

# Monday Morning, October 31, 2005

## Applied Surface Science

### Room 206 - Session AS+BI+NS-MoM

#### Nanoscale Analysis: Biomaterial and Other Applications

Moderator: A.M. Belu, Medtronic, Inc.

#### 8:20am AS+BI+NS-MoM1 The Development of NSOM for Live Cell Applications, R.C. Dunn, O. Mooren, University of Kansas

INVITED

Near-field scanning optical microscopy (NSOM) is a scanning probe technique that enables optical measurements to be conducted with nanometric spatial resolution. This technique offers single molecule detection limits, high spatial resolution, and simultaneous force and optical mapping of sample properties. As such, it has found applications in many areas including the study of thin films, polymers, and solid-state materials. Perhaps its greatest potential, however, lies in the biological sciences, where fluorescence techniques are well developed for tagging specific proteins or structures or following dynamic processes such as calcium signaling. To date, NSOM measurements on viable cells remains problematic due to the forces involved in maintaining the tip close to the sample. Our laboratory has been actively developing new methods for conducting NSOM measurements that are amenable with soft and fragile samples such as living cells. We recently reported a new NSOM tip design built around a conventional atomic force microscopy tip that can be used to make high resolution fluorescence measurements on living cells. The development of these techniques and their application to the study of lipid rafts and nuclear pore complexes in the nuclear envelope will be discussed.

#### 9:00am AS+BI+NS-MoM3 Local Mobility in Membranes: Atomic Force Microscopy and Fluorescence Correlation Spectroscopy, A.R. Burns, D.J. Frankel, Sandia National Laboratories

The lateral organization and dynamics of lipids and proteins in membranes are critical to cellular signaling processes. Fluorescence imaging and atomic force microscopy (AFM) are both effective ways to map the location and structure of membrane components and domains (e.g., lipid rafts) in supported membranes. Since dynamical processes like translational diffusion of lipids and proteins are dependent on the local membrane structure and molecular interactions, it would be advantageous to correlate dynamics with detailed topography mapped out with AFM. We do this by performing fluorescence correlation spectroscopy (FCS) at specific sites imaged by simultaneous AFM and submicron confocal fluorescence microscopy. We have thus examined the relative partitioning and diffusion coefficients for both tail and head labeled GM1 ganglioside, as well as for head and tail labeled phospholipids, in phase separated domains. Our results indicate significant mobility changes in the micron-scale domains due to differences in lipid packing and ordering. We also observe a large reduction in the mobility of GM1 when bound to cholera toxin B fragments. The effects of membrane proteins will be discussed as well. This research was supported in part by the Division of Materials Science and Engineering, Office of Basic Energy Sciences, U.S. Department of Energy. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the U.S. Department of Energy under Contract DE-AC04-94AL85000.

#### 9:20am AS+BI+NS-MoM4 Molecular Orientation Imaging with sub 10-nm Resolution by Vector Piezoresponse Force Microscopy, B.J. Rodriguez, North Carolina State University; S. Jesse, A.P. Baddorf, Oak Ridge National Laboratory; A. Gruverman, North Carolina State University; S.V. Kalinin, Oak Ridge National Laboratory

Functional properties of calcified and connective tissues are determined by the relative ordering and orientation of a relatively small number of biopolymers, such as collagen. Here we present a new approach for local molecular orientation imaging in biological systems by Vector Piezoresponse Force Microscopy (Vector PFM). Vector PFM is capable of determining the local electromechanical activity and orientation in piezoelectric materials with a spatial resolution below 10 nm. The applicability of Vector PFM to biological systems is demonstrated for objects from butterfly wings to bones. Electromechanical characterization of enamel and dentin layers in human tooth is demonstrated. The vector electromechanical response of a bundle of collagen molecules in human tooth dentin has been visualized with 5 nanometer resolution. A method for imaging the local orientation of biomolecules from Vector PFM data has been illustrated using collagen molecules embedded in a hydroxyapatite matrix. As another example, 2D piezoelectric properties and local elasticity of a butterfly wing are measured with nanoscale resolution and interpreted in terms of the relative orientation of chitin molecules in the wing scales. The ubiquitous presence of electro-activity in biopolymers, such as chitin,

keratin, collagen, and cellulose, suggests that Vector PFM has exceptional potential for orientation imaging of biological materials on the sub-10 nanometer length scale. Research was sponsored by the U.S. Department of Energy, under contract DE-AC05-00OR22725 with UT-Battelle, LLC and by the National Science Foundation grant DMR-0072998 (AG). Research partially performed as a Eugene P. Wigner Fellow (SVK).

#### 9:40am AS+BI+NS-MoM5 Nanoscale Raman and Fluorescence Microscopy of Carbon Nanotubes, A. Hartschuh, H. Qian, A.J. Meixner, University of Tuebingen, Germany; N. Anderson, L. Novotny, University of Rochester

INVITED

Spectroscopic methods with high spatial resolution are essential for understanding the physical and chemical properties of nanoscale materials including biological proteins, quantum structures and nanocomposite materials. Optical techniques are of special interest because the energy of light quanta is in the range of electronic and vibrational transitions. Advances in near-field optics open up new means to overcome the diffraction limit and extend the range of optical measurements to the length scales of most nanosystems. Recently, a near-field optical technique based on local field enhancement has been demonstrated which allows to perform spectroscopic measurements with 20 nm spatial resolution. The method makes use of the strongly enhanced electric field close to a sharp metal tip under laser illumination. In this approach the metal tip is held a few nanometers above the sample surface so that a highly localized interaction between the enhanced field and the sample is achieved. Raster scanning the sample then allows for simultaneous optical and topographic imaging. Single-walled carbon nanotubes (SWCNTs) have been the focus of intense interest due to a large variety of potential nanotechnological applications. We demonstrate near-field Raman and fluorescence imaging of the same individual single-walled carbon nanotube and show that a spatial resolution of less than 20 nm can be achieved. The high-resolution capability and chemical specificity of the presented method is used to study local variations in the optical spectra of SWCNTs which would be hidden in farfield measurements. The technique has great potential for becoming a routine tool for the chemical analysis of surfaces at high spatial resolution. E. J. Sanchez et. al, Phys. Rev. Lett. 82, 4014 (1999). A. Hartschuh et. al, Phys. Rev. Lett. 90, 095503 (2003).

#### 10:20am AS+BI+NS-MoM7 Scanning Atom Probe Study of Fragmentation of Organic Molecules, O. Nishikawa, M. Taniguchi, Kanazawa Institute of Technology, Japan

Fragmentation of two organic molecules, crystal violet [(C<sub>25</sub>N<sub>3</sub>H<sub>30</sub>)<sup>+</sup>Cl<sup>-</sup>: 408 amu] and tetra-n-butyl-ammonium hydroxide [N(C<sub>4</sub>H<sub>9</sub>)<sub>4</sub><sup>+</sup>OH<sup>-</sup>: 259 amu], was studied at atomic level by mass analyzing the dissociated fragments with the scanning atom probe (SAP). In the SAP analysis the molecules and their fragments are field evaporated as positive ions and detected one by one. Since the field evaporation is a static process, it does not disorder surface structure breaking atomic bonds by external energy. Accordingly, evaporated positive ions reflect the binding state in the molecules. For example, the radical of polythiophene, SC<sub>4</sub>H<sub>2</sub>, is field evaporated as doubly charged ions indicating that the atoms forming the radical are strongly bound. A thin layer of crystal violet was deposited on a tungsten substrate. Since the crystal violet is non conductive, the molecules are field evaporated applying a DC high voltage to the tungsten substrate and irradiating the specimen with a pulsed laser beam, 2nd harmonic of YAG laser, 532 nm. Although non-dissociated molecule ions are detected, most molecules are dissociated showing the ions such as C<sub>13</sub>H<sub>2</sub>, C<sub>13</sub>NH<sub>4</sub> and C<sub>8</sub>NH<sub>2</sub>. The detected fragments suggest that no double bonds are broken. When the molecule layer was deposited on a titanium oxide layer, all molecules were dissociated possibly due to the photocatalytic function of titanium oxide. The most abundant fragment is C<sub>4</sub>NH<sub>2</sub>. The ratio of the number of carbon atoms to that of nitrogen atom was found to be nearly 8:1 as expected. Although the dissociation of tetra-n-butyl-ammonium hydroxide molecules at the boundary with the tungsten substrate is noticeable, the dissociation is insignificant at non-boundary areas. It was also found that hydroxide of the molecules is dissociated and oxygen atoms are bound with tungsten. This may suggest that tungsten also have catalytic function.

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10:40am **AS+BI+NS-MoM8 Surface Potential Mapping of DNA-protein Complex at Molecular Level**, *E. Mikamo, F. Yamada, T. Matsumoto, T. Kawai*, Osaka University, Japan

Atomic force microscopy (AFM) is a valuable method for the study of biomolecules such as DNA, RNA and proteins at real-space. The biomolecules have generally been adsorbed on the insulating substrate as mica to observe by AFM. However, it is very hard to measure the local electric properties of the insulating substrate and the conductive substrate has been commonly used. Recently our group demonstrated the measurement of electric properties of DNA and Au nanoparticles on mica and sapphire substrate. This result encouraged us to measure the complex of biomolecules on the insulating substrate at molecular level. We report here surface potential and capacitance measurement of DNA, protein and DNA-protein complex on the insulating substrate. The experiments are based on frequency mode non-contact AFM (FM-ncAFM). The FM-ncAFM is able to detect the high-sensitive local electrostatic forces and prevent the charge injection caused by tip-sample contact. We observed the surface potential mapping and topographic image simultaneously. The topographic images clearly showed DNA and protein as line and dot structure. The surface potential of corresponded structures is observed as bright contrast. Our results indicate that surface potential of DNA, protein and DNA-protein complex is higher than insulating substrate surface. The potential images resolve the double strand DNA, thin structure less than 2 nm, and protein at single molecular level. To estimate the capacitance of individual molecules, we measured  $d(\Delta F)$  per  $dV$  images. The measurement of surface potential and capacitance indicate that this technique is able to discriminate the individual molecules on an insulating substrate. This work was supported by grants from the New Energy and Industrial Technology Development Organization (NEDO).

11:00am **AS+BI+NS-MoM9 The Importance of Aberration Corrected SEM and TEM to the Semiconductor Industry**, *A.C. Diebold*, SEMATECH & AMRC, US; *B. Foran*, ATDF & AMRC; *M.J. Yacaman, B.A. Korgel*, UNIVERSITY OF TEXAS & AMRC

INVITED

Microscopy continues to be a critical need for the semiconductor industry. Feature sizes continue to shrink with logic having a two-year cycle for introduction of each new technology generation. Over the next fifteen years, the gate length of transistors will rapidly shrink to less than 10 nm. The interconnect technology connecting the transistors will keep pace with this size reduction. Research and development needs occur well ahead of manufacturing needs. Thus, there already is a need for microscopy capable of imaging and characterizing the interfaces, film layers and structures for future devices. Recent advances in electron optics technology have corrected for chromatic and spherical aberrations that have long limited resolution in scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Commercially available advances include monochromators to reduce the energy spread of the electron source and lens correctors to reduce spherical aberration. Resolution of state of the art scanning TEM and High resolution TEM has been proven below 0.1 nm. Aberration correction technology is also now commercially available for SEM and allowing resolution to 0.6 nm. In this paper we discuss the advances in imaging that aberration corrected lenses have enabled along with semiconductor industry applications. We will discuss near-term applications such as the characterization of interfaces in the transistor gate stack and measurement of strain in the transistor channel, and then also discuss long-term research applications such as nanowires and nanodots. Aberration correction will not solve all microscopy problems, and we will discuss specific cases such as sample or analytical limitations that can obviate any benefit of aberration correction technology.

11:40am **AS+BI+NS-MoM11 Scanning Tunneling Microscope Assisted with Inner-Shell Excitation by Hard X-ray Micro-Beam**, *A. Saito*, Riken Harima Inst., Japan; *J. Maruyama, K. Manabe*, Osaka Univ., Japan; *K. Kitamoto*, Riken Harima Inst., Japan; *K. Takahashi*, Osaka Univ., Japan; *Y. Tanaka*, Riken Harima Inst., Japan; *M. Yabashi, M. Ishii*, Japan Synchrotron Radiation Res. Inst.; *M. Akai-Kasaya*, Osaka Univ., Japan; *S. Shin, T. Ishikawa*, Riken Harima Inst., Japan; *Y. Kuwahara, M. Aono*, Osaka Univ., Japan

A scanning tunneling microscope (STM) system was developed for in-situ experiments under the irradiation of highly brilliant hard x-rays of synchrotron radiation (SR). It appears attractive to excite the core electrons of specific level under the STM observation, because it may enable to analyze the elements or control the local reaction with the spatial resolution of STM. To surmount a small probability of the core-excitation by hard X-rays, SR of the highest brilliance at the SPring-8 was used. To prevail the difficulties produced by the highly brilliant SR (damage around

the STM scanner, thermal and electrical noise, and instability of the system such as thermal drift), the beam size was limited to  $\sim 10 \mu\text{m}$ . The small beam size serves also to obtain a high signal to noise ratio and high spatial resolution by restraining the electrons emitted from a wide area. The in-situ STM observation was enabled by developing an accurate "three-body (invisible micro-beam, tip-end, and sample surface)" alignment system in ultrahigh vacuum. Despite a noisy condition of SR facility and radiation load around the probe tip, STM images were successfully obtained with atomic resolution. The analysis of the clean Si(111) surface revealed that the thermal expansion affects to the behavior of the tip much strongly than reported in the past reports. Next, the tip-current spectra were obtained on Ge nano-islands on the clean Si(111) surface, by changing the incident photon energy across the Ge absorption edge. A current modification was detected at the absorption edge, with a spatial resolution of the order of 10 nm. This system will serve to observation or manipulation with atomic resolution, which is based on the interaction between the surface atoms and the hard X-ray photons.

## 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. Laracuenta, 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 to 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 PDDT 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 ( $\sim 1 \text{ G}\Omega/\text{day}$ ).

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We have also found that a high resistance state can be restored by exposure to H@sub 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@sub 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 20x110 nm "nano-surfboards" (<5 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  $\mu\text{m}/\text{min}$  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 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  $\text{\AA}^\circ\text{C}$ ), 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  $\sim 30\%$  and  $\sim 40\%$  of their bulk melting points (W at 3410  $^\circ\text{C}$  and Ru at 2334  $^\circ\text{C}$ ), 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  $\sim 75$  nm and an average length of  $\sim 500$  nm and the Ru nanorods have an average width of  $\sim 75$  nm and an average length of  $\sim 370$  nm. These nanorods were isolated from each other with gaps  $\sim 20$  nm. The nanorods were vacuum-annealed at various temperatures in the range of 700-1000  $^\circ\text{C}$  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  $\sim 1000$   $^\circ\text{C}$  and  $\sim 950$   $^\circ\text{C}$ , 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

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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.

## Nanometer-Scale Science and Technology Room 210 - Session NS2-MoM

### Nanowires

Moderator: C.R. Marrian, IBM

8:20am **NS2-MoM1 Probing Growth Defects Inside Nanowires**, *J. Eriksson, A. Mikkelsen, E. Lundgren*, Lund University, Sweden; *W. Hofer*, University of Liverpool, U.K.; *N. Skold, L. Samulesson, W. Seifert*, Lund University, Sweden

Free-standing semiconductor nanowires are perceived as future components in nanoelectronics and photonics. In fact, applications such as for example, bio/chemical sensors, n- p- type diode logic and single nanowire lasers have already been realized in the laboratory. @footnote 1@ Because of the extremely small dimensions of a nanowire, atomic scale structural features can have a significant impact on their properties. As a result, structural methods that address all these issues are highly desirable. Recently we have demonstrated a new method to image individual atoms inside III-V semiconductor nanowires using a combination of STM and a novel embedding scheme. @footnote 2@ In this way, we are able to image areas of the nanowire with atomic resolution both along the wire, and through the face of the wire. In this contribution we present a cross-sectional STM study of the structure and the electronic properties of stacking faults inside a GaAs nanowire containing an embedded GaInAs segment. The stacking faults are created due the formation of twins as the nanowire is grown. Spectroscopy measurements performed directly on a stacking fault are compared to density functional theory calculations, and the influence of the stacking fault on the electronic properties of the wire will be discussed. @FootnoteText@ @footnote 1@L. Samuelson, Mater. Today 6 (2003) 22. @footnote 2@A. Mikkelsen et al, Nature Materials. 3 (2004) 519.

8:40am **NS2-MoM2 Optical Activation of Implanted Impurities in ZnS Nanowires**, *D. Stichtenoth, D. Schwen, S. Mueller, C. Borchers, C. Ronning*, University of Goettingen, Germany

Nanostructures of zinc sulfide (ZnS), a II-VI compound semiconductors with a direct band-gap of 3.66 eV in the cubic phase and 3.74 eV in the wurtzite phase, show interesting optical properties, making it a promising candidate for optoelectronic devices. Single crystalline nanobelts and -wires were synthesized in a computer-controlled process according to the VLS mechanism. We investigated the morphology, structure and composition by scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy dispersive spectroscopy (EDS), and X-ray diffraction (XRD). The optical properties have been studied by temperature dependent photo- (PL) and cathodoluminescence (CL). The synthesized ZnS nanowires were implanted with nitrogen and boron as potential donor and acceptor, respectively. The implanted nanowires were investigated directly after ion implantation and showed a high quantity of defects resulting into non-luminescence material. Annealing procedures recovered the crystal structure and the optical properties, and we found varying and new PL-lines indicating the activation of the implanted impurities.

9:00am **NS2-MoM3 Metal, and Conducting Polymer Nanowires for Gas and Biomolecule Sensing**, *M. Yun*, University of Pittsburgh; *C. Lee, R. Vasquez*, Jet Propulsion Laboratory; *N. Myung*, University of California at Riverside; *J. Wang, H. Monbouquette*, University of California at Los Angeles; *A. Mulchandani*, University of California at Riverside  
Single Palladium (Pd), Polyaniline(PANI), and Polypyrrole(PPY) nanowires from 70 nm to 300 nm in diameter and up to 7 Åµ in length have been synthesized using e-beam lithography and electrodeposition. This

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fabrication method enables the use of various materials for single nanowire sensors, such as polymers, metal oxides, and semiconductors. These fabricated Pd nanowires are used to sense hydrogen gases and have achieved a sensitivity of 0.02% H<sub>2</sub>. In addition, we have observed that the resistance of the 200 nm wide avidin-functionalized PPY nanowires increased rapidly to a constant value upon addition of 1 nM of the biotin-DNA conjugate and the resistance increased with increasing concentrations up to 100 nM. At last, we will present that arrays of nanowires with controlled dimensions are fabricated on substrates, optionally as integral parts of multilayer structures, by means of a high-yield process based on ion milling on steps (IMOS). To demonstrate the utility of functionalized IMOS nanowires as sensors, we have successfully demonstrated Pt nanowire array and precisely assembled glucose oxide (GOx) on Pt nanowire array by co-deposition with electropolymerized PPY. A mixture of GOx and pyrrole is used in PBS solution for electrochemical polymer formation and GOx immobilization. It has been verified by measuring the current sensitivity of 0.3 nA/nM to the glucose with IMOS Pt nanowires.

9:20am **NS2-MoM4 Determination of the Mechanical and Electromechanical Properties of 1D-nanostructures**, A. Heidelberg, B. Wu, J.G. Sheridan, J.J. Boland, Trinity College Dublin, Ireland

Nanowires (NWs) have attracted considerable interest as nanoscale interconnects and as the active components of both electronic and electromechanical devices. Nanomechanical and nanoelectromechanical measurements are a challenge but remain key to the development and processing of novel NW-based devices. Here, we report a general method to measure the spectrum of NW mechanical properties based on NW bending under the lateral load from an atomic force microscope (AFM) tip.<sup>1</sup> For electromechanical measurements bending experiments have been carried out with simultaneous measurement of the NW's conductivity. Mechanical measurements on Li<sup>+</sup>/Mo<sub>3</sub>Se<sub>3</sub> NW bundles<sup>2</sup> with a diameter range between 25 and 200 nm have been carried out using a SPM-nanomanipulator. In these experiments NWs were deposited out of solution across trenches on SiO<sub>2</sub>.<sup>2</sup> To prevent any slippage of the NWs during the manipulation, they were pinned down by E-beam induced deposition of Pt at the trench edges in a dual beam FIB/SEM system. Taking into account the wire shape and dimensions as well as the AFM cantilever dimensions, the Young's modulus and the maximum bending strength of the NWs can be calculated from the force-displacement traces obtained by the lateral manipulations. The Young's modulus for Li<sup>+</sup>/Mo<sub>3</sub>Se<sub>3</sub> NWs shows a strong radius dependence. It increases exponentially with decreasing NW diameter which can be attributed to shear effects between the individual NWs in the NW bundles. For NWs with a radius of 30 nm a modulus of 1.22 TPa is found. The NWs show brittle failure and the bending strength increases with decreasing wire radius. Electromechanical properties of NW bundles were also measured and compared to data obtained on metallic (Au, Cu) and semiconducting (Si) NWs.<sup>1</sup> @FootnoteText@<sup>1</sup> B. Wu, A. Heidelberg, J. J. Boland, Nat. Mater. (accepted)<sup>2</sup> A. Heidelberg et al., Z. Phys. Chem. 217 (2003) 573.

9:40am **NS2-MoM5 Nanowires: From Biological Sensing to Computing and Much More!**, C.M. Lieber, C. Yang, Harvard University **INVITED**

Nanotechnology offers the promise of producing revolutionary advances in many areas, extending from biology and medicine to electronics and computing, and thus may impact in a substantial way our future lives. This presentation will provide an overview to the bottom-up paradigm for nanotechnology enabled using nanowire building blocks. First, the growth of nanowires, with composition controlled down to the atomic scale, their fundamental electronic properties, and parallel assembly and interconnection will be described. Second, nanowire devices configured as electrically-based biosensors will be discussed with an emphasis on disease detection and ultimate sensitivity limits of these nanodevices, as well as the potential linkage to hybrid information processing systems. Third, studies of nanowire based electronic circuits and nanocomputing systems will be critically examined. Lastly, challenges that must be met to realize these and other nanotechnologies in the future will be summarized.

