

Nanometer-Scale Science and Technology Room 204 - Session NS1-MoM

Nanometer Scale Structures

Moderator: S.V. Kalinin, Oak Ridge National Laboratory

8:20am **NS1-MoM1 Morphological Control of Nanoporous Gold by Surfactants, J. Biener**, Lawrence Livermore National Laboratory; *M.M. Biener*, Harvard University; *T. Nowitzki*, Universitaet Bremen, Germany; *A.V. Hamza*, Lawrence Livermore National Laboratory; *C.M. Friend*, Harvard University; *M. Baeumer*, Universitaet Bremen, Germany

Nanoporous Au (np-Au) prepared by electrochemically-driven dealloying of Ag-Au alloys has attracted considerable interest due to potential sensor and actuator applications. The material exhibits an open sponge-like morphology of interconnecting ligaments on the nanometer length scale. Due to the very high surface-to-volume ratio of np-Au, the surface chemistry should play an important role in controlling the pattern formation during dealloying. Ion-bombardment of Au surfaces can be used as a model system to study the mechanisms of pattern formation during dealloying: Both processes generate a supersaturation of Au adatoms and vacancies, which in turn results in the nucleation of Au adatom clusters and vacancy islands. The actual morphology evolving under these conditions strongly depends on the mobility of vacancies and adatoms, and in particular on the stabilization of undercoordinated Au atoms by adsorbate species. Here, we report on oxygen and argon ion sputter experiments on Au(111) surfaces which allow us to study the influence of oxygen adsorption on pattern formation. The resulting surface morphologies were characterized by scanning tunnelling microscopy (STM), and the amount of adsorbed oxygen was measured by X-ray photoemission spectroscopy (XPS). Specifically, our experiments demonstrate that adsorbed oxygen stabilizes a rougher surface morphology by stabilizing undercoordinated Au atoms. Our results thus open a new door to control the morphology of nanoporous metals by means of surfactants. This work was performed under the auspices of the U. S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

8:40am **NS1-MoM2 Characterization of Polymer Nanostructures Deposited with Thermal DPN, A.R. Laracuate**, *M. Yang*, *P.E. Sheehan*, Naval Research Laboratory; *W.P. King*, Georgia Institute of Technology; *L.J. Whitman*, Naval Research Laboratory

We have developed a new variant of dip-pen nanolithography (DPN) called thermal DPN (tDPN), where a heated atomic force microscope cantilever controls the deposition of a solid "ink." Using this technique we have successfully deposited semiconductors, insulators, and metals, and extended it into UHV. As an example, we have deposited poly(3-dodecylthiophene) (PDDT), a polymer that shows great promise as an active component in organic electronic devices. PDDT nanostructures with lateral dimensions below 100 nm have been written on silicon oxide and gold surfaces. Using a unique UHV instrument that combines a scanning electron microscope (SEM), a scanning Auger, and in-situ four-probe measurements, we have characterized PPDT nanostructures written across prefabricated Au electrodes. I-V measurements show the nanostructures to be initially insulating ($>10\text{ G}\Omega$); however, the resistance unexpectedly drops several orders of magnitude (to as low as $33\text{ k}\Omega$) upon prolonged exposure to the SEM electron beam. When the beam is turned off, the resistance gradually increases ($\sim 1\text{ G}\Omega/\text{day}$). We have also found that a high resistance state can be restored by exposure to H_2 , suggesting that the polymer film is not damaged by the electron beam, but rather that charged H vacancies are generated in the PPDT film by the high-energy electrons, and that the vacancies can be reversibly filled by H_2 exposure. @FootnoteText@ @footnote 1@ P. E. Sheehan, et al., Appl. Phys. Lett. 85, 1589 (2004).

