

# Friday Morning, October 19, 2007

## Thin Film

Room: 613/614 - Session TF2-FrM

## Nanoparticles

Moderator: T.M. Klein, the University of Alabama

8:00am **TF2-FrM1 Preparation and Characterization of Supported Metal Sulfide Nanoclusters Using Size-Selected Deposition**, *M.G. White*, Brookhaven National Laboratory, *J.M. Lightstone*, SUNY Stony Brook, *P. Liu*, Brookhaven National Laboratory, *M.J. Patterson*, *J.C. Lofaro*, SUNY Stony Brook

INVITED

The layered (S-M-S) structure of the bulk metal sulfides leads to unusual structures at the nanoscale (disks, fullerenes, tube) that exhibit a size-dependent band gap and/or unique catalytic properties. For example, MoS<sub>2</sub> is widely used as a commercial catalyst for hydrogenation and hydrodesulfurization, where it is dispersed as nanoparticles (10-30 Å) on a high surface area support. It is generally accepted that the active sites for reaction are associated with Mo atoms (with Ni/Co "promoter" atoms) located at defects or edges of the nanoparticle, however, many questions remain about the inter-relationship between nanocluster size, structure (atomic and electronic) and metal-sulfur composition, and how these physical properties influence catalytic activity. In this work, we are using mass (size) selected cluster ion beams to explore the size dependent reactivity of small nanoclusters of the early transition metal sulfides (Mo, W). Specifically, we use reactive sputtering in a magnetron source to generate gas-phase cluster cations which are then mass-analyzed to yield a beam of clusters with a precisely defined mass (size) and metal-sulfur composition. The mass-selected clusters are deposited at low kinetic energies ("soft landing") onto a solid support, e.g., Au(111) and Al<sub>2</sub>O<sub>3</sub>, for preparing model nanocatalysts whose properties can be studied by conventional surface science techniques. To date, we have explored the structure and stability of several prominent Mo<sub>x</sub>S<sub>y</sub><sup>+</sup> and W<sub>x</sub>S<sub>y</sub><sup>+</sup> cluster species (x/y = 2/6, 3/7, 4/6, 5/7, 6/8, 7/10, 8/12) in the gas phase and deposited on surfaces. These clusters are substoichiometric relative to the bulk material (sulfur to metal ratio < 2), and generally have exposed metal atoms (edge sites) that are available for adsorbate binding and reaction. Using thermal desorption (TPD) and electron spectroscopy (Auger, XPS), we have studied the reactivity and thermal stability of molybdenum sulfide nanoclusters deposited on a Au(111) surface. This work was motivated by recent theoretical calculations that predict that the highly symmetric and stable Mo<sub>4</sub>S<sub>6</sub> and Mo<sub>6</sub>S<sub>8</sub> clusters bind to the Au(111) surface via relatively strong Au-S linkages, but with little distortion of the cluster structure. Experiments indicate that the clusters can be deposited intact, with adsorbate binding energies that depend on cluster size and atomic composition, and the presence of the Au substrate.

8:40am **TF2-FrM3 Chemical States of Sn Present in SnO<sub>2</sub> Nanomaterial Sensors**, *D.L. Lahr*, *J.K. Evju*, *K.B. Benkstein*, *J.L. Hertz*, *S. Semancik*, National Institute of Standards and Technology

Tin(IV) oxide (SnO<sub>2</sub>) has been studied extensively as a chemiresistive sensing material. Increasingly, it has been shown that morphologies of SnO<sub>2</sub> with nanoscale dimensions have improved sensing properties compared to the bulk material. We report on the observation of chemical states of tin present at the surfaces of a variety of nanoscale SnO<sub>2</sub> materials using X-ray Photoelectron Spectroscopy (XPS). Nanoparticles, nanowires and nanostructured thin films with a nominal stoichiometry of SnO<sub>2</sub> actually contain a range of oxidation states of tin, from tin(IV) to tin(0), at their surfaces. Depth profiling reveals the underlying tin(IV) oxide in each of these materials, and provides information on the relative amounts of the various chemical states present as a function of depth. In addition, we present methods to control the extent of oxidation of these materials, as monitored by XPS. We propose that the relative amounts of the chemical states of tin at the surfaces of sensors composed of these materials influence their sensitivity and stability. Control of the composition of the chemical states of tin can lead to improved sensor performance.