10:20am **NS2-MoM7 Direct Atomically Resolved Imaging of Nanowire Heterostructures and Nanowire Substrate Interaction**, A. Mikkelsen, Lund University, Sweden; J. Eriksson, L. Ouattara, E. Lundgren, Lund University, Sweden; T. Knaapen, Eindhoven Technical University, The Netherlands; N. Skold, W. Seifert, L. Samuelson, Lund University, Sweden

Self-assembled semiconductor nanowires are among the most interesting systems for doing low dimensional physics, as well as for realizing many

future electronic and optoelectronic devices.<sup>1</sup> Due to efficient strain relaxation a wide range of heterostructures, not possible in the bulk, can be grown in nanowires, and as a result, a multitude of complex nanowire based heterostructure devices has been realized in recent years. Very recently it has even been possible to grow optically active III-V structures on Silicon substrates.<sup>2</sup> Because of the seeding type growth process of the wires, it is further possible to grow the wires by self-assembly in well defined positions for example on a chip. Using Scanning Tunneling Microscopy (STM), we address both the issue of heterostructure growth, the initial growth of the nanowire on the substrate and the influence of nanowire growth on the substrates - with atomic scale resolution. We apply our newly developed scheme to image individual atoms inside III-V semiconductor nanowires using a combination of STM and embedding.<sup>3</sup> Using this method we have imaged GaInAs segments in GaAs wires with atomic resolution. We show that while the GaInAs segments are in principle perfectly defined on the atomic scale, an In distribution exists above the segment and also on the side facets of the wire. We further image GaAs nanowires at the GaAs(001) substrate interface, revealing intriguing details about both the initial growth of the nanowire along the surface, and the subsequent growth of the out-of-plane free standing wire. Finally we have investigated the influence of the nanowire growth, by Au seed particles, on the surrounding substrate - revealing that significant structural changes can occur. @FootnoteText@<sup>1</sup> L. Samuelson, Mater. Today 6 (2003) 22.<sup>2</sup> @Footnote 2@ T. Maartensson et al, Nano Lett 4 (2004) 1987<sup>3</sup> @Footnote 3@ A. Mikkelsen, et al, Nature Materials. 3 (2004) 519.

10:40am **NS2-MoM8 Near-field Scanning Photocurrent Microscopy of a Nanowire Photodetector**, Y. Gu, E.-S. Kwak, J.L. Lensch, J.E. Allen, T.W. Odom, L.J. Lauhon, Northwestern University

One-dimensional nanomaterials such as semiconductor nanowires (NWs) are being considered for a variety of device technologies, including nanoscale photodetectors (PDs). The mechanisms of carrier photogeneration in nanoscale PDs have been addressed in a number of studies, but the charge transport and collection mechanisms have received comparatively little attention and are not well understood. In this regard, photoconductivity measurements with uniform illumination (spot size larger than the device) may be insufficient to establish the operational principles of NW devices because (1) the internal electric fields may be highly non-uniform, and (2) similarities between conventional and NW device characteristics may be fortuitous. To understand the global response and the ultimate potential of NW PDs, an understanding of the photoresponse on a smaller length-scale is desirable. We have developed a new technique, near-field scanning photocurrent microscopy (NSPM), to explore the local photoresponse of semiconductor NW devices. A near-field scanning optical microscope (NSOM) was used to image the photocurrent induced by local illumination (excitation spot size less than device size) along the length of a metal-semiconductor-metal (MSM) PD based on a single CdS NW. Under uniform monochromatic illumination, the MSM PDs exhibited photocurrents ~10<sup>5</sup> larger than the dark current (< 2 pA). Under local illumination, the response of the devices was limited to regions near the M-S contact. Analysis of the spatial variation and bias dependence of the local photocurrent allowed the mechanisms of photocarrier transport and collection to be identified. The NSPM technique we describe can be readily extended to other NW-based devices with similar geometries, and provide insight into the operation principles of these devices. NSPM therefore has the potential to significantly advance the understanding and development of NW device technology.

11:00am **NS2-MoM9 Fabrication of Silicon Nanowires with Addressable Au-coated Si Islands**, C. Wang, K.S. Ma, M. Madou, University of California, Irvine

With the increasing interest in various aspects of nano devices, it is becoming apparent that controlled growth is the key to manufacturing. The ability to control the growth of materials on the nanometer scale is important since it determines the device applications. Within many various material, Si nanowires (SiNWs) have attracted intensive research efforts in the synthesis and characterizations. The vapor-liquid-solid mechanism is the rife technique to growth SiNWs. The SiNWs were grown by decomposition of SiH<sub>4</sub> as the Si atom sources. Most recently, the other approach, e.g. the solid-liquid-solid, has been developed. In this, the bulk Si wafers were used as either the substrates or Si sources. A thin Au layer was deposited on the substrate as catalyst. In this method, the SiNWs were directly deposited onto the conducting substrate. The post-growth processes are needed to employ those SiNWs as building blocks for the electronics. Herein, we report an alternative method to fabricate the

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SiNWs by adopting SLS mechanism. The addressable Au-coated Si islands were fabricated by lithography with lift-off on the SiO<sub>2</sub> pre-coated substrate. The substrates were then heated to 900 Å°C in N<sub>2</sub>/H<sub>2</sub> gas. By this isolated Si islands technique, the grown SiNWs were settled down on the insulated substrate. By e-beam or optical lithography, the conducting electrodes can be fabricated on the wires. The islands are the starting point of the growth which can be served as the marker to localize the positions of SiNWs. By engineering design the size and position of the islands, the post-growth fabrication will be much easy instead of using alignment technique under the microscopes. We demonstrated a convenient technique to fabricate SiNWs of controllable position using SLS mechanism. The synthesized SiNWs were deposited on the non-conducting substrates. The widths of the wires are in the tens of nanometer range. The characterizations of synthesized SiNWs were carried out.

11:20am **NS2-MoM10 Mechanical and Electromechanical Properties of Metallic Nanowires**, *B. Wu, A. Heidelberg, J.J. Boland*, Trinity College Dublin, Ireland

Here, we present a general method to measure the full spectrum of nanowire (NW) mechanical properties: ranging from Young's modulus  $E$ , yield strength, plastic deformation and failure. This method is based on NW bending under the lateral load from an atomic force microscope tip, and involves the manipulation of NWs after they have been mechanically pinned at the edge of a trench using a focused ion-beam. We find that for Au and Cu NWs the Young's modulus ( $E$ ) is essentially independent of diameter, while the yield strength is largest for the smallest diameter wires, with strengths up to 100 times that of bulk materials and substantially larger than that reported for bulk nanocrystalline metals (BNMs). In contrast to BNMs, NW plasticity is characterized by strain-hardening demonstrating that dislocation motion and pile up is still operative down to diameters of 40 nm. Possible origins for the different mechanical properties of NWs and BNMs are discussed. The application of this method has also been extended to electrical measurement of NW systems under mechanical strain. For metallic and conducting polymer NWs, the resistance was monitored when NWs were subjected to loads by AFM tip. The potential applications will be discussed.

11:40am **NS2-MoM11 In Situ Resistance Measurement of Epitaxial Silicide Nanowires**, *H. Okino, R. Hobara, Y. Hosomura, I. Matsuda, S. Hasegawa*, University of Tokyo, Japan; *P.A. Bennett*, Arizona State University

We present in situ resistance measurements for CoSi<sub>2</sub> nanowires (NWs) on Si(110), using a custom-built multi-tip UHV-STM. We have shown elsewhere that self-assembled epitaxial silicide NWs can be formed with a variety of transition metals (Co, Ni, Fe, Ti, Pd, Dy) on Si(100), Si(111) or Si(110) surfaces, in various combinations (Phys. Rev. Lett v93, 2004, p256102). In most cases, these form via a new "endotaxial" growth mechanism, in which the silicide grows into the substrate along inclined Si{111} planes, breaking the symmetry of the surface and leading to the long, thin island shape. These NWs are metallic, single-crystal structures with potential applications as interconnects, nano-electrodes or as functional elements for nano-electronic devices. Four independent STM tips can be positioned to contact a single NW. Each tip is pushed ~ 10nm beyond the point of tunneling to make good electrical contact with the NW. Four-point measurements on a single NW yield typical values of 600 @ohm@ and 60 @ohm@ for the NW and contact resistance, respectively, for a NW with dimensions 60 nm wide, 40 nm high and 2 microns long. Similar values are obtained from a 2-point configuration by measuring the resistance vs. tip separation. The corresponding resistivity is @rho@ = 20-30 μ@ohm@/cm, which is similar to that for high-quality epitaxial films of CoSi<sub>2</sub> at 300K. This indicates that defect- and/or surface-scattering is small for these structures. We also find that the NWs are isolated from the substrate by a Schottky barrier with zero-bias resistance of ~ 10@super 7@ @ohm@. The good isolation results from a surface depletion layer near the NWs.

## Nanometer-Scale Science and Technology Room 204 - Session NS1-MoA

### Nanotribology

**Moderator:** H.J. Mamin, IBM Research Division

**2:00pm NS1-MoA1 Scaling Effects in Tribology: Micro- and Macroscale Studies of Diamond Like Carbon Nanocomposite Coatings, R.R. Chromik,** North Carolina State University; **K.J. Wahl,** Naval Research Laboratory

The formation of a transfer film is a key part of how solid lubricant and protective coatings provide low friction and resist wear. These interfacial films, or "third bodies," are found to be chemically and mechanically different from the original mating surfaces, and the evolution of contact behavior is tied intimately with their dynamic nature. While the role of transfer films in macroscopic contacts has received considerable study, the effects of scaling on friction, transfer film formation and dynamics remains largely uninvestigated. To this end, we have studied the microtribology of DLC nanocomposite coatings using a commercially available nanoindentation system. Reciprocating sliding tests at speeds of 1-4  $\mu\text{m/s}$  were conducted using diamond and sapphire counterfaces having radii of 10 and 150  $\mu\text{m}$ , respectively. These geometries resulted in two regimes of contact stresses: 0.25 to 0.85 GPa for sapphire and 1.5 to 5.5 GPa for diamond. The friction behavior as a function of contact stress was explored in the elastic regime. Microcontact friction behavior fit a Hertzian contact model over a broad load range. Diamond vs. DLC gave shear stress similar to macroscopic values, while sapphire vs. DLC showed lower interfacial shear strength but higher friction overall. Ex situ optical microscopy, atomic force microscopy and micro-Raman spectroscopy suggest that friction response is correlated with formation of transfer films on the counterface. Scharf and I.L. Singer, Tribology Letters 14, 3 (2003). Ex situ optical microscopy, atomic force microscopy and micro-Raman spectroscopy suggest that friction response is correlated with formation of transfer films on the counterface. Singer, S.D. Dvorak, K.J. Wahl and T.W. Scharf, J. Vac. Sci. Technol. A21, S232 (2003).

**2:20pm NS1-MoA2 The Effect of Filling Carbon Nanotubes on Their Tribological Behavior, S.-J. Heo, S.B. Sinnott,** University of Florida

As microengineering technology continues to evolve, the design of MicroElectroMechanical System (MEMS) / NanoElectroMechanical System (NEMS) devices is increasingly more complicated. At the same time, the need to consider the tribological properties of the materials that are likely components in future MEMS/NEMS devices has increased. Carbon nanotubes are one of the candidate materials for use in MEMS due to their high stiffness in the direction of the nanotube axis, low Young's modulus perpendicular to the nanotube axis and relative ease with which they slide against one another in bundles as a result of their van der Waals interaction with each other. In addition, nanotubes can stand high compressive and tensile forces prior to failure due to their flexibility. Here we investigate the responses of a bundle of single-walled nanotubes (SWNTs) and filled SWNTs to compressive and shear forces between two hydrogen-terminated sliding diamond surfaces by using classical molecular dynamics simulations. After constructing the systems, they are allowed to equilibrate completely at the room temperature. Then, the topmost diamond substrate moves to compress the nanotubes and then slides relative to the lower diamond surface in order to shear the nanotube bundle. The forces on the atoms are calculated by using the reactive empirical bond-order (REBO) potential for hydrocarbons coupled to Lennard-Jones Potentials. The results elucidate the role of filling on the tribological responses of SWNT bundles. This work is supported by the NSF-funded Network for Computational Nanotechnology (grant no. EEC-02288390).

**2:40pm NS1-MoA3 Nanometer Scale Mechanical and Electronic Properties of Molecular Films, M. Salmeron,** Lawrence Berkeley National Laboratory

**INVITED**

Molecular thin films are intensely studied in connection with applications in chemical recognition, molecular patterning and manipulation, molecular electronics and as tribological films to modify friction and adhesion in nano- and micro-scale devices. I will present studies aimed at understanding the relation between structure, mechanical stability and electronic properties of molecular films. Our studies reveal the strong interdependence between structure and properties and the role of externally applied pressure. Examples include Self-assembled and Langmuir-Blodgett films made of molecules with saturated alkane chains, aromatic and unsaturated bonds, oligothiophenes, etc.

**3:20pm NS1-MoA5 On the Influence of Structure on Friction: The Amorphous-Crystalline Transition in Antimony Nanoparticles, C. Ritter,** Humboldt University Berlin, Germany; **M. Heyde,** Fritz-Haber Institute of the Max-Planck Society, Germany; **K. Rademann,** Humboldt University Berlin, Germany; **U.D. Schwarz,** Yale University

This work addresses two of the crucial points in nanotribology, namely the dependence of friction on effective contact area and interface structure. As model system, antimony nanoparticles grown on graphite are used. Such particles can be easily prepared with different sizes, and the effective particle/substrate contact area can be deduced from scanning force microscopy images. Moreover, the particles are undergoing a structural transition from amorphous to polycrystalline during the growth process at about 10000-15000 nm in size. This feature can be used to establish a correlation between structure and friction. Antimony islands have been pushed over atomically flat substrate areas using the tip of a dynamic force microscope while the power dissipation necessary to move the islands was measured. To fully cover the amorphous-crystalline transition, to check on reproducibility, and to obtain sufficient statistics, 95 measurements including 57 islands (areas between 1370 nm<sup>2</sup> and 112000 nm<sup>2</sup>) and four different cantilevers were performed. The threshold value of the power dissipation needed for translation of the crystalline islands depends linearly on the contact area between the islands and the substrate. With the assumption of a linear relationship between dissipated power and frictional forces, this implies a direct proportionality between friction and contact area. The amorphous islands, however, also fit with a linear law, but the slope is a factor of three lower than the one found for the larger particles, leading to significantly lower energy dissipation. This change and their tentative relation to the structural transition within the particles will be discussed.

**3:40pm NS1-MoA6 Combined Nanoindenter and Quartz Microbalance Studies of Realistic Tribological Contacts and Ultrathin Lubricant Films, B. Borovsky, A. Booth,** Grinnell College

For emerging technologies such as micromachined devices, it is increasingly important to understand high-speed, multi-asperity, microscale contacts lubricated with films as thin as a single molecule, and to control the effects of humidity. Most theoretical and experimental studies of small contacts do not directly access this physical regime. We have therefore used a combined nanoindenter and quartz crystal microbalance (QCM) to study the contact between a sapphire sphere and a polycrystalline gold electrode undergoing transverse shear at speeds on the order of 1 m/s. For the first time, we have used this combined system to study both dry and lubricated contacts, by applying monolayer octadecanethiol films. We have extended previous work by adding continuous monitoring of the QCM resonance bandwidth during indentations. We find that both the frequency and bandwidth of the QCM track changes in the contact area, as derived from the contact stiffness. Depending on the roughness of the gold electrode, variations in the frequency with contact area follow either the single-asperity or multi-asperity limits of the elastic no-slip model of the interface. However, this model fails to account for the large levels of dissipation observed during indentations and the dependence of the bandwidth on contact area. We attribute this to dissipation in outer portions of the contact subject to interfacial slip. We also report a reversible humidity effect whereby the levels of dissipation in lubricated contacts increase and decrease reproducibly with the amount of water incorporated into the octadecanethiol film. We will discuss refinements of the interaction model to account for frictional processes and the response of the polymer film to humidity, confinement, and high-frequency shear. Research supported by NSF, Research Corporation, and Hysitron, Inc. Borovsky, J. Krim, S.A. Syed Asif, and K. J. Wahl, J. Appl. Phys. 90, 6391 (2001).

**4:00pm NS1-MoA7 Effect of Temperature on the Nanomechanics of Lipid Bilayers Studied by Force Spectroscopy, S. Garcia-Manyes, G. Oncins, F. Sanz,** University of Barcelona, Spain

The effect of temperature on the nanomechanical response of supported lipid bilayers has been studied topographically and by Force Spectroscopy with Atomic Force Microscopy. An AFM equipped with a high temperature stage heater has been used. It has been experimentally proved that the force needed to puncture a phosphatidylcholine lipid bilayer (yield threshold force,  $F_y$ ) deposited on mica and tested in liquid environment is extremely temperature-dependent. The quantitative measurement of the evolution of  $F_y$  with temperature has been related to the structural changes (phase transitions) that the bilayer undergoes as observed through AFM images. These studies have been carried out with three different

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phosphatidylcholine bilayers that exhibit different main phase transition temperatures (TM), namely, 1,2-Dimyristoyl-sn-glycero-3-phosphocholine(DMPC), 1,2-Dipalmitoyl-sn-glycero-3-Phosphocholine (DPPC) and 2-Dilauroyl-sn-glycero-3-Phosphocholine (DLPC). The solid-like phase shows a much higher  $F_y$  than the liquid-like phase, which also has been proved to exhibit a jump (breakthrough) in the force-curve. Within the solid-like phase  $F_y$  decreases as temperature is increased, and suddenly drops as it approaches TM. Interestingly, a well in the  $F_y$  vs. temperature plot occurs around TM, thus proving an anomalous mechanical softening around TM. Such mechanical softening has been predicted by experimental techniques and also by MD simulations and interpreted in terms of water ordering around the phospholipid headgroups. A further temperature increase when the phospholipid bilayer is in the liquid phase does not change  $F_y$  significantly. Furthermore, ion-binding has been demonstrated to increase  $F_y$  and its influence on both solid and liquid phases has also been discussed. @FootnoteText@ @footnote 1@Garcia-Manyes,S.; Oncins,G.; Sanz,F.:(Submitted to Biophysical Journal).

4:20pm **NS1-MoA8 Understanding the Frictional Response of Organic Monolayer Coatings using Atomic Force Microscopy, E.E. Flater, R.W. Carpick**, University of Wisconsin-Madison

Motivated by the lack of fundamental understanding of friction, and that friction and wear are major limiting factors for surface micromachined devices, we use atomic force microscopy (AFM) to determine the nanoscale frictional properties of alkylsilane monolayers commonly used in these microscale devices to reduce adhesion and friction. Quantitative single asperity measurements of friction and contact stiffness are performed using SiO<sub>2</sub>- and monolayer-terminated AFM tips on monolayer-terminated silicon. Using octadecyltrichlorosilane (OTS) and fluorinated monolayers (FOTAS), we observe that friction for these systems depends on the type of molecule and its packing properties. For the OTS monolayer there are two phases evident; the liquid condensed phase shows measurably lower friction at low loads than the liquid expanded phase, demonstrating that lower friction is associated with higher molecular packing density. However, the films exhibit the same frictional response at higher loads, indicating that compressed forms of both phases are tribologically equivalent. For FOTAS monolayer interfaces, fluorination increases friction at most loads, in agreement with measurements of micromachined interfaces. We find that frictional variation, as well as overall friction and adhesion for monolayer-coated tips are significantly reduced as compared with uncoated tips. Thus, the behavior of uncoated tips is highly dependent on the scanning history. This has wider importance for the acquisition of reproducible AFM nanotribology measurements in general, and strongly suggests that AFM researchers should strive to characterize and control the chemistry and structure of their tips to obtain meaningful measurements. We acknowledge Robert Ashurst for preparing the OTS samples, and Maarten de Boer and Alex Corwin for providing the FOTAS samples and microscale friction coefficients.

4:40pm **NS1-MoA9 The Observation of Nanoscale Melting at Sliding Interface, S.M. Lee, J. Krim**, North Carolina State University

Tribological phenomena occurring at buried interfaces undergoing shear are extremely difficult to characterize experimentally, especially since the characterizations must ideally be performed at both atomic length and time scales. We report here one such investigation, involving a scanning probe tip sliding along the metal film electrode of a quartz crystal microbalance (QCM). The atomically sharp STM tip allows the generation of the nano-scale interface area while the sharp resonance of QCM allows measurement of the interaction forces applied to its surface. This in turn yields fundamental information on energy dissipation mechanisms associated with the sliding. For a W-tip sliding along a copper surface, we have observed nano-scale melting that is attributable to the rubbing action of the tip. As the rubbing velocity at the interface increases, the frequency shift converted from the positive to the negative when the interface area melts. Additionally, QCM amplitude shifts are enhanced by ~ 5 times upon melting of the interface. This observation implies that the nano-scale local temperature can be controlled by the rubbing velocity at the film-tip interface. And the temperature rise by rubbing can easily go over 1000°C, since the melting point of copper is 1084.62°C. The experimental results will be discussed with in the context of an extended Laschitsch and Johannsmann (LJ) model. @footnote 1@ @FootnoteText@ @footnote 1@ B. Borovsky, J. Krim, S. A. Syed Asif, and K. J. Wahl, J. Appl. Phys., 90, 6391 (2001) @footnote \*@ This work has been supported by the DOE and the AFOSR Extreme Friction MURI program.

5:00pm **NS1-MoA10 Quantitative Elastic and Electromechanical Imaging: The Probe Dynamics of Vector Piezoresponse Force Microscopy, S. Jesse, A.P. Baddorf, S.V. Kalinin**, Oak Ridge National Laboratory

Piezoresponse Force Microscopy (PFM) is a nanoscale probe of the local coupling of electronic and mechanical properties, including domain imaging, polarization switching, hysteresis measurement, and orientation imaging of ferroelectric and piezoelectric materials. The image formation mechanism in PFM is controlled by the voltage dependent mechanics of the tip surface junction and the dynamics of the cantilever. A detailed analysis of the nanoscale tip-surface junction electromechanics junction shows that, for a conductive tip, the PFM signal is independent of tip shape, as in case for Atomic Force Acoustic Microscopy (AFAM). We analyze the frequency and DC bias dependent dynamic response of vector PFM, in particular, the transmission of vertical, lateral, and longitudinal surface vibrations to the tip, using modeling and 2D frequency-bias spectroscopy. We demonstrate that for an electrical tip excitation, the contact resonances are determined solely by the elastic properties of the material. Therefore, the tracking of contact resonance frequency permits local mechanical characterization, absent the numerous stray resonances inherent to piezo-actuators used in AFAM. The frequency dispersion of the nulling bias, the DC bias at which the measured response to AC excitation is zero, yields a measurement of electrostatic vs. electromechanical contrast. The differences between transduction for vertical and in-plane response components are analyzed. It is shown that lateral PFM imaging is optimal at low frequencies, while vertical PFM is best at high frequencies where dynamic stiffening reduces the electrostatic and longitudinal contributions. Finally, we discuss the measurements of all three components of the electromechanical response vector using a single PFM scan. Implications for molecular orientation imaging are also discussed. Research was performed as a Eugene P. Wigner Fellow (SVK) at ORNL, managed by UT-Battelle, LLC under DOE contract DCE-AC05-00OR22725.

## Nanometer-Scale Science and Technology

### Room 210 - Session NS2-MoA

#### Nanometer Scale Assembly

**Moderator:** D.W. Carr, Sandia National Laboratories

2:00pm **NS2-MoA1 Seeing SAMs, R.G. Nuzzo**, University of Illinois, Urbana-Champaign

**INVITED**

We have begun a new program that exploits optics as a tool for exploring complex forms of surface chemistry. In this talk, I will describe the progress made in our recent work in this area, one that exploits the use of SAMs in several areas of technology. Of particular interest in this regard is the development of new SAM-based assembly systems-and chemistry for their modification-that allows their use as a platform for array-based proteomic assays. I will highlight in this presentation recent work that has led the development of new protocols-ones exploiting assembly, surface modification, soft lithography, and microscopy-that possess considerable potential for chemical sensing. The enabling of label free detection of protein binding events using non-spectroscopic methods of detection based on new imaging protocols will be discussed. The hope for SAMs, in this context then, is to demonstrate that seeing is believing.