9:00am **NS1-MoM3 Growth Modification of Ferromagnetic Core-Shell Nanomaterials by a Magnetic Field, K.T. Leung**, University of Waterloo, Canada

Our recent work on metal nanoparticles (Cu, Ni, Co) electrochemically deposited on an ultrathin polypyrrole film grown on a gold-coated silicon electrode shows that the morphology (size, shape, density and distribution) of these nanostructured materials can be easily controlled by varying the wet deposition conditions (pH, electrolyte concentration, deposition potential, charge, and current density), and the thickness and morphology of the polypyrrole film. Using similar electrochemical techniques, we have

recently obtained mono-sized, uniformly distributed Fe core-shell nanoparticles with two different morphologies: quantum dots of 4-10 nm in diameter and $20\times 110\text{ nm}$ "nano-surfboards" ($<5\text{ nm}$ thick). These nanoparticles are found to primarily consist of a Fe metallic core and a mixed Fe oxides shell (2-3 nm thick). In the present work, we report the first evidence of morphological changes induced by an external magnetic field during growth. Implications of constructing patterned nanostructured materials using this technique will also be discussed. @FootnoteText@ * Work supported by the Natural Sciences and Engineering Research Council of Canada.

9:20am **NS1-MoM4 Fabrication of Defect-free Sub-10nm Si Nanocolumn using Cl Neutral Beam, J.K. Chen, T. Kubota**, Tohoku University, Japan; *U. Uraoka*, *T. Fuyuki*, Nara Institute of Science and Technology, Japan; *I. Yamashita*, Matsushita Electric Industrial Co., Ltd., Japan; *S. Samukawa*, Tohoku University, Japan

We fabricated nanocolumn structure by using a low energy Cl neutral beam and a ferritin iron-core mask. By optimizing beam accelerated energy, extremely high etching selectivity of Si to ferritin iron core masks as well as highly anisotropic etching profile could be realized. As a result, the diameter of the Si nanocolumn structure was 7 nm, which was identical to that of the iron core in the ferritin. We were also able to achieve an extremely high aspect ratio of about 19 (height: 130nm) with maintaining the diameter of 7nm. Additionally, the crystal defects of 7nm Si nanocolumn were observed by using TEM images. We found that defect-free Si nanocolumn etching could be accomplished by using the Cl neutral beam. It is much difficult for conventional plasma etching processes to fabricate such fine structure, because the high-energy photons in the plasma cause low etching selectivity to the iron core mask and generate crystal defects in the silicon.

9:40am **NS1-MoM5 Three-Dimensional Nanochannels Formed by Oxide Deposition and Fast Etching of Polymer, C. Peng, S.W. Pang**, University of Michigan-Ann Arbor

Nanochannels are widely used in biomedical applications such as DNA analysis and biomolecule detection. We report a method using sacrificial polymer and oxide to form three-dimensional (3D) nanochannels. Polymer nanostructures were patterned on Si substrates using optical lithography or nanoimprint lithography, followed by oxide deposition to form the sealed channels. A high-speed dry etching technique for removing the sacrificial polymer was developed using an oxygen plasma at high power, high pressure, and elevated temperature. This dry etching technique provides a fast lateral etch rate of $3.91\text{ }\mu\text{m}/\text{min}$ for the polymer inside nanochannels, which is an order higher than conventional reactive ion etching. High selectivity of 1200 is obtained between the lateral etch rate of polymer inside the nanochannels and the vertical etch rate of oxide. Etch rate dependence on pressure, temperature, and channel width were studied. It was found that the etch rate increases with pressure and temperature. To form multiple levels of nanochannels, the oxide covering the channels was planarized by a photoresist coating and etch-back process. After oxide planarization, the channel formation process is repeated and multiple levels of nanochannels can be stacked to build 3D nanostructures. A two-level nanochannel structure has been demonstrated and more complex 3D system is developed. Since oxide is transparent to visible light and the channels have hydrophilic surfaces, such 3D nanofluidic system is suitable for various biomedical studies.