9:00am **TF2-FrM4 New Carbon Allotropes Produced by Hydrogen Plasma Exposure of Carbon Nanotubes**, *M.J. Behr*, University of Minnesota, *T. Singh*, *D. Maroudas*, University of Massachusetts, Amherst, *E.S. Aydil*, University of Minnesota

Plasma-enhanced chemical vapor deposition (PECVD) using hydrocarbons is a common technique used to grow carbon-based nanostructured materials. It has been well established that hydrogen plays a critical role in

determining these materials' crystallinity. For example, PECVD of diamond films is possible only when hydrocarbon precursors are heavily diluted in hydrogen. The specific role of hydrogen in these carbon systems, however, is unknown. To investigate hydrogen's role, we have exposed multiwalled carbon nanotubes (MWCNTs) and carbon nanofibers (MWCNFs) at room temperature to atomic hydrogen produced by an inductively coupled radio frequency plasma source. We observed hydrogen-induced crystallization of MWCNTs and MWCNFs at room temperature. Nanometer-size crystals of carbon appear gradually during 2-10 hour H-atom exposure of the nanotubes. We characterized these nanocrystals using high-resolution transmission electron microscopy (HRTEM), electron diffraction, and forward recoil elastic spectrometry (FRES). HRTEM of the H-exposed material at room temperature revealed the presence of carbon nanocrystals, ~5 nm in diameter, embedded in amorphous carbon nanorods. The electron diffraction patterns and lattice spacings could not be accounted for by known crystalline phases of carbon, such as diamond and lonsdaleite, or by contaminants. However, two distinct crystalline phases are observed among a variety of others in this amorphous matrix. The observed electron diffraction patterns and lattice spacings from these two phases are consistent with a body-centered cubic (BCC) phase with lattice parameter  $a = 0.30$  nm and a face-centered cubic (FCC) phase with lattice parameter  $a = 0.425$  nm. The lattice parameter of the FCC phase is approximately the same as that of i-Carbon, a previously observed but unidentified phase belonging to the cubic crystal system. However, electron diffraction from i-Carbon and the FCC phase we observe do not follow the same selection rules. First-principles density functional theory calculations within the generalized gradient approximation are used in conjunction with electron microscopy to suggest possible crystal structures for these new phases. Specifically, we consider the possibility that these new ordered phases may contain hydrogen atoms in addition to carbon and examine the dependence of the structural parameters of the crystalline phases on their hydrogen content.

9:20am **TF2-FrM5 Non-Lithographic Organization of Nickel Catalyst for Carbon Nanofiber Synthesis on Laser-Induced Periodic Surface Structures**, *Y.F. Guan*, The University of Tennessee, Knoxville, *A.V. Melechko*, Oak Ridge National Laboratory, *A.J. Pedraza*, *P.D. Rack*, The University of Tennessee, Knoxville

We present a non-lithographic technique that produces organized nanoscale nickel catalyst for carbon nanofiber growth on a silicon substrate. This technique involves three consecutive steps: first, the substrate is laser-irradiated to produce a periodic nanorippled structure; second, a thin film of nickel is deposited using glancing angle ion beam sputter-deposition, followed by plasma heat-treatment; and third, a catalytic dc plasma enhanced chemical vapor deposition (PECVD) process is conducted to produce the vertically aligned carbon nanofibers (VACNF). The nickel catalyst is distributed along the laser induced periodic surface structures (LIPSS), and the Ni particle dimension varies as a function of the location on the LIPSS and is correlated to the nanoripple dimensions. The glancing angle, the distance between the collimators, and the total deposition time all play important roles in determining the final catalyst size and subsequent carbon nanofiber property. Due to the gradual aspect ratio change of the nanoripples across the sample, Ni catalyst nanoparticles of different dimensions were obtained. After the PECVD process, it was observed that in order for the carbon nanofibers to grow, the nickel catalyst dimension should be larger than a certain critical value of ~ 25 nm, below which, the Ni is insufficient to sustain carbon nanofiber growth.