2:40pm **NS2-MoA3 Directed Assembly and Separation of Self-Assembled Monolayers Via Electrochemical Processing, T.J. Mullen, A.A. Dameron, J.R. Hampton, P.S. Weiss**, The Pennsylvania State University

We have directed separation in self-assembled monolayers (SAMs) on Au{111} using electrochemical desorption and characterized them with scanning tunneling microscopy (STM) and voltammetry. Separated domains of 1-dodecanthiolate were created by solution insertion into 1-adamantanethiolate SAMs. The adamantanethiolate domains were selectively desorbed by applying a reductive potential. Subsequently, the samples were immersed in 1-octanethiol solution, thereby producing SAMs with separated domains of dodecanthiolate and octanethiolate. We have investigated the molecular order of each lattice type with STM. The apparent height difference in the STM images and the two distinct cathodic peaks observed with voltammetry indicate distinct separated domains. The fractional coverages of each lattice before and after electrochemical desorption were calculated using both STM images and voltammograms. Using this electrochemical process, high-resolution chemically patterned surfaces with application in areas ranging from microelectronics to biocompatible systems have been assembled and characterized with molecular precision.

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3:00pm **NS2-MoA4 AFM Investigation of the Growth of Self-Assembled MOSUD Layers**, T.Y. *Shih*, B.E. *Koel*, A.A.G. *Requicha*, University of Southern California

Designed fabrication of structures on a nanometer scale often requires progress in the efficiency and control in deposition of self-assembled monolayers, especially in an approach that we have called layered nanofabrication (LNF). We report results demonstrating controlled growth of layers of (10-carbomethoxydecyltrimethylchlorosilane) MOSUD that are used for embedding and planarizing patterns of Au nanoparticles. These studies of the growth of self-assembled monolayers of MOSUD extend previous investigations of modification of silicon surfaces by silane adsorption. In particular, we studied the influence of an anchor layer for stabilizing the Au nanoparticles. Atomic force microscopy (AFM) was used ex-situ to characterize the formation and quality of self-assembled mono and multilayers. In addition, ellipsometry was used to monitor the MOSUD film thickness and characterize the film growth mode. Growth of layers with a uniform packing and constant height could be obtained and the film thickness could be increased without covering the Au nanoparticles.

3:20pm **NS2-MoA5 Submicron Dispersions from Urea-Based Liquid Crystalline Phases**, C. *Fong*, CSIRO Molecular Science, Australia; J. *Booth*, RMIT School of Applied Sciences, Australia; C.J. *Drummond*, I. *Krodziewska*, D. *Wells*, P.G. *Hartley*, CSIRO Molecular Science, Australia

Surfactant self assembly phases such as micelles, vesicles / liposomes, and lyotropic mesophases are of technological importance as carriers for cosmetic formulations, as drug delivery systems, and as protein crystallisation media. Lyotropic mesophases offer particular advantages since under certain conditions they are robust to dilution, temperature and composition. The three dimensional structure also enhances solubilisation of hydrophilic and/or hydrophobic moieties when compared to their liposomal analogues. There are currently a limited number of materials which exhibit dilutable mesophase behaviour. Our aim was to design surfactants capable of self assembling into higher order surfactant liquid crystalline phases, which would be stable to dilution over a broad temperature range. In this study we have explored the urea based surfactants since the conventional wisdom suggested that this class of compounds was unable to form liquid crystalline phases. This work negates this long held view and demonstrates for the first time that surfactant mesophases with the urea head group are favoured by highly splayed hydrophobes with exaggerated cross sections. Hydrophobes such as hexahydrofarnesyl and phytanyl were successful in promoting room temperature inverse hexagonal phases which are stable against dilution and robust for a large temperature and composition regime. The current synthesis strategy has therefore more than doubled the previously known numbers of compounds with these properties. Colloidal dispersions of the bulk inverse hexagonal phase were prepared with average particle size < 300 nm. These nanoparticles have much reduced viscosities over the bulk phase with high surface area and the benefit that the bulk structure has been preserved. Significantly, they are of a suitable size range for applications such as intravenous drug delivery or bioremediation.

3:40pm **NS2-MoA6 Nanometer-scale Structures Created using Molecular Self-Assembly for Building Blocks and Components**, M.E. *Anderson*, C. *Srinivasan*, R. *Jayaraman*, E.M. *Carter*, M.W. *Horn*, P.S. *Weiss*, The Pennsylvania State University

Molecular self-assembly plays an important role in the development of many nanolithographic techniques acting as building blocks and/or an active components for nanometer-scale devices. We have utilized self-assembled multilayers in conjunction with conventional lithography to create metal electrode structures with precise proximal placement in the 10-50 nm regime. By controlled placement and thickness of these multilayers (building blocks), the spacing between the electrodes can be fabricated with single nanometer resolution. Much effort has gone into developing the lithographic process steps to create precise nanometer-scale gaps reproducibly with electrical integrity. We will present methods relevant to the processing parameters and data regarding the electronic characterization of these nanogaps. The optimization of lithographic processes compatible with self-assembly has opened a novel avenue for directed chemical patterning of multi-component self-assembled films. The multilayers themselves are interesting complex nanometer-scale materials; studies are underway to understand and to manipulate their formation and electrical properties. We continue to push this technology toward architectures relevant for device fabrication; these techniques will be discussed. A. Hatzor and P.S. Weiss, Science 291, 1019 (2001). M. E. Anderson et al., Journal of Vacuum Science and

Technology B 20, 2739 (2002). M. E. Anderson et al., Journal of Vacuum Science and Technology B 21, 3116 (2003).

4:00pm **NS2-MoA7 Electric Nanocontact Lithography to the Directed Self-Assembly of Nanoparticle Based Devices**, C.R. *Barry*, A.M. *Welle*, U. *Kortshagen*, S. *Campbell*, H.O. *Jacobs*, University of Minnesota

The first part of this talk will review recent results in the area of Electric Nanocontact Lithography while the second part will discuss the use of electrostatic forces to direct the assembly of nanomaterials. First we report on a programmable, reconfigurable, printing approach for parallel nanofabrication of three different types of structures: patterns of charge, oxide, and e-beam sensitive resist. Our approach that we refer to as Electric Nanocontact Lithography (ENL) is based on previous knowledge in the area of conducting scanning probe lithography which uses a conducting probe to electrically expose and modify a surface. ENL makes use of the same physical principles; however, instead of using a single electrical point contact, we use programmable electrical nanocontacts of different size and shape to expose a surface. In the second part we report on a novel directed self-assembly process to assemble nanoparticle based devices. Nanoparticles are considered potential building blocks for the fabrication of future devices. The use of nanoparticles and nanomaterials in general, however, requires novel assembly concepts. The concept that we present is based on electrostatic interactions. In particular we demonstrate directed self-assembly of nanoparticles onto charged surface areas (receptors) with 40 nm resolution. A liquid-phase assembly process where electrostatic forces compete with disordering forces due to ultrasonication has been developed to assemble nanoparticles onto charged based receptors in 10 seconds. A gas-phase assembly process has been developed that uses a transparent particle assembly module to direct and monitor the assembly of nanoparticles from the gas phase. A process is also being developed to enable the patterning of any organic and inorganic nanomaterials with sub 100 nm resolution. First patterns of bio-molecules will be presented. Currently, the electrostatically directed assembly of sub 10 nm sized proteins, 10 - 100 nm sized metal, 40 nm sized silicon nanocubes, and 30 nm - 3000 nm sized carbon nanoparticles has been accomplished. The application to nanoparticle devices will be discussed and first results on a nanoparticle transistor will be presented.

4:40pm **NS2-MoA9 Self-Assembly Activated by Molecular Motors**, H. *Hess*, University of Florida; J. *Clemmens*, University of Washington; C. *Brunner*, ETH Zurich, Switzerland; R. *Doot*, University of Washington; S. *Luna*, ETH Zurich, Switzerland; K.-H. *Ernst*, EMPA Duebendorf, Switzerland; V. *Vogel*, ETH Zurich, Switzerland

In molecular self-assembly, the transport of the interacting parts is typically diffusive, and thermal forces prevent the mismatched assembly of non-complementary parts. This situation has serious disadvantages: Diffusive transport slows as building blocks become larger, thermal forces are distributed over a wide range which is difficult to adjust, and thermal forces strain even correctly assembled connections. Active transport on a molecular scale, for example powered by biomolecular motors, can overcome these disadvantages and provide strong, tunable, and directed forces which facilitate the ordered assembly of supramolecular structures. Furthermore, the assembled structures can be under internal strain and internally ordered without representing a minimum energy configuration. As a consequence of the transport properties of the system a high degree of long-range order can emerge. We experimentally demonstrated such a self-assembly system relying on active transport of functionalized microtubules by kinesin motor proteins.

5:00pm **NS2-MoA10 Directed Assembly and Real-Time Electrical Detection of Nanowire Bridges**, L. *Shang*, M. *Marcus*, J. *Streifer*, B. *Li*, R.J. *Hamers*, University of Wisconsin-Madison

We have explored the use of dielectrophoretic manipulation combined with biomolecular recognition to control bridging of individual metallic and semiconducting nanowires across micron-sized electrical gaps. While dielectrophoretic manipulation is only temporary, more permanent assembly can be achieved using biomolecular recognition. For example, while biotin-modified nanowires interact only weakly with bare Au electrodes, they bind strongly to avidin-modified electrodes. The bridging of a nanowire across the gap can be detected electrically even though the nanowire is spaced away from the gold contact by the biomolecular

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contact. We have developed a novel method for achieving real-time monitoring of nanowire bridging events, using one AC electric field to manipulate the wires and a second field to measure the changes in electrical response induced by nanowire bridging. Because the change in electrical response is primarily capacitive, detection of bridging events is most sensitively achieved at higher frequencies, on the order of 1 kHz-100 kHz. At a fixed measurement frequency, we observe a step-like increase in current when a nanowire bridges the electrodes. Individual silicon and metal nanowires can be detected visually as well as electrically, allowing visual confirmation of the origin of the electrical response.

## Thin Films

### Room 306 - Session TF+NS-MoA

#### Focused Beam Processing & Fabrication

**Moderator:** J.D. Fowlkes, University of Tennessee

#### 2:00pm TF+NS-MoA1 Beam-Induced Nano-Structuring for Advanced Mask Repair, *T. Liang*, Intel Corporation **INVITED**

Photomask repair is a process of editing local pattern structures by adding or removing materials in order to restore a defective mask to good lithographic condition and, in many instances, it is an enabling step for yielding a defect-free mask. Beam-induced nano-structuring has been developed for such process with the use of photons, ions and electrons. However, it has become ever more challenging to repair advanced photomasks because of the limited extendability of these technologies to meet the critical defect specifications and tight edge placement. Specifically, the use of aggressive optical proximity correction structures, resolution enhancement techniques, such as phase-shifting, and entirely new types such as EUV reflective masks has placed a great need for stringent lateral and vertical dimensional control. A capable repair process removes the defect with sufficient placement precision while at the same time preserves the optical integrity of the repaired site. This essentially requires also a damage-free process. Mask shops have put ever increasing emphasis and effort in mask repair at the back end of the production line to fix every defect possible in order to restore an otherwise defective mask. This invited talk will present an overview of advanced mask repair and the lithographic requirements, followed by an assessment of four repair technologies by comparing their respective uniqueness and limitations. The discussion of underlying mechanisms for different repair processes will provide an insight to the fundamental capabilities and ways for further improvements. Detailed descriptions will be given for examples representing binary Cr-on-glass, phase-shifting and EUV masks including repair qualification. I will present our recent progress in electron beam mask repair development and discuss future directions in mask repair using nano-structuring technologies to support the aggressive lithography roadmap

#### 2:40pm TF+NS-MoA3 Electron Beam Induced Processing Techniques for Advanced Lithography Mask Repair, *D.A. Smith*, University of Tennessee, Knoxville; *J.D. Fowlkes*, University of Tennessee, Knoxville, US; *T. Liang*, Intel Corporation; *P.D. Rack*, University of Tennessee, Knoxville

Producing defect-free photomasks for semiconductor applications is a critical and challenging operation. Enabling nano-processes are being developed for mask repair to meet the defect requirements for advanced 193nm and EUV lithography. To this end, we are investigating electron beam induced deposition (EBID) and etching (EBIE) techniques for mask repair involving material deposition and removal, respectively. The EUV masks are typically composed of multi-layer Mo-Si on a quartz-like substrate, capped with a Ru etch stop layer with an overlying TaBN absorber layer. For material removal, an etchant vapor such as XeF<sub>2</sub> or NF<sub>3</sub> is flowed over the mask surface in an SEM in the presence of an electron beam. The electron beam interacts with the etchant gas to produce an electron induced etch effect, allowing material removal at a controlled rate with nano-scale precision. Repair operations involving deposition are typically carried out with a precursor gas such as cyclopentadienylplatinum (IV)-trimethyl (CpPtMe<sub>3</sub>) which dissociates under an electron beam and adsorbs to the substrate. This presentation will demonstrate the results of a study involving the optimal operating conditions for controlled etching and deposition, including an analysis of the sidewalls, roughness, and spontaneous etching. Monte-Carlo based computer simulations of the material deposition will also be employed to describe the effects of varying system parameters such as operating voltage, gas pressure, current and time.

3:00pm TF+NS-MoA4 Reduction of Laser-Induced Roughness in a-Si:H Surfaces for Vacuum Compatible Lithography, *R.N. Jacobs*, US Army RDECOM CERDEC Night Vision and Electronic Sensors Directorate, 22060; *E.W. Robinson*, *A.J. Stoltz*, *J.H. Dinan*, US Army RDECOM CERDEC Night Vision and Electronic Sensors Directorate; *L.G. Salamanca-Riba*, University of Maryland, College Park

A vacuum compatible lithography technique has recently been demonstrated, whereby amorphous hydrogenated silicon (a-Si:H) films are used as a resist. Following plasma deposition of the a-Si:H film, poly-Si patterns are generated on the surface by excimer laser exposure through a projection mask. Development is then carried out by hydrogen plasma etching for which etch selectivities of over 1000:1 have been achieved for a-Si:H and poly-Si regions. However the rms roughness induced by excimer laser irradiation can be well over 10 times that of the as-deposited a-Si:H surface. This is problematic because the roughness may be transferred to underlying device layers during subsequent pattern transfer plasma etching. We have developed a step-wise laser irradiation procedure that results in a reduction of surface roughness by an order of magnitude to a level of ~1 nm (rms). This value is approximately equal to the surface roughness in the as-deposited a-Si:H film. The irradiation procedure uses multiple pulses with progressive increases in the energy density, in contrast to single high energy density pulses used previously. Transmission electron microscopy and Fourier transform infrared spectroscopy are used to understand and confirm the mechanism behind this process. Our data suggests that the observed reduction in roughness is due both to smaller grain sizes and to a slow rate of H removal from the film surface. While useful for a-Si:H vacuum-lithography processing, our results also hold significance for other applications of laser processed a-Si:H, even where different film properties may be desired. @FootnoteText@ @footnote 1@R.N. Jacobs, A.J. Stoltz, J.H. Dinan, and L. Salamanca-Riba, J. Vac. Sci. Technol. B, 22 1071 (2004).

#### 3:20pm TF+NS-MoA5 Maskless, Direct-Write Nanolithography using Electron Beam-Induced Deposition, *S.J. Randolph*, University of Tennessee, Knoxville; *J.D. Fowlkes*, University of Tennessee, Knoxville, US; *P.D. Rack*, University of Tennessee, Knoxville

Several groups have investigated electron beam-induced deposition (EBID) as a nanoscale direct-write fabrication technique. The EBID process is similar to focused ion beam processing; however deleterious damage associated with ion implantation is mitigated when using an electron beam. Our group has been investigating this technique as a tool for rapid nanoscale device prototyping as well as for device and lithography mask repair. More recently, we have investigated EBID as a technique to be coupled with a massively parallel electron beam lithography concept-the so-called Digital Electrostatic E-beam Array Lithography (DEAL) system. The goal is to develop an alternative ultra-thin resist scheme for the DEAL low energy electron beam lithography system. We have developed a single layer and bilayer resist scheme using a tetraethylorthosilicate (TEOS) and tungsten hexafluoride precursors to deposit SiO<sub>2</sub> and tungsten resist layers. In this presentation our experimental procedure and EBID system will be described and the DEAL lithography concept briefly reviewed. The fundamental EBID process will be explained, and we will describe the relevant EBID parameters that affect the single and bilayer EBID resist schemes. The effects of secondary, backscattered, and forward scattered electrons on the resolution and exposure requirements will also be explained, and dose requirements for optimum exposure as a function of beam energy will be illustrated. Pattern transfer of sub-100 nm features requires excellent control of etch selectivity and profile control. The effects of RIE parameters such as pressure, power, and chemistry as they are related to etch selectivity and profile will also be presented.

#### 3:40pm TF+NS-MoA6 Focused Ion Beam Sculpting of Curved Shapes in Metals and Amorphizable Solids, *D.P. Adams*, *M.J. Vasile*, Sandia National Laboratories

We describe how focused ion beams can be used to sculpt predetermined micron-scale, curved shapes in a variety of initially planar solids. Using a vector-scanned focused Ga ion beam system, we sputter different shapes including hemispheres, paraboloids and sine waves having dimensions from 1-50 microns. Ion sculpting is accomplished by varying pixel dwell time (i.e., dose) within individual boustrophedonic scans. The pixel dwell times determined for a given shape account for the material-specific, angle-dependent sputter yield, Y(theta), the beam current and the ion beam spatial distribution. We highlight new results that show how this sculpting technique can be applied to a large set of materials. Using appropriate sets of dwell times, we sculpt semiconductors (Si, C) amorphized by the high-energy beam, and single crystal metals (Au, W)

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that remain crystalline with ion exposure. The ion-milled features, in most cases, match the intended shape with milled feature depths repeatedly within 5% of intended values. Finally, we describe techniques that minimize the deleterious effects of redeposition. This includes a method that determines the optimal range of pixel dwell times and research of gas-assisted FIB sculpting techniques.

4:00pm **TF+NS-MoA7 Focused Electron and Ion Beam Processing and Fabrication**, *J. Melngailis*, University of Maryland; *I. Utke*, EMPA, Thun, Switzerland; *P. Hoffmann*, EPFL, Lausanne, Switzerland **INVITED**

Beams of electrons and ions are now fairly routinely focused to dimensions in the nanometer range. Since the beams can be used to directly alter material, they represent direct nanofabrication tools. We will focus here on direct fabrication rather than lithography which is indirect in that it uses the intermediary of resist. In the case of both ions and electrons material addition or removal can be achieved using precursor gases. In addition ions can also alter material by sputtering (milling), by damage, or by implantation. Many material removal and deposition processes employing precursor gases have been developed for numerous practical applications, such as mask repair, circuit restructuring and repair, and sample sectioning. In many cases the minimum dimensions at which these processes can be realized are considerably larger than the beam diameters. The detailed atomic level mechanisms responsible for the precursor gas activation have not been studied in detail in most cases. We will review the state of the art and level of understanding of direct ion and electron beam fabrication and point out some of the unsolved problems. We will present recent results on beam deposited contacts to carbon nanotubes, nanowires and nanofibers.

4:40pm **TF+NS-MoA9 Sub-Micron Features Using a Focused Ion Beam and Novel Resist Structures**, *M.H. Ervin*, U.S. Army Research Laboratory

Typically, sub-micron features are written with an e-beam lithography tool. However, e-beam tools are very expensive and availability is an issue. A method for writing sub-micron features (e.g. short gate-length contacts) using a focused ion beam (FIB) is described. It is not just a matter of milling a pattern into any resist. To avoid sputtering the substrate, the mill has to be incomplete, and the partially milled resist may be cross-linked due to the ion irradiation damage. The cross-linked resist is then resistant to solvent development or plasma ashing. This might make it useful as a negative resist, but for positive resist applications write times would be problematic. Instead, two metal films are deposited on top of the resist. The top layer (e.g. Au) is cut through by the FIB to form the pattern, and the underlying layer (e.g. Ti) is the backstop layer which prevents the FIB Ga ions from penetrating through to the resist. The backstop layer is then selectively wet etched. The etch is allowed to produce an undercutting of the pattern layer features for good lift-off. Similarly, the underlying resist can be plasma ashed to expose the substrate. One has to be careful with the ashing temperature to prevent blistering of the resist/metal layers. Subsequent metallization and lift-off can produce features below a quarter micron. Of course, if the substrate is vulnerable to resist solvents, one could omit the resist entirely if the backstop layer can be used to provide lift-off at the end. Another potential advantage for sensitive substrate materials, is that the substrate is never irradiated with ions or electrons as is the case in e-beam lithography.

## Magnetic Interfaces and Nanostructures

### Room 204 - Session MI+NS-TuM

#### Magnetic Nanostructures, Surfaces, and Interfaces

**Moderator:** R.A. Lukaszew, University of Toledo

8:20am **MI+NS-TuM1 Size Effect and Chemical Ordering in [FePt]<sub>x</sub>Cr<sub>1-x</sub> Nanoparticles**, C. Srivastava, G.B. Thompson, J.W. Harrell, D.E. Nikles, University of Alabama

FePt nanoparticles have received considerable attention as candidate materials for achieving ultra-high areal storage densities. Recent experimental and modeling studies have suggested that FePt must achieve a critical size near 4 nm for the chemically ordered L1<sub>0</sub> phase to be stable. We report the use of Cr in controlling the size and ordering temperature in FePt nanoparticles. Two series of [FePt]<sub>x</sub>Cr<sub>1-x</sub> nanoparticles (x = 5, 10 and 16 at. %) were chemically synthesized by a high-temperature salt-decomposition process yielding as-prepared diameters of 2 nm and 4 nm. XRD and STEM-EDS confirmed that the Cr formed a solid solution within the A1 FePt phase. Upon annealing, the as-synthesized 4 nm [FePt]<sub>x</sub>Cr<sub>1-x</sub> particles ordered at 450°C while maintaining ~4 nm size. In contrast, the as-synthesized 2 nm [FePt]<sub>x</sub>Cr<sub>1-x</sub> particles ordered at 550°C. It was noted that the initial 2 nm particles had achieved an ~4 nm sintered particle size at 550°C. Thus, the initial particle size is critical before chemical ordering can commence. Once the critical size is achieved, Cr was able to reduce the ordering temperature. The initial 4 nm FePt nanoparticles ordered at ~500°C and experienced rapid particle sintering at the onset of its ordering temperature. In contrast, the Cr alloyed nanoparticles were shown to have reduced grain growth at elevated temperatures. Magnetometry measurements of the nanoparticles indicated that the coercivity is reduced with Cr content.