10:00am **NS1-MoM6 Chemical Vapor Deposition onto Size-Selected, Aerosolized Silicon Nanoparticles, J.T. Roberts, J. Holm, Y.-C. Liao, A. Nienow**, University of Minnesota

We describe a method for depositing metal oxide layers onto the surfaces of aerosolized nanoparticles. Chemical vapor deposition was used to deposit group IV metal oxides, including zirconium dioxide, onto silicon. The film precursors were anhydrous metal nitrates. Layers were deposited on silicon particles of initial diameter between 10 and 20 nm. The results are important because they describe a new approach for manipulating interfacial properties of nanoparticles that have materials applications. More fundamentally, the results are among the first kinetic and mechanistic studies of surface reactivity in aerosolized nanoparticles. Deposition was investigated using tandem differential mobility analysis (T-DMA) and transmission electron microscopy (TEM). Aerosolized, crystalline silicon nanoparticles were extracted from a plasma synthesis chamber into an atmospheric pressure flow tube reactor. The particle streams were sent through a furnace for thermal activation, through a bipolar diffusion charger to establish a known charge distribution on the particles, and then through a differential mobility analyzer (DMA-1). DMA-1 was used to

Monday Morning, October 31, 2005

create a stream of monodisperse particles; selected diameters were in the 10-20 nm range. The monodisperse particle streams were swept into a reaction zone, which was a heated copper tube with a valve for the precursor introduction. The reaction zone was designed for maximal flexibility, with variable temperature (25-200 Å°C), particle residence time (1-10 s), and gas-phase composition. Particles that exited the reaction zone were analyzed in two ways: (1) for size changes, with a second DMA capable of measuring diameter changes as small as 1%, and (2) for morphological changes that are induced by deposition, using TEM.

10:20am **NS1-MoM7 The Electronic Structure of Diamondoids Measured with Synchrotron Radiation**, *T.M. Willey*, Lawrence Livermore National Laboratory; *C. Bostedt*, Technische Universität Berlin, Germany; *T. van Buuren*, Lawrence Livermore National Laboratory; *J.E. Dahl*, *S.G. Liu*, *R.M.K. Carlson*, MolecularDiamond Technologies, Chevron Texaco; *T. Möller*, Technische Universität Berlin, Germany; *L.J. Terminello*, Lawrence Livermore National Laboratory

Although the Group IV semiconductors Si and Ge show quantum confinement effects in nanoparticles, diamond particles a few nanometers in size do not show this increase in band-gap. However, various calculations on diamond predict increasing HOMO-LUMO gap as the diameter decreases below 1 nm. We have tested this hypothesis and will present the first measurements of the electronic structure of diamond in this near- and sub-nanometer size regime using synchrotron radiation techniques. Pure, defect-free, hydrogen-terminated diamondoids were investigated in the gas phase to eliminate particle-particle interaction and ensure measurement of pristine molecules. X-ray absorption probes the unoccupied electronic states; the carbon K-edge reveals rich electronic structure in these materials. We will present our analysis showing the emergence of a diamond-like band structure and a comparison to the predicted change in HOMO-LUMO gap from several calculations and our own recent X-ray absorption and emission measurements on solid-state diamondoids.

10:40am **NS1-MoM8 Low Temperature Melting of Tungsten and Ruthenium Nanorod Arrays**, *T. Karabacak*, *D.-X. Ye*, *P.-I. Wang*, *G.-C. Wang*, *T.-M. Lu*, Rensselaer Polytechnic Institute

We observed that tungsten and ruthenium nanorod arrays melted at ~30% and ~40% of their bulk melting points (W at 3410 °C and Ru at 2334 °C), respectively. These findings reveal the most dramatic reduction in the melting temperature of nanostructures ever reported in literature. The W and Ru nanorods were grown by an oblique angle sputter deposition technique through a physical self-assembly mechanism due to the shadowing effect. The W nanorods have an average width of ~75 nm and an average length of ~500 nm and the Ru nanorods have an average width of ~75 nm and an average length of ~370 nm. These nanorods were isolated from each other with gaps ~20 nm. The nanorods were vacuum-annealed at various temperatures in the range of 700-1000 °C for 30 minutes at each annealing temperature. The melting process was investigated through the analysis of scanning electron microscopy (SEM) images and X-ray diffraction (XRD) spectra. W and Ru nanorods started to coalesce and formed continuous films at temperatures ~1000 °C and ~950 °C, respectively. In addition, the melting was associated with recrystallization as observed from XRD spectra. After melting, W rods transformed from metastable cubic @beta@(200) phase to bcc @alpha@(110) and Ru rods changed their texture from hcp(100) to a mixture of (002) and (101) crystal orientations. The low temperature melting of the nanorods is explained to be mainly due to their small size and increased surface/volume ratio, which results in the "premelting". The premelting is believed to be further enhanced by the presence of interstitials (due to the atomic peening of energetic Ar, W, or Ru particles of tens of eV) or impurity (O in the case of @beta@-W rods) atoms in the lattice structure of the rods accompanied during sputter deposition.

