is used to coat half of their surface with Pt and to make them as Janus motors. A new bubble propelled quasioscillatory translational motion is observed only for big motors. The motion coincided with bubble growth and burst resulting from catalytic reaction. A physical model was proposed which explained that bubble growth imparts a growth force on the motor to move it forward and instantaneous local pressure depression due to bubble burst causes the motor to move backward. The competition of the two processes generates a net forward motion. The bubble propulsion mechanism involves hydrodynamics, growth kinetics, and mass/momentum transport. In order to understand the detailed mechanism, we have investigated the mass transport in microtubular jet engines, a major bubble propelled motor. A one dimensional mass transport model using basic principles of diffusion and reaction is built to explain the effect of environmental factors such as fuel concentration and of geometry on the motion. Numerical investigations of the motion-related parameters, such as O$_2$ flux, bubble generation rate and frequency, and average speed of the microjet motors during bubble growth, are found to depend closely on the length and opening radius of the microjet and the concentration of H$_2$O$_2$ in the surrounding environment. The theoretical results are in good agreement with the motion of Graphene oxide tubular microjet motors we have fabricated.

10:00am **MG+AS+EM+NS+SA+SE+SP+SS+TF-FrM6 Erosion Resistant Physical Vapor Deposition Coatings for High Temperature Polymer Matrix Composites Applications**, *S. Dixit*, M. Chin, R. Dixit, Plasma Technology Inc.
The advantages of replacing metals in aircraft turbine engines with High-Temperature Polymer Matrix Composites (HTPMC's) include weight savings accompanied by high strength to weight ratio, and lower manufacturing costs. Most of the nacelle of a modern aero gas turbine is made of HTPMC, a component that accounts for approximately 25% of the weight and 20% of the cost of the power plant. Unfortunately, they are limited to applications where they are not exposed to high-temperature

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* TFD James Harper Award Finalist

oxidizing atmospheres and/or particulates from ingested air. This is because oxidation and erosion occur on the surface, leading to weight loss, and/or cracking on the surface and a consequent decline of mechanical properties over time. Resistance to surface erosion is one rarely reported property of HTPMC's in engine applications because HTPMC's are generally softer than metals and their erosion resistance suffers.

Although prior research has shown that oxidation can be slowed down when metallic or ceramic coatings are applied onto HTPMC's, there remains a need for erosion-resistant coatings that protect HTPMC's from high-velocity particulates in the engine flow path. These erosion-resistant coatings could extend the life of polymer composites and also reduce the overall cost of the turbine assembly. Hence in this paper we report the development of coating materials that are compatible with HTPMC's such as Avimid N and AFR-PE-4 using Cathodic Arc Physical Vapor Deposition (CAPVD). We report the feasibility of applying multilayer PVD TiN coatings onto the HTPMC substrates and characterize their adhesion, microstructure and erosion resistance. We also show the effectiveness of duplex process of thermal spray and PVD to enhance the overall adhesion of the multilayer coating.

10:20am MG+AS+EM+NS+SA+SE+SP+SS+TF-FrM7 Poking Tips at Surfaces: Mechanical and Electronic Properties of Atomically Defined Interfaces, *P. Grutter*, McGill University, Canada **INVITED**
How does stuff break? An important step in this process is inelastic deformation of the material, the formation of a first disclocation. We report on the for the first experiments which due to the small size and atomic scale control of the indenter allow a direct quantitative comparison with molecular dynamics simulations and state-of-the-art electronic transport theory.

We have studied the formation of the smallest permanent indentation in the Au(111) model surface by a combination of scanning tunneling microscopy (STM) and atomic force microscopy (AFM) in ultrahigh vacuum (UHV). We use field ion microscopy (FIM) to characterize the nanometer scale spherical apex of the W(111) indenter in UHV prior to the indentation experiments [1,2]. Knowledge of the indenter geometry is necessary to extract quantitative parameters such as contact pressures and stresses within the sample during indentation.

Traditional nanoindentation measures depth to high precision, but typically does not possess the force resolution (nN) to detect initial plastic events [3]. Indentation with standard AFM allows for excellent force resolution, but large piezo displacements required to load the contact with a soft cantilever hamper the extraction of true indentation depth because of quantitative optical beam deflection calibration issues (beam placement, sensitivity to mode shape, etc.) and piezo creep. I will describe how our set-up overcomes these limitations and allows us to quantitatively assess elastic and plastic behaviour in an indentation curve.

We report on the transition from elastic to plastic deformation in the indentation of Au(111). This is done by producing arrays of indentations to forces near the plastic yield point and examining the resulting force-displacement curves for both elastic and plastic indentation sites. Plasticity can be identified by features in the force displacement curves, such as the sudden displacement excursions of the tip (pop-ins), the work done by the indenter, and the sink-in depth measured at mild repulsive loads. These indicators of plasticity can also be correlated with the permanent impressions in the surface imaged by STM. The measured forces at the initial yield points correspond to shear stresses lower than those expected for the homogeneous dislocation nucleation. We suggest that heterogeneous nucleation involving surface effects and atomic scale indenter roughness is likely to play a role in the observed plastic behaviour.

[1] W. Paul et al. Nanotechnology 23, 335702 (2012) [2] D. J. Oliver et al., PNAS **109**, 19097 (2012) [3] Minor et al., Nature Materials **5**, 697 (2006)

11:00am MG+AS+EM+NS+SA+SE+SP+SS+TF-FrM9 Functionalized Shape Memory Polyester Biomaterials, *V. Sheares Ashby*, University of North Carolina at Chapel Hill **INVITED**
Functionalized Shape Memory Biomaterials

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Shape memory polymers (SMPs) are a class of smart materials that can change their shape in a predetermined fashion when exposed to the appropriate external stimulus. Since Langer and Lendlein first demonstrated the tremendous potential of SMPs in biomedical applications there has been a growing interest in utilizing these materials as intelligent medical devices and minimally-invasive implants. Our research focuses on several areas: micro- and nanotopography, reactive functionality and switching stimuli.

Recently, we have developed thermally responsive micro-patterned poly(ε-caprolactone) (PCL) shape memory films to examine the interaction of human mesenchymal stem cells (hMSCs) with dynamic surface patterns using PRINT™ (pattern replication in non-wetting templates). We have also begun research on novel polymer structures containing functionality with the goal of developing SMPs capable of micro- or nanoscopic shape memory and post-functionalization. Finally, there have been several examples of dual (one temporary shape) and triple shape memory (two temporary shapes). Our efforts focus on the synthesis of novel bifunctional monomers and biodegradable polyester prepolymers containing photo-responsive side groups (cinnamamide or cinnamate) using a polycondensation method to allow uniform repeat units each possessing a photo group, followed by end-functionalization and crosslinking to create networks with photo and thermal shape memory switches. The synthesis of these materials, which has led to shape memory polymers with switching temperatures near physiological temperature and unique functionality, in addition to characterization of thermal and shape memory properties, will be presented. Fabrication of the patterned surfaces, initial cytotoxicity and cellular response to dynamic shape switching will also be discussed.

Authors Index
Bold page numbers indicate the presenter