8:40am **MI+NS-TuM2 Core Size Effects on Core-Shell Structured Fe/FeO<sub>x</sub> Nanoparticles**, A. Ceylan<sup>1</sup>, S. Shah, University of Delaware; K. Hasanain, Quaid-e-Azam University, Pakistan

In this study, we examined the particle size dependence of magnetic properties of Fe/Fe-oxide core/shell structured nanoparticles. Inert gas condensation has been used to synthesize the nanoparticles. Structural and magnetic properties of the samples have been investigated by various techniques. It has been observed that the effect of AFM shell can be relatively enhanced by decreasing the core size such that much higher exchange bias than larger particles is obtained. Furthermore, as an indication of pinned spins, which are attributed as one of the reasons of higher exchange bias field, at the AFM-FM interface, a vertical shift at the hysteresis loops has also been observed in small nanoparticles. Room temperature magnetic measurements have revealed that small particles show superparamagnetic behavior. However, the system does not reach to saturation even at 4T which indicates high anisotropy. These observations reveal that superparamagnetic behavior is related to the small size rather than a lack of anisotropy.

9:00am **MI+NS-TuM3 Magnetic Field Effects in Ferromagnetic/Organic Hybrid Structures**, J. Shi, University of Utah **INVITED**

Spin injection/detection and coherent spin transport are key ingredients in Spintronics, which were first demonstrated in the giant magnetoresistance or GMR effect in all-metal systems. In this talk, I will present our recent progress using organic semiconductors. In spin valves consisting of two ferromagnetic layers (La<sub>2</sub>/3Sr<sub>1</sub>/3MnO<sub>3</sub> or LSMO and Co) and an organic semiconductor spacer (Alq<sub>3</sub>), we have successfully shown electrical spin injection/detection and coherent spin transport through the GMR effect. In addition, we have also found a high-field magnetoresistance effect in these structures. Our work shows that this high field effect originates from the magnetic field enhanced carrier injection due to the anomalous Fermi level shift in double exchange ferromagnets such as LSMO.

9:40am **MI+NS-TuM5 Magnetic Stripes at the Spin Reorientation Transition of a Magnetic Thin Film**, Z. Qiu, University of California at Berkeley **INVITED**

One fundamental issue in magnetic nanostructure research has concerned the presence of magnetic long-range order in a two-dimensional (2D) magnetic system. It has long been established that an isotropic 2D Heisenberg system does not carry long-range order at nonzero

temperature. The magnetic order observed in ultrathin films is usually attributed to the existence of magnetic anisotropy. In an ultrathin film with perpendicular magnetocrystalline anisotropy, the spin direction could exhibit the so-called spin reorientation transition (SRT) from perpendicular to the in-plane direction of the film. At the SRT point, the perpendicular magnetocrystalline anisotropy is balanced out by the dipolar shape anisotropy and the system approaches to an isotropic Heisenberg system. Thus an investigation of the magnetic phase near the SRT point is expected to reveal the magnetic origin of 2D magnetic systems. In this talk, I will present an overview and our most recent experimental result on this subject. Using photoemission electron microscopy (PEEM) to do element-specific measurement, we studied the SRT in magnetically coupled sandwiches. We show that a crossover from the anisotropy length to the dipolar length governs the formation of the magnetic stripe phase.

10:20am **MI+NS-TuM7 Inhomogeneous Magnetic States in Gd/Fe and SmCo/Fe Nanolayers**, D. Haskel, Argonne National Laboratory **INVITED**

The reduced size and dimensionality of layered magnetic nanostructures enhances the role that surfaces and interfaces play in determining their magnetic structures. This can result in inhomogeneous magnetic states, wherein the local magnetization varies with distance away from surfaces or interfaces. Using hard x-ray magnetic circular dichroism and x-ray resonant magnetic scattering, we explore the nature of such inhomogeneous states in Gd/Fe metallic multilayers and SmCo/Fe spring magnets. In collaboration with Y. Choi, J. Lang, D. Lee, G. Srajer, C. Kmety, J. Pollmann, C. Nelson, R. Camley, J. Meersschaut, J.S. Jiang, S.D. Bader Work at Argonne is supported by the U.S. Department of Energy, Office of Science under contract No. W-31-109-ENG-38.

11:00am **MI+NS-TuM9 Magnetic Quantum Tunneling and Relaxation in Molecular Magnets**, L.J. de Jongh, A. Morello, F. Luis, M. Evangelisti, F. Mettes, Leiden University, The Netherlands **INVITED**

For strongly anisotropic magnetic clusters, like Fe<sub>8</sub> and Mn<sub>12-ac</sub>, quantum tunneling of the cluster spins below their blocking temperatures T<sub>B</sub> of a few K has been observed by several groups, and is expected to be triggered by the dynamic hyperfine interaction of the cluster spins with their surrounding nuclear spins, as recently predicted by Prokof'ev and Stamp.<sup>1</sup> In that model, however, the ensuing relaxation of the electron spins is towards the nuclear spin system, leaving open the question if and at what stage, by which mechanism and at what rates the nuclear and electronic spin systems relax to the lattice phonons. That such phonon relaxation channels are indeed operative even deep in the quantum regime, could be proven unambiguously by our measurements of the specific heat contributions of both nuclear and electronic spin systems at temperatures T << T<sub>B</sub>.<sup>2-4</sup> Nuclear Magnetic Resonance is the technique of choice for studying the nuclear spin-dynamics involved in these processes. In addition, since the nuclear spins have to relax to the lattice via the electron spin system, also the dynamics of the latter is probed. In the talk such data (taken down to 20 mK), will be presented<sup>5</sup> and analysed in the light of earlier developed theories for dynamic nuclear polarization and nuclear relaxation by paramagnetic impurities in insulating compounds, leading to new insights in the quantum relaxation mechanisms in molecular nanomagnets.<sup>6</sup> <sup>Footnote 1</sup> N.V. Prokof'ev and P.C. Stamp, Phys. Rev. Lett. 80, 5794 (1998). <sup>Footnote 2</sup> F.L. Mettes et al. Phys. Rev. B64, 174411 (2001); Phys. Rev. Lett. 85, 4377 (2000). <sup>Footnote 3</sup> M. Evangelisti et al. Phys. Rev. Lett. 93, 117202 (2004). <sup>Footnote 4</sup> A. Morello et al. Phys. Rev. Lett. 90, 017206 (2003). <sup>Footnote 5</sup> A. Morello et al. Phys. Rev. Lett. 93, 197202 (2004).

## Nanometer-Scale Science and Technology

### Room 210 - Session NS+EM-TuM

#### Nanoscale Electronic Devices & Detection

**Moderator:** P. Grutter, McGill University

8:20am **NS+EM-TuM1 Single Electron Spin Detection in Si-Based Semiconductor Structures**, H.W. Jiang, UCLA **INVITED**

Several schemes for electron spin based qubit in compound semiconductor structures have been proposed recently for quantum information processing. In order to physically implement any of the proposals, it is essential to measure the state of a single spin. Towards this end, we have done a sequence of measurements to probe the spin state of a single paramagnetic spin center adjacent to a sub-micrometer silicon metal-oxide-semiconductor field-effect transistor. Stochastic switching between

<sup>1</sup> Falicov Student Award Finalist

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two discrete values of channel current, known as random telegraph signal (RTS), has been used as a tool to sense the single spin. Magnetic-field-induced Zeeman splitting of the single spin center was measured. Using microwave radiation, we have observed that the statistical distribution between the two states changes when the electron spin resonance condition is matched. Experiments with a series of pulsed gate voltages showed promise of using the field effect transistor channel for single-shot spin state read-out. Our ongoing effort of single spin measurements in electrostatic quantum dots in a Si/SiGe 2D electron gas will be described.

9:00am **NS+EM-TuM3 Few Electron SiGe Quantum Dots**, *L.J. Klein, S. Goswami, K.A. Slinker, S.N. Coppersmith, D. Savage, M.G. Lagally, M.A. Eriksson*, University of Wisconsin

Spins in silicon quantum dots are promising qubits for quantum information processing. Here we present an approach to combine trenchline and metal gates to fabricate quantum dots in modulation doped Si/SiGe heterostructures. Electron-beam lithography and reactive ion etching are used to define single and tunnel coupled double dots. Both Schottky and in-plane two-dimensional electron gas gates are used. Transport measurements at 0.2 K for the single and tunnel coupled double dots show Coulomb blockade with single electron charging. For the double quantum dots a transition from a single to split peaks are observed as voltages applied to the gates became more negative. A transition is observed from a large single dot to two tunnel coupled quantum dot with a well defined tunnel coupling between pairs of quantum dots. The tunnel coupling between the dots is determined by the width of the channel between the dots. To achieve a higher control of the tunnel coupling between the dots we integrate metal gates on the top of the channel in addition to side gates. The fabricated quantum structures are stable over long periods of time with minimal charge noise fluctuations. We also discuss progress towards the achievement of few electron dots using both etched and Schottky gates for electrostatic confinement.

9:20am **NS+EM-TuM4 Top-gated Quantum Dots in Silicon / Silicon-Germanium Two-Dimensional Electron Gases**, *K.A. Slinker, L. McGuire, K.L.M. Lewis, C.C. Haselby, S. Goswami, L.J. Klein*, University of Wisconsin - Madison; *J.O. Chu*, IBM Research Division, T. J. Watson Center; *M. Friesen, M.A. Eriksson*, University of Wisconsin - Madison

Electrons in silicon/silicon-germanium two-dimensional electron gas (2DEG) quantum dots are a promising architecture for spin based quantum computation. Schottky gated quantum dots allow precise tuning of electron shape and interdot coupling; however, up until now top gates on Si/SiGe heterostructures have not been used to deplete into the tunneling regime, most likely due to problems with gate leakage. We have overcome these problems by reducing the active 2DEG area into sub-micron mesas and back gating the 2DEG to tune the carrier concentration to be depleted by the top gates. We report on the depletion characteristics of these Schottky gates as well as successful Si/SiGe quantum dot architectures incorporating top gates. For one quantum dot device, an 800 nm channel is fabricated by electron beam lithography and subsequent reactive ion etching. Metal gates are deposited across the channel to define the leads of the dot, and an etch-defined side gate is used to vary the potential in the dot. The sides of dot are defined by surface depletion from the etched sidewalls. In another device, six metal gates are used to electrostatically define the dot on all sides - a set of pincher gates on each lead and two plunger gates. Properties of the dots are presented and compared.

9:40am **NS+EM-TuM5 Spin Physics in Few-Electron Quantum Dots**, *L. Kouwenhoven*, Delft University of Technology, The Netherlands **INVITED**

Few-electron quantum dots are realized in various semiconductor materials. The conventional system for transport studies is an AlGaAs/GaAs heterostructure in which quantum dots are defined by surface gates. We have studied the spin states in one and two-electron dots. The spin states are resolved in a magnetic field that splits the one-electron spin states and also the triplet states for two electrons. We manipulate the spin states using a pulse technique that allows to determine the spin of individual electrons. As a spin off we measure the spin relaxation times under various circumstances (e.g. magnetic field). The obtained time scales are in good agreement with theory based on spin-orbit and hyperfine interaction. A new class of materials are semiconductor nanowires. We have fabricated quantum dot devices in InP and InAs wires with diameters around 50 nm. We observe discrete states and resolve Zeeman splitting of the spin states in a magnetic field. In addition we have used superconducting contacts to bias the nanowires with supercurrents.

10:20am **NS+EM-TuM7 Single Spin Detection Using Magnetic Resonance Force Microscopy**, *H.J. Mamin*, IBM Research Division; *R. Budakian*, University of Illinois at Urbana-Champaign; *B.W. Chui, D. Rugar*, IBM Research Division

**INVITED**

Magnetic resonance force microscopy (MRFM) has been proposed as a method for greatly improving the sensitivity and spatial resolution of magnetic resonance imaging, perhaps even to the atomic level. In this talk, I describe recent experiments at IBM that demonstrate an important step toward this goal, namely the detection of an individual subsurface electron spin. In this technique, the spin is detected via the attonewton-scale force it exerts on a 150-nm sized magnetic tip that is attached to the end of an ultrasensitive micromachined cantilever. The spin, which is associated with a dangling bond in silicon dioxide, is manipulated by cantilever-driven cyclic adiabatic inversion, which results in a slight frequency shift of the cantilever. With this method, we were able to unambiguously detect a single spin located more than 100 nm below the magnetic tip of the cantilever and obtain a spatial resolution of 25 nm in one dimension. I will also describe recent experiments on relatively small ensembles of nuclear spins, and discuss the challenges of pushing the technique toward single nuclear spin detection. This work was supported by the DARPA-QUIST program administered through the Army Research Office.

11:00am **NS+EM-TuM9 Fabrication and Characterization of Nanolayered Electron Emitters**, *A.A. Dixit, A. Raigoza, T. Engstrom, A. Lapicki, K. Akutsu, D.C. Jacobs*, University of Notre Dame

Nanolayered electron emitters (vertical dimension  $\sim 100$  nm), based on a Metal-Insulator-Metal (MIM) architecture, are fabricated by sequential deposition of thin films. A combinatorial approach is employed to efficiently screen different materials and fabrication conditions, and an array of 24 devices is fabricated in each batch. The electrical performance of each device is characterized as a function of the voltage bias applied across the metal electrodes. The total vacuum emission of electrons exhibits a non-linear increase as a function of the applied voltage bias. The kinetic energy distribution of emitted electrons is recorded at a series of bias voltages by a hemispherical energy analyzer. The energy distribution is quasiballistic with minimal inelastic losses. A change in the applied voltage bias results in a corresponding linear shift in the position of the peak in the energy distribution. The role of defects on the electron transport mechanism is discussed.

11:20am **NS+EM-TuM10 Low Temperature Scanning Tunneling Spectroscopy on Cleaved InAs Quantum Dots**, *A. Urbietta*, IEMN, (CNRS, UMR 8520) France; *B. Grandidier, J.P. Nys, D. Deresmes, D. Stiévenard*, IEMN, (CNRS, UMR 8520) France; *Y.M. Niquet*, CEA/DRFMC/SP2M, France

InAs quantum dots (QDs) have attracted increasing attention in recent years due to their application in optoelectronic devices such as infrared solid state lasers.<sup>1</sup> Therefore, a complete knowledge of the electronic structure of the mentioned dots is essential in order to improve device design, performance and reliability. QDs are zero-dimensional structures also known as artificial atoms since they exhibit three dimensional confinement leading to atomic-like electronic states. Much effort has been devoted in the last decade to determine the characteristics of these states from both theoretical and experimental viewpoints. The spectroscopic mode of scanning tunneling microscope (STM) at cryogenic temperatures is a powerful tool to study low dimensional structures, since it enables a detailed characterization of their local electronic properties with high resolution. Actually, electron states in free-standing InAs QDs grown on n-type GaAs have been successfully investigated using this technique.<sup>2</sup> However, a complete characterization of QD-related hole states is still lacking. In this work, scanning tunneling spectroscopy at low temperatures has been used to investigate the electronic structure of cleaved InAs quantum dots growth on p-type (001) GaAs. Several peaks related to energy levels of electrons and holes confined in the dots have been observed. The experimental results are compared with tight-binding calculations of the electronic structure of similar quantum dots, which allow us to determine both the ground state and first excited states of electrons and holes. Wave function mappings have been also carried out in order to assess the symmetry of the QDs states. <sup>1</sup>Y. Qiu, P. Gogna, S. Forouhar, A. Stintz and L. F. Lester, Appl. Phys. Lett. 79, 3570 (2001). <sup>2</sup>T. Maltezopoulos, A. Bolz, C. Meyer, C. Heyn, W. Hansen, M. Morgenstern and R. Wiesendanger, Phys. Rev. Lett. 91, 196804 (2003).

# Tuesday Morning, November 1, 2005

11:40am NS+EM-TuM11 Nanometer Spaced Electrodes on Ultra Flat GaAs-AlGaAs Heterostructures for Molecular Electronics Applications, S.M. Luber, F. Zhang, S. Strobel, A. Hansen, Walter Schottky Institut, TU Muenchen, Germany; D. Schuh, Universitaet Regensburg, Germany; M. Bichler, M. Tornow, Walter Schottky Institut, TU Muenchen, Germany

Current efforts in molecular electronics both aim for novel devices as well as the fundamental understanding of the electronic transport in molecular "wires". Here one of the major challenges is the preparation of well defined electrodes which allow reliably contacting and electrically investigating molecules of a given size. We pursue a novel strategy to fabricate nanometer spaced (nanogap) metal electrodes which is based on a cleavage plane of a GaAs-AlGaAs heterostructure. This allows for a precisely predetermined spacing of the electrodes. In recent studies<sup>1</sup> we successfully fabricated, characterized and verified the electrical functionality of such nanogap electrodes. Using Molecular Beam Epitaxy (MBE) we embedded a thin (5-20nm) GaAs layer in between two AlGaAs layers. By cleaving the substrate and selectively etching the GaAs layer, the remaining AlGaAs layers are used as a support for deposited metal (Au) electrodes. This device is especially useful for measuring plenty of nanoscale objects in parallel, as the lateral size of the electrodes is defined by optical lithography. In our contribution we will report on a) first electrical investigations on thiolated  $\pi$ -conjugated aromatic molecules assembled on 5nm spaced electrodes, and b) on our recent progress to reduce the lateral electrode size to a few nanometers only. Such electrode shape will allow for the contacting of merely a few or even single nanoscale objects. The downsizing is possible by the insertion of a second MBE growth step perpendicular to the first growth direction using the Cleaved Edge Overgrowth (CEO) technique. We successfully fabricated metallized electrodes of various widths (5-50nm) and various distance (15-30nm). We investigated these electrodes by AFM and SEM and made a first electrical characterization. <sup>1</sup>SM Luber, S Strobel, HP Tranitz, W Wegscheider, D Schuh, and M Tornow, Nanotechnology 16 (2005), in press.

## Nanometer-Scale Science and Technology

### Room 210 - Session NS+BI-TuA

#### Molecular and Biological Applications of Nanostructures

**Moderator:** M.C. Hersam, Northwestern University

2:00pm **NS+BI-TuA1 Nano-Patterned Surfaces Induce Bio-Molecules Oriented Immobilization**, *A. Valsesia, P. Colpo, T. Mezzani, P. Lisboa*, EC-JRC-IHCP Italy; *M. Lejeune, F. Rossi*, EC-JRC-IHCP Italy, Italy

The immobilization of biomolecules in domains with the typical size of the nano-meter or few tenth of nano-meters is one of the most challenging issues of the actual research in the field of biosensors and biochips. In particular the ability to create nanopatterned bio-active surfaces should be addressed to improve the performances of biosensing devices and to study new fundamental problems. From the technological point of view the nano-patterned surfaces can improve or modulate the absorption of proteins, minimize their non-specific absorption, increase the active surface density. In the last few years nano-soft lithography, dip-pen lithography, nano-fountain pen lithography and colloidal lithography were able to produce nano-patterned surfaces with fouling-antifouling contrast. The selective immobilization of the biomolecules on the fouling regions was demonstrated as well as the reduction of the nonspecific absorption in the antifouling matrix. In this work we developed a nano-patterning method which combines the spontaneous formation of molecular monolayers (SAM) and plasma based colloidal lithography. By this approach we have shown that the nano-patterning resolution is not limited in principle and can be accurately controlled by the plasma processing parameters. The techniques was employed for the creation of chemical nano-patterned surfaces with 100 nm motives with a hexagonal 2-D crystalline structure, characterized by COOH terminated SAM nano-spots in a CH<sub>3</sub> terminated thiols matrix. By combining the information arising from the different characterization techniques, it was possible to demonstrate the creation of a chemical contrast with a resolution of 100 nm, without a meaningful change in the morphological properties of the surface. An effective orientation of the biomolecules immobilized on these nano-patterned surfaces was demonstrated by AFM measurements and confirmed using an ELISA antibody immobilization protocol.

2:20pm **NS+BI-TuA2 Surface Nanopatterning for the Control of Cell Behavior**, *C.M. Dekeyser, J. Marchand-Brynaert, A.M. Jonas, Ch.C. Dupont-Gillain, P.G. Rouxhet*, Université Catholique de Louvain, Belgium

Cell adhesion is mediated by proteins of the extracellular matrix, called adhesion proteins. RGD (arginine-glycine-aspartic acid) is the most widely spread peptide sequence responsible for these recognition events. It has been shown that a surface covered by adhesion proteins or grafted with the RGD sequence can induce different cell behaviors, depending on the distribution of the ligands. The aim of the work is to get a better insight into the influence on cell behavior of the distribution of ligands at the nanometer scale. This involves four aspects: creating a nanostructured surface, grafting a RGD ligand or adsorbing an adhesion protein according to defined motifs, passivating the rest of the surface with respect to protein adsorption and evaluating the cell behavior. The nanopatterns are created by means of electron-beam lithography. The challenge here is to draw small motifs (100 nm) on an area (500\*500 μm@super 2@), large enough to allow cell adhesion to be studied. This was realized by juxtaposition of patterns (143\*143 μm@super 2@) on which electron-beam lithography allowed continuous and regular lines to be drawn. In order to minimize non specific protein adsorption, the passivation of the surface is realized by self-assembly of oligo(ethylene glycol)-terminated silanes on silicon. The influence of various parameters has been examined in order to optimize the treatment in terms of cleanliness, thickness and density (AFM, X-ray reflectometry, XPS) of the obtained layer. Adsorption of different proteins is used to evaluate the inertness of the background and the selective adsorption on the patterns. RGD immobilization is realized by photografting an azide which bears an active ester able to react with the NH@sub 2@ groups of the ligand. The influence of the nanopatterned surfaces on the adhesion and spreading of neural cells will be examined.

2:40pm **NS+BI-TuA3 Enzymatic Nanofabrication: Step-wise Synthesis of DNA Scaffolds on Nanopatterned Oligonucleotide Templates**, *D. Chow, W.-K. Lee, S. Zauscher, A. Chilkoti*, Duke University

Nucleic acid nanopatterns can serve as a template for step-wise synthesis for a variety of complex molecular nanostructures and have significant

potential in materials science, molecular electronics, and biosensing. However, most nanofabrication techniques of nucleic acid scaffolds require DNA to be synthesized separately prior to self-assembly or manipulation at the nanoscale. Enzymes that can polymerize DNA are potentially useful molecular tools for the in situ synthesis of DNA scaffolds. Although these proteins are well studied and commercially available, they have not been previously exploited for enzymatic nanofabrication. This study demonstrates that terminal deoxynucleotidyl transferase repetitively adds mononucleotides to the 3' end of oligonucleotides on gold substrate nanopatterned by e-beam lithography. Without complex multi-step chemistry or biochemistry, the step-wise synthesis of DNA scaffolds leads to significant extension of DNA. This strategy can be modified to create more complex DNA nanostructures by simply replacing natural mononucleotides with unnatural ones, which serve as specific recognition sites along the single-stranded DNA. This enzyme-mediated nanofabrication methodology offers a new route to selectively dock nanoscale components of interest along the vertical direction with nanometer-level precision, and also provides a foundation for fabrication of hybrid molecular ensembles of biotic and abiotic components.