11:00am **NS1-MoM9 Self-Assembly and Photoluminescence of CdSe Quantum Dots from Buffer-Layer-Assisted Growth**, *V.N. Antonov*, *P. Swaminathan*, *J.S. Palmer*, *J.H. Weaver*, University of Illinois at Urbana-Champaign

Nano-particles of II-VI semiconductors (quantum dots) exhibit well-known size-dependent optical properties due to the quantum confinement of their charge carriers. The principal routes of their synthesis have been chemical and thus difficult to integrate with silicon technology. In this paper, we demonstrate that CdSe quantum dots can be self-assembled and delivered on almost any substrate with the help of buffer-layer-assisted growth (BLAG). In BLAG, physical vapor deposition of atoms or molecules on multilayers of van der Waals solids leads to spontaneous formation of

clusters. Subsequent warm-up and desorption of the buffer causes the clusters to diffuse and aggregate into larger structures. The extent of this aggregation is controlled by the thickness of the buffer. Here, sub-monolayer depositions of CdSe on Xe buffers ranging from 4 to 35 ML result in formation of quantum dots ranging from small 2 nm clusters to extended ramified islands with typical branch width of 3 nm. The diffusivity of CdSe nano-particles on solid Xe is determined from the evolution of particle density with buffer thickness. The photoluminescence spectra of the CdSe dots are measured at 3 K, and their maxima shift through a large portion of the visible range with particle size. The spectra are analyzed in terms of the measured size distributions of the dots and the existing models of quantum confinement in CdSe. BLAG should be applicable for the synthesis of quantum dots of any II-VI semiconductor on almost any substrate.

11:20am **NS1-MoM10 Comparative Study of ZnO Nanorods Grown by MOCVD and Solution Method**, *Y. Tak*, *K. Yong*, POSTECH, Korea

ZnO nanomaterials have been intensively studied due to their characteristic properties and possible applications in nano-device fabrication. Various synthesis techniques of ZnO nanomaterials have been developed such as vapor liquid solid (VLS) method, metalorganic chemical vapor deposition (MOCVD), physical vapor deposition (PVD) and solution method. Among these methods, MOCVD and solution method can be easily applicable to low temperature process. We report on the comparative study regarding characteristics of ZnO nanorods grown by MOCVD and solution method, respectively. For MOCVD growth of ZnO nanorods on silicon, diethylzinc (DEZn) and oxygen were used as reactants. The growth temperature was 400 ~ 500 @super o@C and thin ZnO layer was used as a buffer layer. For solution method, Zn or ZnO coated silicon substrate was placed in a solution containing Zn(NO@sub 3@)@sub 2@ and hexamethylenetetramine (HMT) or ammonia water. The reaction temperature and time were 60 ~ 90 @super o@C and 6h, respectively. Large quantities of well-aligned ZnO nanorod could be prepared by both MOCVD and solution method. The morphology and crystallinity of the samples grown by two different methods were compared using field-emission scanning electron microscopy (FE-SEM) and X-ray diffraction spectroscopy (XRD). High-resolution transmission electron microscopy (HR-TEM) and X-ray photoelectron spectroscopy (XPS) were used to analyze atomic structures and element composition. Photoluminescence properties of the samples were compared using He-Cd (325nm wavelength) laser as an excitation source.