9:40am **TF2-FrM6 Matilda : A Mass Filtered Magnetron Nanocluster Source**, *G.H. Kwon*, *T.M. Klein*, The University of Alabama, *W. Hale*, AJA International, Inc., *G.J. Mankey*, The University of Alabama

Matilda, a nanocluster source, consists of a cluster source, a Retarding Field Analyzer (RFA) and a Magnetic sector. A moveable AJA A310 Series 1"-diameter magnetron sputtering gun enclosed in a water cooled aggregation tube serves as the cluster source. The sputtering pressure in the aggregation tube is controlled in the range of 0.03 - 1 Torr using a mass flow controller. The mean cluster size is found to be a function of gas flow rate, sputtering power, and aggregation length. The kinetic energy distribution of ionized clusters was measured with the RFA. The RFA also serves as a high pass filter which allows only ions having a higher kinetic energy than the cluster charge times the retarding voltage to pass. A silver target was used for initial testing and cluster sizes were measured using a transmission electron microscope. At high Ar flow rates, the mean cluster size is 60 nm and for lower flow, the mean cluster size is reduced to 2 nm. Finer control of cluster size can be achieved using a mixture of He and Ar as the sputtering gas. Our results show the He gas pressure can be optimized to reduce the cluster size variations. The cluster sizes can also be selected using a magnetic

sector. The sector is downstream from the RFA, and the magnetic field is applied in a direction perpendicular to the direction of ion motion. The ions are dispersed on a substrate laterally according to size. This new method of fabrication allows the study of size effects on a single substrate to increase throughput. This work was funded by the US DOE under grant number DE-FG02-01ER45867 and shared equipment from NSF-DMR-02-13985.

10:00am **TF2-FrM7 Controlled Synthesis of Single and Multi-Component Metallic and Ceramic Nanoparticles Via Matrix Assisted Pulsed Laser Evaporation**, *A.T. Sellinger, E.M. Leveugle, L.V. Zhigilei, J.M Fitz-Gerald*, University of Virginia

The need to obtain nanoparticles with narrow size distributions has prompted the development of alternative processing methods. As an emerging area, laser processing has evolved into several widely accepted fields spanning from thin film growth, etching, lithography, and industrial fabrication to name a few. Within this field, the use of matrix-assisted laser processing has been successfully utilized in the deposition of soft materials in thin film form. One class of materials amenable to solution processing are acetates [X(OAc)<sub>2</sub>]. Acetates are a widely favored metallorganic precursor for thin film processing on various substrates due to their decomposition behavior under ultraviolet irradiation and/or low temperature. In this research, a dry method to synthesize nanoparticles from frozen salt solutions is reported. Synthesis of Pd, Au, and Ag nanoparticles including their binary and ternary compositions were grown by photochemical decomposition of starting metal acetates within host matrices of chloroform and water using an excimer laser operating at 248 nm. Frozen composite targets were ablated at fluences ranging from 0.10 J/cm<sup>2</sup> to 1.0 J/cm<sup>2</sup> at a processing pressures ranging from 10 mTorr to 1 Torr. The ejected nanoparticles were deposited on continuous carbon coated and lacey carbon transmission electron microscopy grids at ambient temperature. Characterization was performed by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and energy dispersive x-ray spectroscopy (EDXS). High-resolution TEM analysis showed definitive evidence of elemental composition and confirmed that the size distributions which were narrow for the Pd system which exhibited mean diameters ranging from 2 to 3 nm while the Ag and Au systems were on the order of 10 nm with evidence of large particles. Additional research concerning the growth of complex, multi-component oxide nanoparticles will be presented as time permits.

10:20am **TF2-FrM8 The Characterization of Stress Induced Crystallization of Polycrystalline Silicon Thin Film Transistor with Vertically Aligned Carbon Nanofibers**, *J. Park, S.Y. Kwon*, The University of Tennessee, *S.-I. Jun*, dpiX, *A.V. Melechko, T.E. McKnight, M.L. Simpson*, Oak Ridge National Laboratory, *P.D. Rack*, The University of Tennessee

Thin film transistors (TFT) with vertically aligned carbon nanofibers (VACNF) are an attractive electronic switching device for nanoscale electroanalysis and delivering biological material into live cells. In our previous work, we have demonstrated an amorphous silicon TFT array integrated with VACNFs for delivering biological material into live cells. To enhance the device performance, we have explored a polycrystalline silicon active layer with a bottom-gate structure. For the poly silicon device, source/drain and gate metals and gate dielectric thin films were RF magnetron sputter deposited. We have examined several enhanced crystallization strategies including DC bias stress during amorphous silicon deposition and stress induced crystallization (SIC) using dielectric silicon nitride caps with relatively lower process temperature and higher crystallinity silicon than conventional annealing. The silicon films have been characterized by x-ray diffraction, scanning electron microscopy, and Raman spectroscopy. In this presentation, we will demonstrate the process flow of fabricating polycrystalline silicon with the stress effects and the characteristics of polycrystalline silicon will be discussed. Furthermore, the electrical characteristics of the TFTs with this active layer will be demonstrated.

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