3:00pm **NS+BI-TuA4 Surface Modification and Morphological Stabilization of Silver Nanoparticles**, *V.H. Perez-Luna, A. Dalwadi, S. Lee*, Illinois Institute of Technology

Metallic nanoparticles exhibit unique optical properties due to the oscillation of surface plasmons when excited by visible light. These optical properties are shape dependent and different modes of excitation can occur for anisomeric nanoparticles (e.g. due to transversal and longitudinal oscillation of surface plasmons). Thus, the optical properties of these systems can be changed without modifying their chemical composition. A wide variety of methods for the synthesis of anisomeric metallic nanoparticles (e.g.; triangular slabs, multipods, nanorods) have been developed over the last couple of decades. However, technological applications of these systems have not been extensively implemented in spite of their great potential for surface enhanced emission of fluorescence and Raman scattering. One of the biggest obstacles is the inherent morphological instability of these systems and processing difficulties that may lead to irreversible aggregation. Surface modification of gold and silver nanoparticles with alkane thiol based self-assembled monolayers could help circumvent these problems and allow for technological applications with great potential in biodetection assays. Experimental studies will be presented illustrating the improved morphological stability and tailored properties of surface modified nanoparticles. Experimental evidence of the strong influence exerted by metallic surfaces on emission of fluorescence will be presented. The potential of surface modified Ag and Au nanorods will be discussed with particular emphasis on biological detection assays.

3:20pm **NS+BI-TuA5 Functionalization and Electrical Characterization of Vertically Aligned Carbon Nanofibers**, *K.-Y. Tse, S.E. Baker, E.A. Hindin, T.L. Clare, R.J. Hamers*, University of Wisconsin-Madison

Vertically Aligned Carbon Nanofibers (VACNFs) represent a new form of carbon with potential applications ranging from biosensing to energy storage. We have explored the electrical properties of bare and chemically-functionalized VACNFs in electrolyte solutions using electrical impedance spectroscopy and cyclic voltammetry. Electrical measurements show that the capacitance of the nanofiber forests is directly proportional to the average nanofiber length, demonstrating that the entire fiber surface is electrically active. A comparison of nanofiber forests with planar electrodes shows that the forests have approximately 7 times higher effective surface area. Measurements of DNA hybridization with DNA-modified VACNFs show a similar ratio, showing that the nanofibers have good biological accessibility. We will discuss the factors that control the electrical properties of nanofibers in electrolyte solutions, the effects of nanofiber aggregation, and prospects for the application of nanofibers for biosensing.

3:40pm **NS+BI-TuA6 Single Porphyrin Molecules as Information Storage Elements**, *H. Kim, Y. Kuk*, Center for Science in Nanometer Scale (CSNS), Korea

Redox behaviors of porphyrin molecules have been widely studied for the possible application to molecular-based information storage for two main reasons; i) they form stable radicals whose redox potentials can be tuned by the synthetic design and chelating metal ions. ii) Assembled on the substrate adequately, they exhibit considerably long charge retention times. Recently, it was shown that they can survive silicon device processing, @footnote 1@ which provides a new possibility to molecular electronics. It was, however, confirmed only for a close-packed monolayer of porphyrins to act as information storage. We separated porphyrin

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molecules both from each other and from the substrate by making a mixed self-assembled monolayer of alkanethiol-derivatized porphyrins and alkanethiols on a Au(111) surface. Alkanethiol monolayers can act as an organic insulating layer whose resistance shows approximately exponential dependence on the chain length and the HOMO-LUMO gap is about 9eV. These properties allow us to investigate more intrinsic behaviors of organic molecules attached to alkanethiol monolayers on surface. By means of scanning tunneling microscopy and spectroscopy, we identified the porphyrin groups on the insulating alkanethiol monolayer and resolved the redox states and the charge retention time of a single porphyrin molecule. @FootnoteText@ @footnote 1@ Molecular memories that survive silicon device processing and real-world operation, Z. Liu et al., Science 302, 1543 (2003).

# Tuesday Afternoon Poster Sessions, November 1, 2005

## Nanometer-Scale Science and Technology Room Exhibit Hall C&D - Session NS-TuP

### Nanometer Scale Science and Technology Poster Session

**NS-TuP1 Free-standing Nanosheets from Cross-Linked Biphenyl Self-Assembled Monolayers**, *W. Eck*, Universität Heidelberg, Germany; *A. Küller*, *M. Grunze*, Universität Heidelberg, Germany; *B. Völkel*, *A. Götzhäuser*, Universität Bielefeld, Germany

Self-assembled monolayers composed of biphenyl units are cross-linked by electron irradiation. These monolayers can be released from the underlying surface by dissolution of the substrate or by scission of the anchor group-substrate bonds. This way, free-standing nanosheets with the thickness of a single molecule and lateral dimensions in the micrometer range are obtained. Gold nanoparticles have been deposited on the sheets and successfully imaged by electron microscopy suggesting their use as substrates for microscopy applications.

**NS-TuP2 Pulse Thermal Processing of FePt Thin Films**, *A.C. Cole*, *G.B. Thompson*, University of Alabama; *R.D. Ott*, Oak Ridge National Laboratory; *J.W. Harrell*, The University of Alabama

The L1<sub>0</sub> phase of FePt is a candidate material for next generation magnetic storage because of its high magnetocrystalline anisotropy. When FePt is sputter-deposited onto an ambient temperature substrate, it adopts a metastable solid-solution face-centered-cubic phase that is superparamagnetic. A subsequent anneal is required to chemically order FePt into the L1<sub>0</sub> phase with its superior magnetic recording properties. A consequence of conventional annealing is grain growth in the film, which is detrimental to increasing areal storage density. We report the use of multiple pulsed-thermal-processing with a high density infrared plasma light source at exposure times of 100 and 250 ms to chemically order FePt films. Upon ordering, no grain growth of the 15 nm diameter columnar grains was observed in 100 nm thick specimens. As the thin film thickness was decreased, grain growth became more prevalent for similar processing conditions. Moreover, for the smaller grain sizes, we observed a strong evolution of texture upon ordering. The morphology of the films pre- and post- processing has been characterized using high-resolution TEM and XRD. Magnetometry of the samples has also been performed. The results of this work will address the consequences of pulsed-thermal-processing on phase and morphological stability at the nanometer-scale.

**NS-TuP3 Etch of Sub-Micron High Aspect Ratio Holes in a Bilayer of SU-8/PMMA Resist Stack for Photonic Crystal Devices**, *J.H. Sung*, *K.J. Lim*, *B.H. O*, Inha University, Korea; *Y.H. Choe*, LG Electronics Institute of Technology, Korea

Sub-micron hole array in a bilayer of SU-8 for core and poly-methyl-metacrylate (PMMA) for clad have been successfully etched for the fabrication of photonic crystal (PC) structures. In the PC waveguides, the etched holes need to be extended into the cladding layer to ensure the proper optical characteristics. The fabrication started from coating multiple materials on a glass substrate to form a multi-layer of hydrogen silsesquioxane (HSQ)/PMMA/SU-8/PMMA. Using a nano-patterned stamp, PC patterns are imprinted into the top HSQ layer at room temperature. After the pattern transfer by a dry etch in our inductively coupled plasma (ICP) system, Cr sputtering was followed for a lift-off process. The Cr pattern was successfully formed on the top of 1- $\mu$ m-thick SU-8 and 2- $\mu$ m-thick PMMA resist stack. Using this Cr pattern as a hard mask, sub-micron holes are etched also in the ICP etcher. Various gas chemistries are attempted to achieve vertical profiles and a high aspect ratio. The best etch conditions for a PC structure with high aspect ratio and vertical side-wall profile will be discussed.

**NS-TuP4 An Innovative Approach to Nanoscale Device Fabrication**, *E.A. Akhador*, *A.H. Mueller*, *M.A. Hoffbauer*, Los Alamos National Laboratory

A recently developed technology exclusive to LANL, called Energetic Neutral Beam Lithography/Epitaxy (ENABLE), offers exceptional opportunities for producing nanoscale structures and for synthesizing thin film materials. ENABLE utilizes reactive neutral atomic species (O and N) having kinetic energies comparable to chemical bonds strengths (a few eV) for etching very high-aspect-ratio features into polymers and for growing oxide and nitride thin films at low temperatures. Using energetic oxygen atoms, numerous nanoscale structures have been fabricated into polymer films that contain sub-100 nm features with very high aspect ratios (in some cases >35:1). For example, using a nanosphere-defined mask a

polyimide film was etched to form a periodic array of 5.4 micron tall, 250 nm diameter pillars. As a novel application, nanoscale polymer templates can be fabricated and used for growing nitride (AlN, GaN, etc.) and oxide (Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, etc.) structures. This novel fabrication approach can easily be expanded to make 2- and 3-dimensional structures and devices with multiple functionalities. The latest results utilizing ENABLE for producing photonic crystals, MEMS and NEMS devices, microfluidic channels, and novel electronic devices will be discussed.

**NS-TuP5 Compositional and Structural Characterization of Tungsten Nanostructures Produced by Electron Beam-Induced Deposition**, *K.L. Klein*, University of Tennessee & ORNL; *S.J. Randolph*, *P.D. Rack*, University of Tennessee; *M.L. Simpson*, University of Tennessee & ORNL

Electron beam-induced deposition (EBID) is an emerging technique for the synthesis of nanostructures and nanopatterning. The high degree of precision associated with EBID, (i.e. precise location, size, and shape) makes it a prime candidate for a wide variety of applications ranging from fiber tips for field emission sources to lithography mask repair strategies. Furthermore, a wide array of materials - as governed by the choice of precursor gas - can be deposited by EBID, thus adding to the versatility of the technique. As is the case with all deposition processes, it is critical to be able to control the composition and structure of the deposited material by varying simple process parameters. Thus far there has been very little characterization of the chemical composition and internal structure of EBID materials. Previous results have suggested a significant incorporation of impurities into the deposited material. The deposition conditions as well as precursor composition can impact the resulting chemical composition and nanostructural properties of the deposit. In order to better control these deposit properties, we report on the effects of beam energy, beam current, and localized precursor pressure on tungsten nanostructures deposited by EBID from a tungsten hexafluoride precursor. The results of high resolution TEM, STEM, and EDS on as-deposited tungsten nanostructures will be reported. In addition, the effects of post-deposition processes, such as thermal treatments will be discussed.

**NS-TuP6 Formation of Nanometer-scale Structures Based on a Plasma Ashing and Lift-off Technique**, *G.-S. Kim*, Sungkyunkwan University, Korea; *Y.-H. Roh*, Sungkyunkwan University, Korea, Republic of Korea

Realization of nano- and/or bio-electronic devices requires the formation of nanometer-scale structures. Recently the fabrications of structures with a nano gap dimension have been demonstrated by using advanced techniques such as electron-beam lithography, focused ion beam lithography, or advanced optical lithography. However, these techniques are very slow, and moreover require a high production cost. Recently, our group proposed the new technique to overcome a resolution limit of an optical lithography for forming nanometer-scale structures. The technique utilizes a well known and a well established processing technique known as a photoresist (PR) ashing. In this technique, the minimum linewidth can be formed by ashing the PR pattern defined by the conventional optical lithography. In this work, we further developed this technique to form the various shapes of nanometer-scale structures including the line-and-space pattern and nanometer-scale holes. In this particular case, we used a negative PR (PMER) instead of a conventionally used positive PR since the final patterns of PMER after treating the ashing process result in the high aspect ratio, reversal echelon formation and excellent property for fine patterning in general. In turn, the lift-off step that is required to form the highly aligned nanometer-scale structures can be easily followed. Based on the current investigation, we found that various types of nanometer-scale structures can be easily formed using semiconductor, metal and insulator materials. These results may open the possibilities to fabricate the unique tools for the vertical-type field effect transistors and highly aligned emitters.

**NS-TuP7 Si Nanoclusters Embedded in SiO<sub>2</sub> Layers Produced by Reactive RF Sputtering**, *E. Sanchez-Meza*, ESFM-IPN, Mexico; *A. Garcia-Sotelo*, *M. Melendez-Lira*, *A. Mendoza-Galvan*, *S. Jimenez-Sandoval*, Cinvestav-IPN, Mexico

The production of silicon nanoclusters is an active topic of research because the possibility to produce efficiently light on a silicon based material. We have taken advantage of the morphologic characteristics of the films deposited by the sputtering technique to produce silicon nanoparticles. We have grown silicon nanoclusters embedded in SiO<sub>2</sub> layers employing reactive RF sputtering. Different partial pressures of Ar/O<sub>2</sub> were employed to produce the plasma, a 99.999 % pure silicon disk was employed as target. Samples were deposited on substrates of silicon (100) and commercial glass at 400 °C. Samples were characterized

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by X-ray diffraction, atomic force microscopy and room temperature infrared, ellipsometry, photoluminescence and Raman spectroscopies. X ray diffractograms shown that samples grown on silicon present a crystalline structure while films grown on glass are amorphous. Atomic force microscopy shown in both cases the presence of ellipsoidal mounds with axis lengths around 100 nm. Raman spectroscopy presents Raman shifts located at 470 cm<sup>-1</sup> due to Si-nanoclusters. Ellipsometry results indicated, in good agreement with the growth procedure, that sample structure correspond to a a-Si+c-Si layer of around 10 nm embedded in layers of SiO<sub>2</sub>. Our results shown that reactive sputtering has a good potential to produce, at low cost, uniform nanoclusters. @FootnoteText@ @footnote 1@work partially funded by CONACyT-México.

**NS-TuP8 Recent Lithography Results from the Digital E-beam Array Lithography (DEAL) Concept, W.L. Gardner, L.R. Baylor, Oak Ridge National Laboratory; X. Yang, University of Tennessee; R.J. Kasica, D.K. Hensley, Oak Ridge National Laboratory; S.J. Randolph, R.B. Rucker, D.C. Joy, P.D. Rack, S. Islam, B. Blalock, University of Tennessee**

The Digital E-beam Array Lithography (DEAL) concept is currently under development at Oak Ridge National Laboratory (ORNL). This concept incorporates a digitally addressable field emission array built into a logic and control integrated circuit to function as the write head for a massively parallel e-beam lithography tool. Each field emission device comprises three electrodes separated 1 μm from each other by SiO<sub>2</sub>. The first electrode functions as the cathode and contains a single vertically aligned carbon nanofiber as the field emitter. The second is an extraction aperture and the third is an aperture functioning as an electrostatic focusing lens. Field emission and focusing tests on prototype devices demonstrated that the emission follows Fowler-Nordheim characteristics, the beams can be focused as anticipated from numerical simulations, and the extraction and focus apertures in well-aligned devices collect less than 1% of the emitter current. Preliminary lithographic results on PMMA coated substrates demonstrated that variations in linewidth measured as a function of the focus lens voltage are in agreement with device modeling. Recently, we obtained the capability to fabricate thick electrodes, which, based on model results, should provide better focusing and depth of field. Furthermore, progress has been made to obtain better aperture alignment and fabricate individually addressable cathodes. Our research objective is to demonstrate lithography using a full 3x3 array of operating devices. We will discuss our recent results in detail as well as ongoing work to achieve <100-nm linewidths and full array implementation.

**NS-TuP9 Characteristic of Carbon Nanotubes Synthesized by Pin-to-Plate Type Atmospheric Pressure Plasma Enhanced Chemical Vapor Deposition at Low Temperature, S.-J. Kyung, J.H. Lee, C.-W. Kim, M. Voronko, G.Y. Yeom, Sungkyunkwan University, Korea**

In this study, carbon nanotubes (CNTs) were grown on glass substrates coated with NiCr by an atmospheric pressure plasma enhanced chemical vapor deposition and their structural and electrical characteristics were investigated as a possible application to the field emitter of field emission display (FED) devices. NH<sub>3</sub> gas flow rate (150sccm~ 270sccm) in He/C<sub>2</sub>H<sub>2</sub>/NH<sub>3</sub> and the substrate temperature (400~500i,°C) were varied and the increase of NH<sub>3</sub> flow rate to 270sccm and the increase of growth temperature to 500i,°C increased the length of the grown CNTs and decreased the diameter of the CNTs. The ratio of defective carbon peak to graphite carbon peak of the CNTs grown at 500i,°C with 270sccm of NH<sub>3</sub> measured by fourier transform(FT)-Raman was 0.772. When field emission properties were measured, the turn-on field was 3.5V/um and the emission field at 1mA/cm<sup>2</sup> was 5.25V/ um.

**NS-TuP10 A Method of Coating and Implanting Carbon Nanotube with Iron Nanoparticles by Inductively Coupled Plasma, J.S. Kim, G.H. Kim, C.I. Kim, O.J. Yoon, J.K. Jung, Chungang University, Korea**

We describe a new method of coating and implanting Single-Walled Carbon Nanotube with Iron Pentacarbonyl(FeCo@sub 5@) using Inductively Coupled Plasma(ICP). We control the pressure of chamber by hydrogen gas. First, Iron Pentacarbonyl(FeCo@sub 5@) in bubbler was evaporated by heating. Second, Plasma treatment process was performed with hydrogen gas and the evaporated Iron Pentacarbonyl(FeCo@sub 5@), at rf-bias voltage. The result of this work shows Fe nanoparticles coated and implanted on Single Walled Carbon Nanotube(SWCNT). The morphology and structure was investigated by scanning electron microscopy (SEM), transmission electron microscopy(TEM), and energy dispersive x-ray(EDX).

**NS-TuP11 Carbon Nanotube Copolypeptide Bionanocomposites, C. Lovell, University of Virginia; E. Worthington, University of California, Santa Barbara; T.J. Deming, University of California, Los Angeles; G.D. Stucky, University of California, Santa Barbara; J. Kang, K.E. Wise, National Institute of Aerospace; J.S. Harrison, NASA Langley Research Center; J.M. Fitzgerald, University of Virginia; C. Park, National Institute of Aerospace**

Due to their helical structures, several biopolymers exhibit high shear piezoelectricity. Unfortunately, few natural biopolymers exhibit adequate physical properties to endure practical utilization of their sensing capabilities. Thus, this investigation seeks to explore the shear sensing potential of a synthetic biopolymer. By combining peptides and polymers, synthetic polypeptides should bridge the gap between expensive, functional peptides and inexpensive, less functional polymers. Further augmentation of their electroactive potential and mechanical properties can be achieved by addition of carbon nanotubes (CNTs) to form a nanocomposite material with very low density . Functional characterization of drop-casted thin films was performed, including electrical and dielectric measurements, as well as mechanical tests. It was found that several properties, including conductivity, permittivity, tensile strength, Young's modulus, and toughness increased with SWNT loadings. However, one of the main limiting factors in achieving the best performance of CNT-polymer composites is a sharp increase of material viscosity at high concentrations (5-6 wt.%) of CNTs, which limits the capabilities of conventional fabrication techniques. In order to exploit the unique properties of CNTs in macroscopic composites, significant progress has to be made in the development of new advanced fabrication and processing methods, allowing control over spatial distribution and alignment of CNTs in the matrix. For this reason, a novel process termed "matrix assisted pulsed laser evaporation" (MAPLE) was used in creating several CNT-copolypeptide nanocomposites. These results, as well as the preliminary investigation of the copolypeptide's shear piezoelectric properties, will be presented. @FootnoteText@ @footnote 1@ S. B. Sinnott and R. Andrews, Carbon nanotubes: synthesis, properties, and applications, Crit. Rev. Sol. State Mat. Sci. 26, 145, 2001.

**NS-TuP12 Double-walled Carbon Nanotubes Grown on Co Tip Catalysts by Chemical Vapor Deposition, C.-M. Yeh, C.-J. Huang, M.-Y. Chen, J.C. Hwang, National Tsing Hua University, Taiwan, R. O. C.**

A cobalt tip structure has been used as the catalysts for the grown of double-walled carbon naotubes (DWCNTs) by catalytic chemical vapor deposition at 900~1000°C. The cobalt tip catalysts were fabricated by a pre-deposition of a cobalt thin layer of 0.5~10 nm on Si(100) and a sequential microwave plasma treatment at 450°C. The outer and inner tube diameters of the DWCNTs are in the range of 3~4 and 2~3 nm, respectively, determined by transmission electron microscopy. The density of DWCNTs can be enhanced by the Co tip catalysts, which structure is superior to ball-like Co islands for the growth of CNTs.

**NS-TuP13 Oxide Electrolyte Nanostructures for Low Temperature SOFC Operation, S. Thevuthasan, L. Saraf, V. Shutthanandan, O.A. Marina, C.M. Wang, S. Azad, Y. Zhang, A. El-Azab, Pacific Northwest National Laboratory**

Development of electrolyte materials that possess high oxygen ion conductance at relatively low temperatures is essential to improve the performance of electrochemical devices. Ceria, doped with a divalent or trivalent cation, exhibits higher ion conductance compared with yttria-stabilized zirconia, the electrolyte currently used in solid oxide fuel cells. In this research, we have investigated layer by layer structures of highly oriented gadolinia doped ceria and zirconia in order to determine the nanoscale effects on the ion conductance. Highly oriented multilayered nanostructures of gadolinia-doped ceria and zirconia with interfaces parallel and perpendicular to the substrate surfaces were grown on sapphire substrates using molecular beam epitaxy and glancing angle sputter deposition, respectively. These structures were characterized by several bulk and surface sensitive characterization techniques. At relatively low temperatures, the oxygen ion conductance in highly oriented layered structures was found to increase with increasing number of layers in the films with interfaces parallel to the substrate surfaces. Theoretical calculations were also performed to understand the effects of space charge regions induced by the thermodynamic equilibrium and impurity segregation as well as the influence of the grain microstructures on the electric transport processes in these materials. In addition, labeled oxygen diffusion measurements were carried out by 18O(p,α)15N nuclear reaction analysis (NRA) and the diffusivity correlation is established with ionic transport by measuring the oxygen ionic conductivity using impedance spectroscopy. These results will be discussed along with the

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results from stability tests of these layered structures at elevated temperatures.

**NS-TuP14 Hydrogen Effects on the Field Emission of Carbon Nanostructures, P. Miraldo, R.A. Outlaw, X. Zhao, J.J. Wang, B.C. Holloway,** College of William & Mary

Field emission from carbon nanostructures such as carbon nanotubes (CNT), carbon nanofibers (CNF) and carbon nanosheets (CNS) is greatly influenced by the presence of hydrogen adsorbed on the surface and dissolved in the bulk. The amount and site location of the hydrogen and how it affects electron emission has, to date, not been determined. Temperature desorption spectroscopy, electron energy spectroscopy and time of flight-secondary ion mass spectrometry were employed to examine some of these characteristics. Hydrogen was desorbed from CNS via vacuum firing ( $T \sim 1000^\circ\text{C}$  for 2h for full depletion) and via thermal conditioning at emission currents of greater than 500  $\mu\text{A}$  for periods of 30 min to > 2h. Following conditioning of the CNS, there was a marked improvement in the repeatability, stability and magnitude of the field emission current. Field emission was observed to increase by over an order of magnitude corresponding to the complete removal of hydrogen from CNS. Turn on voltages less than 0.8 V/ $\mu\text{m}$  and current densities greater than 2 mA/ $\text{mm}^2$  have been observed. Raman spectroscopy performed on the CNS after conditioning revealed a significant reduction in the D/G ratio. Comparisons to the reported decrease in electron emission with hydrogen removal from CNT are presented.