11:40am **NS1-MoM11 Heat Conduction across Nanolaminates of Alternating Metal-Dielectric Materials**, *Y.S. Ju*, UCLA

High density of interfaces can strongly impede heat conduction across nanolaminates. This can be exploited to create superior thermal barrier coatings without compromising mechanical or chemical protection characteristics. Thermal barrier coatings are critical elements that help reduce power requirements of solid-state phase change memory devices and thermally assisted magnetic recording media. Previous theoretical and experimental studies have improved our understanding of the thermal interface resistance. Significant discrepancy, however, still exists between theoretical predictions and experimental data at elevated temperatures. We will present experimental and theoretical studies of energy transport across interfaces between nanoscale metal and dielectric thin films. We will describe details of sample preparation and data analysis procedures we developed to address challenges involved in accurate measurements. The thermal interface resistance between Ta and amorphous AlOx is found to be considerably smaller than previously reported values for comparable metal-dielectric interfaces, which suggest that the intrinsic interface resistance is closer to the model prediction than previously suggested. We also report the thermal resistance of nanolaminates consisting of alternating layers of metal and dielectric materials. The thermal conductivity of the nanolaminates is found to be well-below the minimum thermal conductivity limit of each component and is consistent with our single interface thermal resistance data. We will also describe a continuum two-fluid model we develop to examine the impact of spatial non-equilibrium between electron and phonon on the thermal resistance of nanolaminates. Fundamental understanding of nanoscale energy transport across interfaces will allow systematic design and engineering of interfaces to either enhance or suppress heat conduction in nanolaminates.

Author Index

Bold page numbers indicate presenter

— A —

Antonov, V.N.: NS1-MoM9, **2**

— B —

Baeumer, M.: NS1-MoM1, **1**

Biener, J.: NS1-MoM1, **1**

Biener, M.M.: NS1-MoM1, **1**

Bostedt, C.: NS1-MoM7, **2**

— C —

Carlson, R.M.K.: NS1-MoM7, **2**

Chen, J.K.: NS1-MoM4, **1**

— D —

Dahl, J.E.: NS1-MoM7, **2**

— F —

Friend, C.M.: NS1-MoM1, **1**

Fuyuki, T.: NS1-MoM4, **1**

— H —

Hamza, A.V.: NS1-MoM1, **1**

Holm, J.: NS1-MoM6, **1**

— J —

Ju, Y.S.: NS1-MoM11, **2**

— K —

Karabacak, T.: NS1-MoM8, **2**

King, W.P.: NS1-MoM2, **1**

Kubota, T.: NS1-MoM4, **1**

— L —

Laracuenta, A.R.: NS1-MoM2, **1**

Leung, K.T.: NS1-MoM3, **1**

Liao, Y.-C.: NS1-MoM6, **1**

Liu, S.G.: NS1-MoM7, **2**

Lu, T.-M.: NS1-MoM8, **2**

— M —

Möller, T.: NS1-MoM7, **2**

— N —

Nienow, A.: NS1-MoM6, **1**

Nowitzki, T.: NS1-MoM1, **1**

— P —

Palmer, J.S.: NS1-MoM9, **2**

Pang, S.W.: NS1-MoM5, **1**

Peng, C.: NS1-MoM5, **1**

— R —

Roberts, J.T.: NS1-MoM6, **1**

— S —

Samukawa, S.: NS1-MoM4, **1**

Sheehan, P.E.: NS1-MoM2, **1**

Swaminathan, P.: NS1-MoM9, **2**

— T —

Tak, Y.: NS1-MoM10, **2**

Terminello, L.J.: NS1-MoM7, **2**

— U —

Uraoka, U.: NS1-MoM4, **1**

— V —

van Buuren, T.: NS1-MoM7, **2**

— W —

Wang, G.-C.: NS1-MoM8, **2**

Wang, P.-I.: NS1-MoM8, **2**

Weaver, J.H.: NS1-MoM9, **2**

Whitman, L.J.: NS1-MoM2, **1**

Willey, T.M.: NS1-MoM7, **2**

— Y —

Yamashita, I.: NS1-MoM4, **1**

Yang, M.: NS1-MoM2, **1**

Ye, D.-X.: NS1-MoM8, **2**

Yong, K.: NS1-MoM10, **2**