**NS-TuP15 Fabrication of Three-Dimensional Nanostructures with a Resolution of 10 nm and Selective Attachment of Biological Molecules using Scanning Near-field Photolithography, R.E. Ducker, M. Montague, G.J. Leggett,** University of Sheffield, UK

Scanning near-field photolithography (SNP) is a new nanolithography tool in which a scanning near-field optical microscope (SNOM) coupled to a UV laser is used to pattern organic monolayers. Here we present a detailed study of the mechanism of formation of nanostructures in self-assembled monolayers (SAM) of alkanethiols adsorbed on gold surfaces. A novel mild etch solution has been developed that can be used to selectively etch gold using a SAM resist. Used in conjunction with SNP this enables the fabrication of structures in gold that are smaller than 10 nm using light with a wavelength of 244 nm. In contrast to electron beam methods, SNP may be used under ambient or even fluid conditions. SNP can also be used to create biological nanostructures via a variety of methods.

**NS-TuP16 Metal Nanostructure Growth on Molecular Buffer Layers of CO@sub 2@, P.S. Waggoner, J.S. Palmer, V.N. Antonov, J.H. Weaver,** UIUC

Buffer-layer-assisted growth (BLAG) occurs when a multilayer of condensed gas acts as the surface on which impinging atoms form clusters that subsequently diffuse and coalesce during buffer desorption. We investigated Au, Cu, and Ni nanostructure formation using buffer layers of solid CO@sub 2@ and compared the results to what has been found for solid Xe buffers. The cluster densities could be controlled from  $\sim 10^8$  to  $10^{12}$   $\text{cm}^{-2}$  by taking advantage of the power law dependence of density on the buffer layer thickness. For Au and Cu, the crossover from compact to ramified structures could be followed. For Ni, even small particles were ramified. The effective activation energies for diffusion of large ramified clusters on CO@sub 2@ were determined to be 0.91, 1.02, and 0.93 eV for Au, Cu, and Ni, respectively. These were significantly higher than observed on Xe, and they reflect the higher polarizability of CO@sub 2@. The diffusion pre-factors increased exponentially with the increase in diffusion barrier, demonstrating a Meyer-Neldel compensation effect. The characteristic energy of this process, 9 meV, was higher than for Xe due to the more energetic phonons of CO@sub 2@. It is comparable to the energies of buffer phonons active during buffer desorption, revealing that cluster motion on CO@sub 2@ is a many-body process fueled by coincidence of activated buffer phonons.

**NS-TuP17 Synthesis of Aligned Carbon Nanotubes by CVD Using Ball-Shaped Microwave Plasma, Y. Oshiro, S. Nishino, Y. Hayashi,** Kyoto Institute of Technology, Japan

Aligned carbon nanotubes (CNTs) have been successfully synthesized by plasma-enhanced chemical vapor deposition using ball-shaped microwave plasma in a quartz bell jar. CNTs are expected to be used as field electron emitters for a display or an X-ray source, because they have the characters of high aspect ratio, small radius of tip curvature and mechanical strength, which are required for long-lived emitters with intensive electric field at their tips even at low applied voltage. Ball-shaped microwave plasma,

which is generated non-contact with a quartz bell jar, has been used for aligned CNTs growth because of high purity CNT synthesis. In the plasma, CNTs are expected to grow in an environment with few impurity inclusion by the sputtering of the wall of a quartz bell jar. 10% methane diluted in hydrogen was introduced in the bell jar chamber and the pressure was kept at 2000 Pa during the growth of CNTs. Microwave power of 450W was induced for the generation of ball-shaped microwave plasma. For the growth of vertically aligned CNTs, we placed a DC cathode plate parallel to a grounded electrode, which plays a role of an end plate for microwave propagation, to apply a uniform and intensive electric field on a substrate. Iron substrates were set on the cathode plate, to which negative bias of 300V was induced. Aligned carbon fibers of 30 nm in diameter and 800 nm in length were observed by scanning electron microscopy. These carbon fibers should be CNTs formed by tip growth, because they were hollow and had cone-shaped particles at their tips, which are generally observed to be those of iron catalytic metal in the tip-growth mode of CNTs.

**NS-TuP18 Arrayed Bundles of Carbon Nanotubes for High-Intensity Field Emission: Parametric Studies of Growth and Field Emission, M.J. Bronikowski, H.M. Manohara, B.D. Hunt,** Jet Propulsion Laboratory, California Institute of Technology

We have found that Carbon Nanotubes (CNT) arranged in arrays of bundles give much greater field emission current densities than either isolated CNT or dense mats of CNT, in excess of 1 Amp/ $\text{cm}^2$  at fields of less than 4 Volts/ $\mu\text{m}$ . As part of ongoing efforts to fabricate high-intensity electron-beam devices based on these arrayed CNT bundles, we have studied CNT bundle growth (by Chemical Vapor Deposition, CVD) as a function of the various CVD processing parameters, and field emission intensity as a function of CNT bundle array geometric parameters such as bundle size, spacing, and CNT length and diameter. Results will be presented from these parametric studies, in which we have optimized both CNT growth and field emission of electrons from arrayed bundles of CNT.

**NS-TuP19 Suspended Carbon Nanotube Electro-Mechanical Tunneling Switch for Wireless Communication, Y. Song, J. Choi,** Wayne State University

Carbon nanotube is one of the best building blocks for future nano electro-mechanical systems especially in wireless communication application. It is originated from the excellent properties of carbon nanotubes such as high mechanical strength, chemical inertness, high aspect ratio, and good thermal conductivity. We directly fabricated laterally suspended carbon nanotube tunneling switch and studied its characteristics and performance as an electro-mechanical switch. The onset of tunneling turn-on voltage of carbon nanotube switch is as low as 2.6 V. The switching behavior of carbon nanotube electro-mechanical switch was modulated by a back gate voltage and investigated by in-situ Raman spectroscopy and impedance spectroscopy.

**NS-TuP20 Experimental Evidence of p-type Doping for Long Channel Carbon Nanotube Transistor, D. Kang,** Samsung Advanced Institute of Technology, Korea; *N. Park,* Dankook University, Korea; *B. Kim, J. Kim,* Chonbuk National University, Korea; *W. Park,* Samsung Advanced Institute of Technology, Korea

Carbon nanotubes (CNT) show dramatic changes in physical and chemical properties under different ambient conditions because of its high surface area. However, the possibility of p-type doping has been controversial for several years. While the thermoelectric power measurement obviously reported the oxygen-induced hole doping in the bundles of nanotubes, transport measurement with single short nanotube revealed that the adsorption effect lead to the work function change of the electrode, rather than the doping the nanotube body. However, in this study, we show that the doping effect would be prominent in the single nanotube transistor when the CNT is long ( $\sim 5 \mu\text{m}$ ). In order to decouple mixed effects from doping and metal work function change, we masked the interface (CNT/metal) and channel (CNT) region of CNT FET with conventional photoresists, respectively and measured  $I_{\text{ds}}\text{-}V_{\text{g}}$  characteristics in air and vacuum. Preliminary data show that p-doping due to adsorption of ambient gas molecules could be possible and another critical factor to govern electrical properties of long channel CNT transistors. In addition, we observe that changes in  $I_{\text{ds}}\text{-}V_{\text{g}}$  and  $V_{\text{th}}$  (threshold voltage) are associated with where it was masked.

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**NS-TuP21 Electrical Properties of a Silicon Nanocrystal Embedded in a SiO<sub>2</sub> Layer,** *J.M. Son, J.M. Kim, S.Y. Seong*, Myongji University, Korea; *Y. Khang, B.K. Kim, K.S. Seol, E.H. Lee, J. Lee*, Samsung Advanced Institute of Technology, Korea; *Y.S. Kim, C.J. Kang*, Myongji University, Korea

Si nanocrystal (Si NC) based device is a promising candidate for the future non-volatile memory. It is advantageous in terms of low power consumption, small device size, excellent stress induced leakage current (SILC) immunity and better retention. Since the characteristics of Si NCs memories in which the conventional poly-Si floating gate is replaced by an array of Si NCs is affected by the electrical properties of each NC, the isolation of Si NCs plays an important role. The Si NC samples produced by laser ablation method were followed by sharpening oxidation steps. In these steps Si NCs are capped with a thin oxide layer of 1~2nm thickness for isolation and the size control. It also affects the interface states of NCs, resulting in the change of electrical properties. To find out this effect, we observed localized electrical properties of a capped Si NC by scanning probe microscopy (SPM). And these results were compared with C-V characteristics of the conventional MOS capacitor structure.

**NS-TuP22 Synthesis of Carbon Nanofibers on TiW Substrates and Their Field Emission Properties,** *K. Hou, J.J. Wang, P. Miraldo, R.A. Outlaw, B.C. Holloway*, College of William and Mary

Spaghetti-like and aligned carbon nanofibers have been synthesized on TiW substrates by DC PECVD at a substrate temperature of 635°C. The morphology transition from spaghetti-like to aligned carbon nanofibers has been observed to be a function of plasma power. It is found that the growth rate plays an important role in determining the morphology of carbon nanofibers. When the growth rate is less than 150 nm/min, aligned carbon nanofibers can be fabricated. Otherwise, spaghetti-like carbon nanofibers are formed. The growth rate of carbon nanofibers fabricated on TiW substrate at 550°C is also measured in this work. The field emission properties of both spaghetti-like and aligned carbon nanofibers grown on TiW substrate at 635°C have also been investigated.

**NS-TuP23 Temperature-induced Control of the Aspect Ratio of Gold Nanorods,** *H.J. Park, C.S. Ah*, Korea Research Institute of Standards and Science; *K.-P. Lee*, Kyungpook National University, Korea; *I.S. Choi*, KAIST, Korea; *W.S. Yun*, Korea Research Institute of Standards and Science

Aspect ratio of gold nanorods can be controlled by simply adjusting the reaction temperature in the seed-mediated synthesis of the nanorods. At various reaction temperatures between 276 and 313 K, the gold nanorods were prepared by the injection of gold nanoparticles of around 4 nm in diameter into a reaction mixture consisting of hydrogen tetrachloroaurate, hexadecyltrimethylammonium bromide, and ascorbic acid. Average aspect ratio of the resulting nanorod increases from 1 to about 40 with decreasing the reaction temperature, which can be attributed to temperature-induced change in the stability of the micellar templates.

**NS-TuP24 Controlled Gold Nanowires using 2-Aminoethanthiol Capped Gold Nanoparticles on DNA Molecule as Template,** *H. Kim, B. Hong*, Sungkyunkwan University, Korea; *Y.-H. Roh*, Sungkyunkwan University, Korea, Republic of Korea

We developed a simple technique to form Au-nanowires (AuNWs) by the conjugation of 2-aminoethanthio-capped gold nanoparticles (AET-AuNPs) and the immobilized DNA molecules on 3-Aminopropyltriethoxysilane (APS) coated Si wafers. The AuNPs coated with AET monolayers have been electrostatically assembled along DNA molecules by careful control of the relative molar quantities of AuNPs and AET. We carried out a variety of AuNPs sizes (2, 5, 10 nm) to form the various nanowires, and the various sizes of nanowires were achieved. The gold nanowires formed in this study were confirmed by atomic force microscopy (AFM). In addition, we measured an electrical conductivity of AuNWs located between microfabricated electrodes. The investigated nanowires exhibit ohmic transport behavior at room temperature.

**NS-TuP25 Synthesis and Characterization of SiC Nanowires and SiC/ZnO Hetero-Nanostructure Grown by Direct Heating Method,** *Y. Ryu, Y. Tak, K. Yong*, POSTECH, Korea

SiC is a suitable material for the fabrication of electronic devices operating at high power, high temperature and high frequency due to its unique physical, mechanical and electronic properties. Cubic phase SiC nanowires were synthesized in large quantity by simply heating NiO catalyzed Si substrates at the growth temperature of about 1050 °C. A carbothermal reduction of WO<sub>3</sub>/C provided reductive environment and also carbon source to synthesize crystalline SiC nanowires. SiC nanowires were 20-50 nm in diameter, and the as-grown

nanowires were coated with SiO<sub>2</sub> sheath of ~ 20 nm thick. The grown nanowires were characterized using SEM, TEM, EDX, Raman spectroscopy, FTIR and XRD. Also, the electron field emission properties of the SiC nanowires and core-shell SiC-SiO<sub>2</sub> nanowires were investigated. The turn on field at the emission current density of 10 μA/cm<sup>2</sup> was below 4 V/μm, and it showed uniform emission image. Hetero-nanostructure of ZnO nanorods(NR)/SiC nanowires(NW) were produced using a two step process: direct growth and metal-organic chemical vapor deposition (MOCVD). Atomically abrupt interface was observed at the heterojunction of ZnO NR/SiC NW. The photoluminescence (PL) of aligned ZnO nanorods will be discussed as well.

**NS-TuP27 Formation of Ge Nanocrystals in Hf based High-K Dielectrics for Nonvolatile Flash Memory Device Application,** *J. Chen*, National University of Singapore; *A.-Y. Du*, Institute of Microelectronics, Singapore; *W.J. Yoo*, National University of Singapore, Singapore; *D.S.H. Chan*, National University of Singapore

Nanocrystals (NCs) floating gate has received considerable attention for the future nonvolatile flash memory devices because its discreteness of charge storage suppresses lateral migration of charges, enhancing immunity to oxide defects compared with conventional flash memories using continuous floating gates. High-K dielectrics in place of conventional SiO<sub>2</sub> can further improve programming efficiency, data retention and read speed of flash memory because of lower F-N tunneling barriers and small equivalent oxide thicknesses. In this work, methods to form Ge nanocrystals embedded in main stream high-K dielectrics, HfO<sub>2</sub> and (HfO<sub>2</sub>)<sub>x</sub>(Al<sub>2</sub>O<sub>3</sub>)<sub>1-x</sub> (HfAlO) were introduced and compared. Temperature dependence of phase separation process in the formation of Ge NCs in HfO<sub>2</sub> and HfAlO matrices was studied using X-ray photoelectron spectroscopy. Transmission electron microscopy and energy dispersive X-ray spectroscopy show that Ge NCs can form in either HfAlO or HfO<sub>2</sub>, and the location of Ge NCs varies depending on the high-K films. It is found that, in HfAlO, Ge NCs are well sandwiched in amorphous HfAlO matrix. However, in HfO<sub>2</sub>, Ge NCs are located in grain boundaries of polycrystalline HfO<sub>2</sub>, and most of Ge NCs are in direct contact with Si substrate or gate electrode of memory devices because of the extrusion effect of the growth of HfO<sub>2</sub> crystal grains on Ge NCs. This results in a significant difference in data retention of memories employing these structures. Flash memories employing Ge NCs embedded in HfAlO can maintain a memory window of 0.5 V in 10 years, whereas flash memories employing Ge NCs embedded in HfO<sub>2</sub> show a memory window closing only within 2 minutes.

**NS-TuP28 Electrical Characteristics of DNA-Nanoparticle Networks using Scanning Probe Microscopy,** *N.J. Lee, Y.J. Kim, J.S. Kim, B.H. Nahm*, Myongji University, Japan; *D. Jeon*, Seoul National University, Korea; *Y.S. Kim, C.J. Kang*, Myongji University, Korea

Transport properties of the DNA-nanoparticle networks constructed by the self-assembly of biotinylated DNAs and streptavidins are studied by scanning probe microscopy (SPM). First, we measured I-V characteristics of DNA network linked between two metal electrodes deposited on mica surface, and these results were classified with respect to the conformational change of DNA molecules. Next, SPM probe tip was used as a counter electrode for the fixed metal electrode. In this experiment, only one end of DNA molecule was attached to the fixed electrode and the tip was scanned over DNA molecules to measure the local property. We also monitored capacitance or potential difference within the networks with SPM while biasing the network. To find out the charging effect in the network, we directly injected charge into the DNA molecule through SPM tip and performed microscopy and spectroscopy. In this talk, local electrical properties of the DNA-nanoparticle networks observed by SPM and their possibility to be applied for nano devices will be presented.

**NS-TuP29 Observation of Broad Strong Red Photoluminescence Band in Indium Oxy-nitride Nanoparticles,** *T.S. Ko, C.P. Chu, W.T. Hsu, H.C. Kuo, S.C. Wang*, National Chiao Tung University, Taiwan

Indium oxy-nitride nanoparticles were synthesized on silicon substrate in nitrogen atmosphere using a method involving thermal evaporation of pure indium. Nanoscale compositional analysis by energy dispersion spectrum showed the existence of indium oxy-nitride compound. Scanning electron microscopy investigations showed shape transformation from amorphous sphere to well-shaped octahedron with an average nanoparticle size from 180 nm to 1 μm when growth temperature of substrate increased from 700 to 900 °C. Photoluminescence study was performed on indium oxy-nitride nanoparticle samples grown at different

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temperatures. It was found that all of samples grown at different temperatures exist a broad emission band centered around 690 nm with a full width at half maximum is about 250 nm, spanning the whole red region. The emission intensity increases with growth temperature, which suggests the formation of high quality indium oxy-nitride nanoparticles with increasing temperature. The photoluminescence results indicate the indium oxy-nitride nanoparticle samples have potentialities of developing into red phosphor system for lamp applications.

**NS-TuP30 Single-Crystal GaN Nanorod Arrays Grown by UHV RF-MOMBE, C.N. Hsiao, C.-C. Kei,** National Applied Research Laboratories, Taiwan; **C.K. Chao,** National Central University, Taiwan; **S.-Y. Kuo,** National Applied Research Laboratories, Taiwan

Well-aligned GaN nanorod arrays have been grown by ultra-high vacuum metal organic molecular beam epitaxy using RF radical nitrogen (RF-MOMBE) on c-sapphire substrates without any catalyst. The corresponding microstructure and growth kinetics of rods were investigated by in-situ reflection high-energy electron diffraction, scanning electron microscopy, transmission electron microscopy, energy dispersive spectroscopy, x-ray diffraction, micro-Raman spectroscopy, photoluminescence and high resolution transmission electron microscopy (HRTEM). It was found that the length and diameter of nanorods varies with the growth temperatures, and the rod number density can reach around  $10 \times 10^8 \text{ cm}^{-2}$ . HRTEM and corresponding diffraction patterns have revealed the GaN nanorods have a dislocation free, single-crystal hexagonal wurtzite structure with preferential (0001) orientation. However, the selected area electron diffraction patterns (SADPs) for the interface were not clear enough to identify corresponding orientation relationship between rod and substrate. Further research about growth mechanism is still needed in this area. The findings in this work show that the size and density of the rods can be controlled by adjusting the III/V ratio, RF plasma power and growth temperature. In contrast to previous works, the process requires neither catalyst nor the effect of nanometer-sized confinement such as carbon nanotubes. Thus, the single-crystal and dislocation-free GaN nanorods arrays might be useful for practical applications in nanoscale optoelectronic and electronic devices.

**NS-TuP31 ZnxCd1-xSe Ternary Semiconductor Nanoalloys, H. Lee, L. Hardison, H. Yang, V.D. Kleiman, P.H. Holloway,** University of Florida

ZnxCd1-xSe quantum dots have been synthesized by a high temperature colloidal method using a trioctylphosphine oxide (TOPO) solution. Oleic acid complexes of Cd and Zn were used for the metal sources in reactions that produced ZnxCd1-xSe nanoalloys. Nanoalloying was achieved during the one-step synthesis process that led to a ZnSe shell on the CdSe core. Reaction temperatures below 250°C led to less alloying and less spectral shifts as compared to dots synthesized at 320°C. Smaller nanocrystals were obtained at lower growth temperature due to a smaller critical radius of nucleation, leading to a large nucleation rate. ZnCdSe nanorods were also synthesized from CdSe/ZnSe core-shell nanorods via a solution thermal alloying process at 270~280°C. CdSe nanorods were prepared using tetradecylphosphonic acid (TDPA)/TOPO surfactants, and a ZnSe shell was grown on CdSe nanorods at 180~190°C. These nanorods were characterized as a function of alloying time using X-ray diffraction, Raman, transmission electron microscopy, and time-resolved photoluminescence spectroscopy. Femto-second transient absorption in the visible emission spectra was used to study the alloying mechanism(s). The decay of luminescence in ZnxCd1-xSe nanoalloys is best fit by stretched-exponential function and the significance of this observation will be discussed.

**NS-TuP32 The Dependence of Photoluminescence Characteristics of In2O3 Nanowires on the Zn Doping Level, C.L. Hsin, J.H. He, L.J. Chen,** National Tsing Hua University, Taiwan, R.O.C.

Nano-scaled materials have attracted increasing attention because of their novelty and potential applications. In this paper, we report the growth of In2O3 nanowires with different zinc doping levels in the vacuum furnace by a vapor transport and condensation method. The photoluminescence properties were measured and discussed. Self-assembled indium oxide nanowires with different zinc doping levels have been synthesized on the silicon wafer in a vacuum furnace. The morphologies, structures and chemical compositions have been studied by field emission scanning electron microscopy and transmission electron microscopy. The photoluminescence properties of the samples were measured at room temperature. The presence of metal particle at the top indicates that the growth of the nanowire is by VLS mechanism. The intensity variation with the doping level of the samples can be seen clearly. The band diagram can explain the photoluminescence characteristics. The photoluminescence

properties are attributed to the radiative recombination between oxygen vacancies, zinc impurities and indium-oxygen vacancy pairs.

**NS-TuP33 Synthesis of One-dimensional Well-aligned ZnO Nanorods on Patterned Structures, C.W. Wang, J.H. He,** National Tsing Hua University, Taiwan, ROC; **L.J. Chen,** National Tsing Hua University, Taiwan, ROC., Taiwan, R.O.C.; **G.C. Wu, C.T. Chia,** National Taiwan Normal University, Taiwan, ROC

The synthesis of one-dimensional (1D) semiconducting oxide nanomaterials has drawn a great deal of attention. ZnO has a wurtzite structure with applications in catalysts, sensors, actuators and transducers. Under controlled conditions, 1D well-aligned ZnO nanorods are synthesized by a simple vapor transport via vapor-liquid-solid (VLS) process on patterned single crystal (11-20) sapphire. The patterning methods include atomic force microscope-tip induced technique and nanosphere lithography. From FESEM images, ZnO nanorods are vertically aligned on the substrate and have uniform diameter of about 100 nm. From TEM images, ZnO nanorods are single crystal and grown along c-axis. Photoluminescence measurements show that a peak occurs at 380 nm which is attributed to band edge emission.

**NS-TuP34 Amorphous Nanotubes by Self-Assembly of Amphiphilic Bi(hexadecylamine) Zinc Sulfato Complex with Size Tunability, G.W. Huang, J.H. Wang, H.C. Chen,** National Tsing Hua University, Taiwan, Republic of China; **L.J. Chen,** National Tsing Hua University, Taiwan, Republic of China, Taiwan, R.O.C.

We describe on the formation of amorphous  $\text{C@sub 16@H@sub 33@NH@sub 2@}@sub 2@ZnSO@sub 4@$  nanotubes based on directional bottom-up self-assembly process. Through catalytic chemical reaction, the bi-hexadecylamine coordinated zinc sulfato complex is generated as a long-period molecular chain. The nanotubes were analyzed by FTIR, ESCA and line-scan EDX analysis to confirm the nanotubes are composed of  $\text{C@sub 16@H@sub 33@NH@sub 2@}@sub 2@ZnSO@sub 4@$  complex. The zinc coordinated bi-hexadecylamine provides a multiple intermolecular hydrophobic interaction and drives these molecular backbones to be close together. The as-built nanotubes were identified through analytical electron microscope observations, which reveal the nanotubes possess outer diameters of 60-90 nm and on inner diameter of 20 nm with length up to several micrometers. Additionally, through stoichiometry adjustment the length could be reduced drastically to hundreds of nanometer. The tunability in length is also reflected from photophysical properties with size-dependent optical characteristics. Further molecular packing profile revealed by small angle X-ray scattering strongly suggests and sustains the long range ordering (ca. 3.99 nm d-spacing) within these nanotubes.

**NS-TuP35 Formation of Ordered Nanodots with Si-Ge Superlattices by One Step Etching Process, H.C. Chen, S.W. Lee,** National Tsing Hua University, Taiwan, Republic of China; **L.J. Chen,** National Tsing Hua University, Taiwan, Republic of China, Taiwan, R.O.C.

Semiconductor superlattices are attracting increasing attention due to their potential applications in thermoelectric and optoelectronic devices. While the 2-dimensional (2D) semiconductor possesses promising properties for optoelectronic devices such as light emitting diode, heterostructure formation in zero-dimension (0D) nanostructure may provide even more attractive characteristics and improve device performance. By the use of comparably low etching-rate and size uniformity of Ge QDs, a method was developed to fabricate nanodots with excellent uniformity over large area, containing Si-Ge superlattices structure. The density of the nanodots is about  $1 \times 10^{10} \text{ /cm}^2$ , equivalent to that of original Ge QDs. Pyramid-like nanodots containing Si-Ge superlattices with 35 nm in height and 80 nm in diameter have been successfully fabricated. The use of Ge QDs/Si-Ge superlattices heterostructure takes advantages of not only Ge QDs with good size uniformity and low etching-rate to obtain nanodots with Si-Ge superlattices structure, but also compatible with the Si/SiGe-based integration technology.

**NS-TuP36 Synthesis of Au Nanotubes with SiO@sub x@ Nanowires as Sacrificial Templates, M.Y. Lu, Y.C. Chang,** National Tsing Hua University, Taiwan, ROC; **L.J. Chen,** National Tsing Hua University, Taiwan, ROC, Taiwan, R.O.C.

Gold nanotubes with  $\text{SiO@sub x@}$  nanowires as sacrificial templates have been synthesized.  $\text{SiO@sub x@}$  nanowires were functionalized by 3-aminopropyl trimethoxysilane (APTMS) that generates a charged surface. The attachment of negatively charged gold nanoparticles was followed. The coverage of Au nanoparticles was initially less than 30 percents. Further coverage was achieved by the reduction of gold hydroxide to grow the

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continuous nanoshell on Au nanoparticles, which serve as nucleation sites. The final coverage of gold nanoshells on SiO<sub>2</sub>@nanowires depends strongly on the relative amount of SiO<sub>2</sub>@nanowires in gold hydroxide solution. TEM images showing the progressive growth of gold shells on SiO<sub>2</sub>@nanowires decorated with Au nanoparticles. FESEM image shows the open ends of Au nanostructures after etching by HF solution confirming the formation of Au nanotubes by a simple route.

**NS-TuP37 Orientation Controlled Growth of Epitaxial SiNWs Networks in Ar Ambient, H.W. Wu, H.C. Chen,** National Tsing Hua University, Taiwan, ROC; **L.J. Chen,** National Tsing Hua University, Taiwan, ROC, Taiwan, R.O.C.; **C.J. Tsai,** National Tsing Hua University, Taiwan, ROC

Epitaxial silicon nanowire networks have been synthesized with a convenient annealing process in Ar ambient. Au nanoparticles were used as catalysts for nanowire synthesis via the vapor-liquid-solid growth mechanism. From the SEM observation, silicon nanowires form rectangular networks on (100) Si, and parallel straight lines on (111) Si. The diameters of silicon nanowires are between 10 and 60 nm. Structural characterization showed that the silicon nanowires grow primarily along the  $\langle 110 \rangle$  directions. The heights of silicon nanowires are between 3 and 20 nm. For applications in nanotechnology, growing silicon nanowires epitaxially on a suitable substrate promises to realize a high density of integrated devices based on nanowires.

**NS-TuP38 QCM Studies of the Slippage of Solid and Liquid Krypton Monolayers on Metal(111) and C60 Surfaces, T. Coffey, J. Krim,** North Carolina State University

We report a Quartz Crystal Microbalance (QCM) study of the nanotribology of solid and liquid krypton monolayers adsorbed on Cu(111), Ag(111), Ni(111), and C60 substrates at 77.4 K. We document the liquid-solid phase transition and compare the slip times of the krypton for the various substrates. The slip times for the solid krypton monolayers are longer than the slip times for liquid krypton monolayers on metal substrates and monolayer C60 films, as observed previously for krypton/Au(111). However, for bilayer C60 films, the jump in slip time at the liquid-solid phase transition is not present. We discuss these topics and the underlying reasons.

**NS-TuP39 Nanotribological Effects of Silicone Type and Deposition Level and Surfactant Type on Human Hair using Atomic Force Microscopy, C.A. LaTorre, B. Bhushan,** The Ohio State University

The atomic/friction force microscope (AFM/FFM) has recently become an important tool for studying the micro/nanoscale structure and tribological properties of human hair. Of particular interest to hair and beauty care science is how common hair care materials, such as conditioner, deposit onto and change hair tribological properties, since these properties are closely tied to product performance. Since conditioner is a complex network of many different ingredients (including silicones for lubrication and cationic surfactants for static control and gel network formulation), studying the effects of these individual components can give insight into the significance each has on hair properties. In this study, AFM/FFM is used to conduct nanotribological studies of surface roughness, friction force, and adhesive force as a function of silicone type, silicone deposition level, and cationic surfactant type. Changes in coefficient of friction as a result of soaking hair in de-ionized water are also discussed.

**NS-TuP40 Morphological, Nanomechanical and Cellular Structural Characterization of Human Hair and Conditioner Distribution Using Torsional Resonance Mode with an AFM, B. Bhushan, N. Chen,** The Ohio State University

Characterization of cellular structure and chemical and physical properties of hair are essential to develop better cosmetic products and advance the biological and cosmetic science. Although the morphology of the fine cellular structure of human hair has traditionally been investigated using scanning electron microscopy (SEM) and transmission electron microscopy (TEM), atomic force microscopy (AFM) can be used for characterization in ambient conditions without requiring specific sample preparations and surface treatment. In this study, tapping mode (TM) and torsional resonance (TR) mode in an AFM are compared for measurements of stiffness and viscoelastic properties mapping of the materials using amplitude and phase angle imaging. The TR mode shows advantages in resolving in-plane (lateral) heterogeneity of materials. The TR mode has been used for investigating and characterizing fine cellular structure of human hair. Various cellular structure (such as the cortex and the cuticle) of human hair and fine sublamellar structures of the cuticle, such as the A-layer, the exocuticle, the endocuticle, and the cell membrane complex

could be easily identified. The distribution and thickness of conditioner on treated hair surface affects tribological properties of hair. The conditioner thickness has been estimated using force distance measurements with an AFM.

**NS-TuP41 Atomic-scale Studies of Friction and Nano-Indentation, T. Filleter, S. Maier, R. Bennowitz,** McGill University, Canada; **E. Meyer,** University of Basel, Switzerland

The development of Scanning Force Microscopy has provided us with tools to study friction and wear on the nanometer scale. The characteristic atomic stick-slip instability in friction force measurements is caused by the jump of the contacting tip from one atomic position to the next. Thermal fluctuations in the combined system of tip, surface, and force sensor play an important role for the development of the stick-slip behavior. We measured the friction force for atomic stick-slip friction of a nanometer-sized tip sliding on a KBr (100) surface in ultra-high vacuum. Our friction force microscope allows us to detect force fluctuations up to 3 MHz, well above the mechanical resonance of the force sensor. We could track thermal fluctuations and found that the duration of the slip event shows a broad distribution even for slips over neighboring atomic positions. The indentation of surfaces by sharp tips is a standard method used to determine hardness and elastic modulus of materials. Scaling these experiments to small lengths can probe the initial stages of permanent deformation. Atomic scale plastic deformation at crystal surfaces has been achieved and characterized by use of non-contact force microscopy in ultra-high vacuum. A sharp silicon tip, first implemented as a nano-indenter, was used to image the atomic structure of displaced material on Cu (100) and KBr (100) surfaces. Under nano-Newton loading conditions the debris reorganizes in crystalline terraces with the same orientation as the underlying crystal.

## Nanometer-Scale Science and Technology

### Room 210 - Session NS-WeM

#### Nanometer Scale Imaging

Moderator: R. Bennowitz, McGill University

8:20am **NS-WeM1 Atomic Scale Analysis of Dielectric Surfaces and Nanostructures**, *M. Reichling*, Universitaet Osnabrueck, Germany **INVITED**  
Nanostructures involving dielectric materials play an increasingly important role in numerous fields of science and technology. Prominent examples are ultra-precision machined optical surfaces, high-k dielectrics and diamond in microelectronics, catalytic surfaces and insulating substrates for sensor applications and molecular electronics. Dynamic scanning force microscopy (SFM) operated in the so-called non-contact mode is the method of choice for an atomic scale characterisation of such structures. The method of dynamic SFM is introduced as the only analysis tool capable of atomic resolution imaging of insulating surfaces and nanostructures. The state of the art in highest resolution dynamic SFM on insulators and challenges for future developments are illustrated for examples from different fields of application. While a detailed interpretation and quantitative understanding of atomic contrast formation is demonstrated for fluoride surfaces, the formation and dynamics of surface defects is discussed for oxide surfaces.

9:00am **NS-WeM3 Bioelectromechanical Imaging by Scanning Probe Microscopy: Galvani's Experiment on the Nanoscale**, *S.V. Kalinin*, Oak Ridge National Laboratory; *B.J. Rodriguez*, North Carolina State University; *S. Jesse*, *A.P. Baddorf*, Oak Ridge National Laboratory; *A. Gruverman*, North Carolina State University

Coupling between electrical and mechanical behavior is a universal feature of biological systems. However, macroscopic studies are inherently limited by the complex structure of these materials. Here, we demonstrate a scanning probe microscopy (SPM) based approach for electromechanical imaging and spectroscopy of biological systems based on Piezoresponse Force Microscopy (PFM). Electromechanical imaging of tooth dentin and enamel has been performed using PFM with sub-10 nm resolution. Characteristic piezoelectric domain sizes and local protein fiber ordering in dentin have been determined. The shape of a single collagen fibril in enamel is visualized in real space and local electromechanical hysteresis loops are measured. We have also shown that the electromechanical response vector is related to the local molecular orientation and provides an approach for molecular orientation imaging in biological systems. This technique is further used to address several biological systems, including cartilage, antler, bone, and butterfly wing. This approach repeats Galvani's experiment on the nanoscale - 230 years later and with a million times higher resolution. The future opportunities of electromechanical SPM for characterization of complex biological systems are discussed. Research performed as a Eugene P. Wigner Fellow (SVK) at ORNL, managed by UT-Battelle, LLC under DOE contract DCE-AC05-00OR22725. AG acknowledges financial support of the National Science Foundation (Grant No. DMR02-35632).

9:20am **NS-WeM4 Bridge Enhanced Nanoscale Impedance Microscopy**, *L.S.C. Pingree*, *M.C. Hersam*, Northwestern University

Bridge Enhanced Nanoscale Impedance Microscopy (BE-NIM) advances the ability to measure the impedance of individual nanoscale conductive pathways in a variety of materials. Similar to Nanoscale Impedance Microscopy (NIM),<sup>1</sup> this technique concurrently monitors the magnitude and phase response of the current through a conductive AFM tip in response to an AC bias. By varying the frequency of the driving potential, the resistance and reactance of nanometer scale conductive pathways can be quantitatively determined. Previously, we have demonstrated the extreme accuracy of NIM on a variety of control systems, such as a set of gold nanowires connected to known impedances, resulting in concurrent current and phase images. In addition, we have performed NIM on 8  $\mu\text{m}$  x 8  $\mu\text{m}$  Organic Light-Emitting Diode (OLED) pixels, which exhibit enhanced negative capacitance.<sup>2</sup> However, the effects of long-range electrostatic interactions impose a detection limit on NIM of  $\sim 1$  pF. These interactions, or fringe capacitance, act as a capacitor in parallel with the sample/tip junction. BE-NIM minimizes the contribution of this capacitance by employing a LRC bridge that improves the detection limit to  $\sim 50$  aF. This improved sensitivity has been demonstrated on metal-oxide-semiconductor capacitors ranging in size from 5 fF to 50 aF. The application of BE-NIM to other materials systems, such as carbon nanotube/polymer composites and sub-micron OLEDs, will also be

discussed. <sup>1</sup>FootnoteText@ <sup>2</sup>footnote 1@ L. S. C. Pingree, et al., IEEE T. Nanotechnol., 4, 255 (2005).<sup>2</sup>footnote 2@ L. S. C. Pingree, et al., Appl. Phys. Lett., 86, 073509 (2005).

9:40am **NS-WeM5 Development of a Tunable Microwave Frequency Alternating Current Scanning Tunneling Microscope to Profile Dopant Density in Semiconductors**, *A.M. Moore*, The Pennsylvania State University; *B.A. Mantooth*, GeoCenters; *P.S. Weiss*, The Pennsylvania State University

We have built a scanning tunneling microscope (STM) capable of profiling dopants in semiconductor devices and test structures at sub-nanometer resolution. The alternating current signals, and thereby the dopant density and type, are obtained through a heterodyned signal. Two frequencies are applied to the STM tip and the nonlinearity of the tunnel junction mixes the frequencies, generating new signals including at the difference of the frequencies applied; this in combination with the DC bias yields information on the dopant density and type. This ultrahigh resolution (<1 nm) profiling tool enhances what is obtained through current metrology tools and will support semiconductor processing as the size scale of devices continues to decrease.

10:20am **NS-WeM7 Single-Electron Charging in InAs Quantum Dot Observed by NC-AFM**, *P. Grutter*, McGill University, Canada **INVITED**

In this paper, we present the first successful observation of single electron charging events in an individual InAs QD by spectroscopic measurement with a 4.5K vacuum non-contact AFM (NC-AFM). The main features of the experimental results agree with a simple theory based on the semiclassical theory of the Coulomb blockade effect.<sup>1</sup> The sample structure consists of a two dimensional electron gas (2DEG) layer used as a back electrode. The uncapped InAs QD were grown on top of a InP spacer layer serving as a tunneling barrier. The resonant frequency shift and the dissipated energy of an oscillating AFM cantilever were measured as a function of the tip-back electrode voltage, and the resulting spectra show distinct jumps when the tip was positioned above a QD. The observed jumps in the frequency shift, with corresponding peaks in dissipation, are attributed to a single-electron tunneling between the dot and the back electrode governed by the Coulomb blockade effect, and are consistent with a model based on the free energy of the system. The observed phenomenon may be regarded as the force version of the Coulomb blockade effect. The peaks in dissipation are essentially due to a single electron back action effect on a micromechanical transducer. This NC-AFM based technique has several advantages: It does not need any leads to be attached to individual QD and is also much less invasive for the measurement of quantum states in the QD because only weak, controllable coupling between the tip and the QD is required. <sup>1</sup>FootnoteText@ <sup>1</sup>footnote 1@ Stomp et al., Phys. Rev. Lett. 94, 056802 (2005).

11:00am **NS-WeM9 Development and Characterisation of Reference Materials for Nanotechnology: High Lateral Resolution Auger Electron Spectroscopy on Semiconductor Heterostructures**, *J. Westermann*, *U. Roll*, Omicron NanoTechnology GmbH, Germany; *M. Senoner*, *W. Unger*, Federal Institute for Materials Research and Testing, BAM, Germany

Today, a broad variety of different techniques and instruments is used to characterise nanoscale materials. However, a comparison between results taken with different instruments is often difficult or impossible. To overcome this gap, the Federal Institute for Materials Research and Testing (BAM), the Physikalisches Technische Bundesanstalt, ION-TOF GmbH and Omicron Nanotechnology GmbH have entered into a project to develop reference samples with nanoscale structures. We report on the characterisation of the first prototype of a semiconductor heterostructure with alternating AlGaAs and GaAs layers. The cross section of the epitaxially grown multilayer stack shows a variety of strips in the thickness range between 700nm and well below 10nm. The strip pattern includes strip gratings, isolated narrow strips and wide strips with step transitions. SEM and Auger measurements with highest lateral resolution (sub 10 nm) reveal the distribution of the various elements on the sample surface, and prove the quality of the sample preparation. We discuss the suitability of the sample to become a widely accepted, certified reference standard for lateral resolution in surface chemical analysis.

11:20am **NS-WeM10 STM and AFM Imaging with In-Situ Tip-Characterization**, *C.J. Chen*, *O. Pietzsch*, *D. Haude*, *R. Wiesendanger*, Hamburg University, Germany

The biggest unknown factor in STM and non-contact atomic-force microscopy (NC-AFM) experiments is tip electronic states. Experimental observations show that the STM and AFM images vary dramatically with

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change of tip structure, either intentionally, or spontaneously. Conceptually, tunneling is symmetric to tip and sample, and the STM and AFM images should be determined by a convolution of tip electronic states and sample electronic states. From the beginning of STM, various attempts to characterize the tip have been proposed and tried, most notably using FIM. However, the correlation between the FIM image of the tip and the tip electronic states relevant to STM and AFM imaging is still not clearly identified. For spin-polarized STM, the azimuthal dependence of spin polarization of tip electronic states often determines the images. Currently, there is no well-defined method to determine the azimuth of spin polarization. We present a new method for determining the tip electronic states and the azimuthal dependence of spin polarization of the tip by imaging the tip with well-understood samples. For general tip states, Si(111)7X7 is an ideal standard sample, because the dangling-bond states on the adatoms are well separated in space and the mean energy levels cover more than 1 eV across the Fermi level. For spin-polarized tips, the Fe monolayers on W(001) system provides a perfect standard sample, because of its well-known properties of providing different ferromagnetic orientations. @footnote 1,2@ Using tips characterized by standard samples to image unknown samples, image interpretation is becoming much more certain. Furthermore, through tip reconditioning and tip characterization, tip properties can be optimized to achieve maximum contrast. @FootnoteText@@footnote 1@M Bode, O Pietzsch, A Kubetzka, S Heinze and R Wiesendanger, PRL 86, 2142 (2001).@footnote 2@A Kubetzka, M Bode, O Pietzsch and R Wiesendanger, PRL 88, 057201 (2002).

11:40am **NS-WeM11 Towards the Fabrication of Ultra High Throughput Optical Fiber Probes**, *B.C. Gibson, S.T. Huntington*, University of Melbourne, Australia; *J. Canning, K. Lyytikainen*, University of Sydney, Australia; *J.D. Love*, Australian National University, Australia

Scanning near field optical microscopy (SNOM) has become an important characterization tool across all major disciplines of science. The ability to "cheat" the resolution limit in optical microscopy has enabled characterization of structures on a nanometer scale. At the heart of the technique is a metal coated scanning probe, which features a sub-wavelength aperture as a source or collector of light that explores the near-field of the sample surface. The key problem with this type of SNOM probe is the excessive loss that occurs, which effectively limits the sensitivity of the microscope. The high loss arises from attenuation through the sub-wavelength aperture, which is unavoidable. In addition, the high loss stems from an interaction with the metal coating at the tapered region of the tip. Preliminary theoretical models of tapered air-silica structured fibers suggest that this interaction with the metal may be reduced with the use of these fibers, along with a new type of fiber called a Fractal Fiber (special class of air-silica fiber), instead of using standard single-mode optical fibers. Tapering of these fibers has been performed using a custom-built CO@sub 2@ laser-based fiber pulling system to produce a prototype ultra high throughput optical probe. Initial optical throughput measurements have shown improved power levels to that of conventional SNOM probes. This suggests that the fiber design and fabrication is critical to the successful advancement of SNOM probes.

## Nanometer-Scale Science and Technology

### Room 210 - Session NS-WeA

#### Nanopatterning and Manipulation

Moderator: S.W. Pang, University of Michigan

#### 2:00pm NS-WeA1 Molecular Ruler Lithography Process with Sacrificial Multilayer Host Structures Incorporating a Barrier Layer, S. Subramanian, J.M. Catchmark, Pennsylvania State University

Molecular ruler lithography has the potential of improving the achievable resolution of conventional lithography techniques, without resorting to new instrumentation. This is accomplished by scaling down the dimensions of functional host structure by selectively assembling organic molecules of precise length on their surface. A novel method for performing molecular ruler lithography using sacrificial host structures has recently been developed and demonstrated using contact lithography. This new approach provides a reproducible, high yield technique for selective removal of the host, fabricating high aspect ratio structures and isolation of the host material from the substrate. In order to make this process widely compatible with optical and electron beam lithography techniques, we introduce a modified molecular ruler lithography process using a sacrificial multilayer host structure which incorporates a barrier layer in between the sacrificial and the host material. This barrier layer prevents the lithography resist, developer and removal chemistries used to pattern the host material from interacting with the sacrificial material. We demonstrate this process by using contact lithographically patterned gold host structures to produce isolated platinum lines. The process consisted of depositing a sacrificial LOR resist (MicroChem) and a chrome barrier layer. A gold host feature was patterned on top of the chrome barrier layer using optical lithography. The chrome barrier was then selectively removed using reactive ion etching. Mercaptohexadecanoic acid molecules were assembled onto the patterned gold layer completing the fabrication of the sacrificial host structure. Platinum was then deposited and the host structure was selectively removed by dissolving the sacrificial LOR layer to leave behind the isolated platinum lines. Hatzor A, Weiss P, Science 291,1019. Subramanian S, Catchmark J, JM3, accepted, 2005.

#### 2:20pm NS-WeA2 High Electric Field Nanoimprint Lithography of Metal Thin Films, N. Farkas, P. Meduri, E.A. Evans, R.D. Ramsier, The University of Akron; J.A. Dagata, National Institute of Standards and Technology

Sputter-deposited ZrN thin films prepared with high nitrogen content exhibit superdiffusive scanning probe microscope (SPM) oxidation kinetics and oxide feature heights of several hundred nanometers. We extend this enhanced single-tip SPM oxidation to parallel writing with an inherently simple method to obtain large areas of submicrometer-scale oxide features on ZrN thin films. To investigate if this nanoimprint lithography technique can be used to create arrays of well-defined features on other metal surfaces, pattern transfer onto iron/iron nitride thin films is studied here. This comparison is of fundamental interest in that Zr oxidation is driven by oxygen migration, whereas Fe oxidizes by metal ion transport. Implication of the use of patterned Zr and Fe nitride thin films for biomedical and magnetic applications are also discussed.

#### 2:40pm NS-WeA3 Thermolithography for Micro- and Nanofabrication, M.-T. Hung, Y.S. Ju, UCLA

An intriguing class of alternative lithography techniques utilize localized heating to create nanoscale features. The so-called thermolithography is very interesting since heat conduction in highly disordered polymer layers is a relatively slow diffusive phenomenon, which can be exploited to fabricate 3D nanostructures. We present our study of one type of thermolithography techniques that induces thermochemical cross-linking in select areas of a thin polymer layer. The patterned polymer layer can serve as part of a device or as a mask for subsequent processing. We demonstrate fabrication of T-gate structures and negative-slope resist profiles advantageous for the lift-off process. The thermal transport properties of polymer layers and kinetics of cross-linking processes are key parameters that determine the speed and resolution limit of the thermolithography techniques. We develop thermal transport property measurement techniques based on microfabricated ultra-thin membrane structures. The thermal conductivity and heat capacity of commercially available image reversal photoresists are determined before and after UV exposure, before and after postexposure bake, and also as a function of

temperature. We also use micro-fabricated heaters coated with a polymer layer to induce precisely controlled heating and study kinetics of cross-linking. The spatial extent of cross-linking is determined by treating the polymer in a developer and examining the profile of the remaining layer using an SEM. The polymer profiles are compared with numerical heat conduction simulation results to extract the threshold cross-linking temperature as a function of heating duration. The present work demonstrates feasibility of a thermolithography technique and provides important data on the thermal transport properties and kinetics of polymerization that help guide further development of micro- and nanoscale thermolithography techniques. Basu, S. McNamara, and Y.B. Gianchandani, J. Vacuum Sci. & Tech. B, 2004, 22, pp. 3217-3220. M. Kuwahara, J.H. Kim, J. Tominaga, Microelectronic Engineering, 2003, 67-68, pp. 651-656

#### 3:00pm NS-WeA4 Direct Deposition of Molecular Electronics Materials using Thermal DPN, P.E. Sheehan, M. Yang, A.R. Laracuenta, Naval Research Laboratory; B.A. Nelson, W.P. King, Georgia Tech; L.J. Whitman, Naval Research Laboratory

We have developed a new technique, called thermal DPN (tDPN), where a heated atomic force microscope cantilever controls the deposition of a solid "ink." The heated cantilever can be used like a nanoscale "soldering iron" or "glue gun" to deposit semiconductors, insulators, or metals. tDPN has several advantages over conventional DPN. Control over writing is much greater--deposition may be turned on or off and the deposition rate changed without breaking contact with the surface. In addition, imaging with a cool tip does not appear to contaminate the surface, thereby allowing in situ confirmation of the deposited pattern. tDPN also expands the range of useable inks to those that are immobile at room temperature. Finally, multi-layer films can be deposited sequentially, enabling 3-D structures and heterostructures to be written directly. One material that is easily deposited by tDPN but which is challenging by other means is poly(3-dodecylthiophene), or PDDT. PDDT is a conducting polymer that shows great promise as an active component in organic electronic devices. Using tDPN, well-ordered PDDT nanostructures have been deposited on silicon oxide and gold surfaces with layer-by-layer thickness control. By adjusting the tip heating power and the writing speed, we can vary the polymer thickness from a single monolayer (~2.6 nm) to tens of monolayers with lateral dimensions below 100 nm. Unlike conventional DPN inks, this low vapor pressure polymer may be deposited in UHV by tDPN, thereby allowing integration with CMOS processing. Along with our success at depositing metallic indium nanowires via tDPN, we now have all the requisite elements for the direct deposition of electronic circuitry. P. E. Sheehan, L. J. Whitman, W. P. King, B. A. Nelson, Appl. Phys. Lett. 85, 1589 (2004).

#### 3:20pm NS-WeA5 Physical Processes in Atom Manipulation and Creation of Novel Nanostructures of Co and Cu Atoms on Cu(111) Surfaces\*, J.A. Stroscio, R.J. Celotta, NIST

INVITED

We are studying the interactions involved in STM atom manipulation using Co and Cu atoms on a Cu(111) surface and building novel CoCu nanostructures using atom manipulation. The interactions responsible for atom manipulation are investigated by measuring the atom dynamics with a STM using both imaging and tunneling spectroscopy methods. Manipulated atom imaging, where the manipulated atom is rastered in the trapping potential of the STM tip, reveals the binding sites of the substrate. Contrast in this new type of image is due to the tip sensing the presence of the adatom, which can reflect atom motion and a variation in the local potential energy surface. Quantitative measurements of atom dynamics are made by studying the tunneling current noise properties during atom manipulation. Two distinct mechanisms of atom motion can be identified in the noise dynamics; quantum tunneling of the adatom between neighboring lattice sites, and vibrational heating of the adatom by inelastic electron scattering. The magnetic Co atom is a Kondo impurity on Cu(111) surfaces at low temperatures. The interaction between Co and Cu can be tuned by varying the Cu coordination in nanostructures built by atom manipulation. These nanostructures show significant changes in the Kondo density of states resonance as a function of Cu coordination. \*This work is supported in part by the Office of Naval Research. J. A. Stroscio and R. J. Celotta, Science 306, 242 (2004).

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4:00pm **NS-WeA7 Chemically Engineering the Motion of Individual Molecules on the Si(100)-2x1 Surface: a Scanning Tunneling Microscopy Study**, *R. Basu, J.D. Tovar, M.C. Hersam*, Northwestern University

Room temperature ultra-high vacuum (UHV) scanning tunneling microscopy (STM) is used to study a unique bond-breaking mediated motion of individual organic molecules on the clean Si(100)-2x1 surface. Specifically 4-methoxystyrene molecules are observed to undergo switching between two cycloaddition conformations mediated by pivotal motion about one Si-C bond. Styrene molecules, on the other hand, do not undergo such lateral translations, thus suggesting that the rotational degree of freedom of the methoxy group is responsible for the apparent motion of 4-methoxystyrene. To test this hypothesis, the rotational degree of freedom of the methoxy group was suppressed by synthesizing an analog molecule (5-vinyl-2,3-dihydrobenzofuran) where the methoxy group is covalently linked back to the aromatic ring. UHV STM imaging of 5-vinyl-2,3-dihydrobenzofuran on clean Si(100)-2x1 indeed confirms the suppression of molecular motion. This study suggests that the motion of organosilicon adsorbates can be controlled by chemically engineering their intramolecular degrees of freedom.

4:20pm **NS-WeA8 Formation of Large-Area Nanostructures on Si and Ge Surfaces during Low-Energy Ion Beam Erosion**, *B. Ziberi, F. Frost, B. Rauschenbach*, Leibniz-Institut für Oberflächenmodifizierung e.V. Leipzig, Germany

In contrast to advanced lithographic methods and subsequent etching procedures for pattern production with structure size < 100 nm, which are complex technological processes, self-organized spontaneous pattern formation during low-energy ion beam erosion is a cost-efficient 'bottom up' approach for the fabrication of large-area nanostructures. The formation of these patterns can be observed on various semiconductor materials and is attributed to a surface instability between curvature dependent sputtering that roughens the surface and smoothing by different surface relaxation mechanisms. In these work results for pattern formation due to low-energy noble gas (Ne@super +@, Ar@super +@, Kr@super +@, Xe@super +@) ion beam erosion of silicon and germanium surfaces at oblique ion incidence with and without sample rotation are presented. Depending on ion beam parameters, i. e. ion energy, ion incidence angle and ion mass, different patterns can evolve on the surface. In the case with sample rotation, very well ordered dot structures evolve on the Si surface at glancing incidence angle of 75° with respect to surface normal, with size varying from 30 nm to 50 nm. Without sample rotation, at small ion incidence angles, remarkably high ordered ripple patterns with wavelength ~ 50 nm can form on both materials for similar sputtering conditions. By further increasing the ion incidence angle a transition from ripples to highly hexagonally ordered dot structures with periodicity of ~ 40 nm are observed. The lateral ordering of nanostructures increases with erosion time, leading to very well ordered and homogenous structures. The mean size of nanostructures can be adjusted with ion energy while maintaining their lateral ordering. Scanning force microscopy (AFM) and high-resolution transmission electron microscopy (HRTEM) were used to study the lateral ordering, shape, and size of these nanostructures.

4:40pm **NS-WeA9 Thermally Assisted Atom Transfer on Surfaces: Between Tunneling and Activated Diffusion**, *J.W. Gadzuk*, NIST

The low temperature rates for site-to-site transfer of single atoms and molecules adsorbed on surfaces have been determined in recent STM studies@footnote 1@ within the temperature regime where the dominant transfer mechanism changes from mostly activated transmission over to thermally assisted tunneling through the inter-site (transition state) barrier, as the temperature is reduced. A model that has provided useful conceptual and quantitative insights into thermally assisted field emission tunneling spectroscopy@footnote 2@ is used here as the basis for theory of site-to-site atom transfer in this temperature range where proper account of tunneling and quantum reflection, for energies below and above the transition state barrier is required. The predicted transfer rates which are very sensitive to barrier shape as well as height, agree well with those observed in the STM studies of Co and Cu on Cu(111) surfaces in the interesting 4K@<=@T@<=@7K transition range which is relevant in the atom-by-atom fabrication of thermally stable surface nanostructures. @FootnoteText@ @footnote 1@J. Repp, G. Meyer, K.-H. Rieder, and P. Hyldgaard, Phys. Rev. Letters, Vol.91, 206102 (2003); J. A. Stroscio and R. J. Celotta, Science, Vol.306, 242 (2004).@footnote 2@J. W. Gadzuk and E. W. Plummer, Phys.Rev.B Vol.3, 2125 (1971).

5:00pm **NS-WeA10 Patterning of Well-Ordered PZT Nanodot Arrays using Silicon Nitride Shadow Mask**, *H.-J. Shin, J.H. Choi, H. Yang, Y.D. Park, Y. Kuk*, Seoul National University, Korea; *C.J. Kang*, Myungji University, Korea

We patterned well ordered arrays of Pb(Zr@sub 0.2@Ti@sub 0.8@)O@sub 3@ nanodots on a SrRuO@sub 3@/SrTiO@sub 3@ substrate by pulsed laser deposition. A silicon nitride shadow mask with ordered holes was used for patterning of PZT arrays. This method have an advantage that deposition could be done at high temperature, which could be applicable to in situ deposition avoiding any possible contamination in dot formation. In addition, we could change the shape or size of the patterns if necessary. The SrRuO@sub 3@ bottom electrode and PZT nanodots were deposited at 760 @super o@C and 660 @super o@C, respectively. The lateral size of the dot was about 120 nm and the height was about 15 ~ 20 nm. The inter-dot distance of PZT dot arrays was about 200 nm, exactly the same as the pore-to-pore distance of the shadow mask. Each dot was fully arranged and well isolated, having dome shape after deposition. The local switching of a single dot was examined using piezoresponce force microcopy. We could observe that the absolute piezoresponce value of positively polarized dot is 28.3 % larger than that of negatively polarized background, and there weren't any noticeable inhomogeneity such as an inversion of center region after polarization. The polarized states were maintained at 61.3 % of initial value after ~ 20 min, which almost relaxed suddenly to noise level after 30 min. A sudden drop of polarization implies that the relaxation is mainly related to the nucleation stages of domain reversal in our case.

## Magnetic Interfaces and Nanostructures Room 204 - Session MI+MS+NS-ThM

### Advanced Magnetic Storage and Manufacturing Processes

**Moderator:** E.A. Dobisz, Hitachi Global Storage Technologies/San Jose Research Ctr.

8:20am **MI+MS+NS-ThM1 Interface Stability between Amorphous Ferromagnetic Layer and Oxide Barriers in Tunneling Magnetoresistive Films at Elevated Temperatures**, X. Peng, D. Kvitik, A. Morone, E. Granstrom, S. Xue, Seagate Technology

Interface stability and microstructure between amorphous ferromagnetic (FM) layers Fe<sub>56</sub>Co<sub>24</sub>B<sub>20</sub> (atomic percent), and oxide barrier layers (AIO) as deposited by physical vapor deposition, in both as-deposited and annealed states, have been studied using magnetic measurement by looper, elemental depth profiling by X-ray Photoelectron Spectroscopy (XPS), and atomic level microstructure by Transmission Electron Microscopy (TEM) respectively. AIO is amorphous on both amorphous Fe<sub>56</sub>Co<sub>24</sub>B<sub>20</sub> and crystalline FM layers. Substantial Fe diffusion towards the AIO layer and Al towards FM layer are clearly observed for Fe<sub>56</sub>Co<sub>24</sub>B<sub>20</sub>/AIO system for annealing beyond 360°C, and will likely cause the MTJ devices made from this system to not functioning.

9:00am **MI+MS+NS-ThM3 Nanoimprint Technologies for Magnetic Recording Media**, T. Ando, C. Haginoya, K. Kuwabara, M. Ogino, K. Ohashi, A. Miyauchi, Hitachi Ltd., Japan

**INVITED**

The discrete-track and patterned media have been developed as future magnetic recording media. Nano-scale patterns are formed on the disk surface of these media. The fine patterning technologies are required for producing the patterned disks. The nanoimprint technology is attractive for the fabrication of nano-scale structures in view of cost and mass production. There are two main types of the nanoimprint technologies. One is the thermal nanoimprint technology that fine structures are formed on thermoplastic polymer layer. Another is the photo nanoimprint technology that ultra-fine structures are formed on photo-curable polymer layer. There are several key points for media application such as pattern formation area, resolution, precise control of pattern transfer, lifetime of nano-mold, alignment and so on. The pattern formation area is important for producing patterned disks. We developed a thermal nanoimprint machine that has the auto-parallel system, two step pressure system and so on. The machine enabled us to imprint fine dots on a 300 mm diameter Si wafer using a 300 mm diameter mold. The pattern formation area is large enough to produce the 65 mm diameter patterned disks. The fine resolution is required for high recording density. Austin et al. formed 6 nm half-pitch structure using superlattice stamper, and this resolution seems enough for Tbps storage era. D. Wachenschwanz et al. and Y. Soeno et al. evaluated write/read performance of the discrete-track media that the grooves and servo patterns were formed by using thermal nanoimprint and etching processes. Nanoimprint is promising way for discrete-track and patterned media. @FootnoteText@ D. Wachenschwanz et al., INTERMAG 2005, no. BB02 @ B.D. Terris et al., INTERMAG 2005, no. BB03 @ Y. Soeno et al., INTERMAG 2005, no. FR04 @ M. D. Austin et al., 3rd Conf. on Nanoimprint Nanoprint Technology 2004, no. III.2

9:40am **MI+MS+NS-ThM5 Ultra Narrow Magnetic Recording Heads: Processing Challenges**, M.-C. Cyrille, HITACHI Global Storage Technologies - San Jose Research Center

**INVITED**

As the areal density of magnetic recording increases well beyond 100Gb/in<sup>2</sup>, the critical dimensions of recording heads continue to shrink at a rate of 30% per year. Today, thin film heads with 100nm or less critical dimensions are being routinely fabricated in manufacturing. By the end of 2006, the physical trackwidth of read head sensors is expected to be less than 60nm. The industry is turning to Direct write E-beam and DUV 193nm as the lithography tools of choice to meet those small dimensions. As the material set used to fabricate thin film magnetic heads is unique to this technology, specific challenges arise when trying to pattern such small devices without loss of performances. Damage due to standard patterning techniques can now be observed on both the reader and the writer as their dimensions become smaller than 100nm and advances in tooling and processes tailored to each kind of magnetic sensor are required to overcome this issue. @FootnoteText@

10:20am **MI+MS+NS-ThM7 Correlated AFM/MFM and Magneto-Optical Studies on Epitaxial L1<sub>0</sub> FePd Thin Films**, R.A. Lukaszew, M. Mitra, J. Skuza, University of Toledo; A. Cebollada-Navarro, J.M. Garcia-Martin, C. Clavero Perez, Institute of Microelectronics in Madrid (IMM) - Spain

The latest trend in data storage exploits perpendicular recording. Magnetic binary alloys (e.g. Fe-Pd, Fe-Pt) are of significant interest in magneto-recording because highly ordered L1<sub>0</sub> structures of these alloys exhibit very large magnetic anisotropy that can withstand the super-paramagnetic limit when reduced in size to accommodate the projected demands for higher areal densities. They can be deposited as films with the anisotropy axis perpendicular to the film plane, making them suitable for perpendicular media. There are practical problems associated with this scheme because usually the experimentally achieved perpendicular anisotropy tends to be too large for writing on this media. Therefore it has been suggested that canted magnetization would be more appropriate. Here we show our correlated XRD, AFM/MFM and magneto-optical studies on two series of epitaxial L1<sub>0</sub> FePd thin films of varying thickness grown on MgO. We have observed that the choice of capping material has significant effect on the resulting magnetic and magneto-optical properties of the films. We will show correlated structural and magneto-optical data for films grown under identical conditions but capped with either MgO or Pd. Our studies demonstrate that in the first case the films exhibit strong perpendicular anisotropy while in the latter the films have a magnetization component along the plane of the films in addition to the perpendicular component, thus yielding a net canted magnetization. In addition the films capped with Pd exhibit smaller coercivities than the ones capped with MgO thus enhancing their prospect use in heat-assisted magneto-recording.

10:40am **MI+MS+NS-ThM8 Magnetic Properties of Epitaxial FeN Thin Films**, R.A. Lukaszew, University of Toledo; R. Gonzalez-Arrabal, University Autonoma of Madrid, Spain; C. Sanchez-Hanke, Brookhaven National Laboratory; R. Loloee, Michigan State University; D. Boerma, University Autonoma of Madrid, Spain

Low anisotropy and low magnetostriction iron based FCC films are attractive candidate materials for inductive thin film write heads in magnetic recording. Currently these are made of permalloy and other Fe alloys with polarization ranging from 1.0-1.6 T. Higher polarization is needed to create sufficient stray field to write on the higher-coercivity media that is needed as head and bit dimensions decrease to allow higher areal densities. Fe-N has been proposed as a possible material for the sensing element in read-head. Fe-N exhibits a variety of phases, some of which have enhance magnetic moment. In particular the meta-stable @alpha@'-Fe16N2 is particularly interesting because has the largest saturation magnetization reported of all known materials. We will present a comparative experimental study on epitaxial Fe-N thin films with varying degrees of @alpha@', @alpha@' and @gamma@' phases. The films were obtained using either sputtering or MBE. In the latter case, the films were grown in the presence of a N flow and the growth conditions were optimised in order to obtain a high content of @alpha@'-Fe16N2. A variety of characterization techniques was used to establish the epitaxial character of the films as well as the amount and kind of phase present. The magnetic properties of the samples was characterized by element specific X-ray Magnetic Circular Dichroism (XMCD).

11:00am **MI+MS+NS-ThM9 Processing Technology for Magnetic Random Access Memory**, M.C. Gaidis, J.P. Hummel, S.L. Brown, S. Kanakasabapathy, E. O'Sullivan, S. Assefa, K. Milkove, D. Abraham, Y. Lu, J.N. Nowak, P. Trouilloud, D. Worledge, W.J. Gallagher, IBM

**INVITED**

Magnetic Random Access Memory (MRAM) offers the potential of a universal memory - it can be simultaneously fast, nonvolatile, dense, and high-endurance. Depending on application, these qualities can make MRAM more attractive than SRAM, DRAM, flash, and hard drive memories, with a market measured in the billions of dollars. Small-scale demonstrations have realized much of the potential of MRAM, but scaling the memory to production on economically-profitable 200 or 300 mm wafer sizes creates unique processing challenges heretofore unseen in a large-scale semiconductor fabrication facility. MRAM read operations rely on electron tunneling through a thin (1 nm) insulating barrier between magnetic films. The exponential dependence of tunnel current on barrier thickness imposes requirements for across-wafer film uniformity on the order of 0.01 nm, made possible only by recent developments in deposition technology. To maximize performance, typical magnetic film stack designs can incorporate more than 10 distinct film layers. Very few of these layers

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can be etched by semiconductor-industry-standard RIE processes, and thus have required development of novel patterning techniques specifically tuned to minimize corrosion and to handle the nonvolatile nature of etch byproducts. The elements in these complex film layers tend to interdiffuse at temperatures below that of back-end-of-line (BEOL) semiconductor processing, thus necessitating the development of low-temperature processes for creating the BEOL wiring and packaging. Although daunting, each of the aforementioned challenges has largely been overcome. This presentation provides an overview of the basic MRAM structure and operation, followed by a discussion of the MRAM-specific processing techniques that have been developed to realize this technology in megabit arrays on 200 mm wafers.

## Nanometer-Scale Science and Technology Room 210 - Session NS-ThM

### Nanotube-based Devices

Moderator: S. Evoy, University of Alberta, Canada

8:20am **NS-ThM1 Quantum-dot Nanodevices with Carbon Nanotubes**, *K. Ishibashi, S. Moriyama, T. Fuse, D. Tsuya, M. Suzuki*, RIKEN, Japan **INVITED**  
Carbon nanotubes are attractive building blocks for extremely small nanodevices. In this paper, we present our effort to fabricate and demonstrate quantum-dot nanodevices, which includes following topics. 1) Single electron devices: A single electron transistor (SET), a single electron inverter that is consisting of two SETs in series, and a single electron XOR that has two input gates to SET, are fabricated in individual single-wall carbon nanotubes (SWCNTs) or multi-wall carbon nanotubes (MWCNTs), and their operation was demonstrated. 2) Quantum computing device (Qubit) and an artificial atom in the SWCNT: We focus on the spin qubit in association with observations of the artificial-atom like behavior. It is shown that the four or two electron shell structure was observed in single electron transport measurements at milli-Kelvin temperatures, and the shell filling of successive electrons and the Zeeman splitting of single particle states were confirmed in the magnetic field evolution of each Coulomb peak. The simple singlet and triplet states were directly observed in excitation spectroscopy measurements when two electrons were contained in a shell. These observations show that the SWCNT is very similar to natural atom with its unique shell structure and an energy scale of submillimeter to THz ranges. Despite the demonstrated wonderful properties as a building block of the nanodevices, we should admit that a breakthrough of device processes suitable for carbon nanotubes is really needed to realize more reliable and reproducible nanodevices.

9:00am **NS-ThM3 Stable Electron Emission from a Multi-Wall Carbon Nanotube in Low Vacuum**, *H. Suga*, Nihon University, Japan; *H. Abe, M. Tanaka*, National Institute of Advanced Industrial Science and Technology (AIST), Japan; *T. Ohno*, Technex Lab Co., Japan; *Y. Nishioka*, Nihon University, Japan; *H. Tokumoto, T. Shimizu*, AIST, Japan

Carbon nanotubes have been studied intensively in order to realize functional devices utilizing their unique electrical and mechanical properties. Then we have tried to fabricate the electron emitter using a multi-wall carbon nanotube (MWNT). Electrons are usually emitted applying several kilo volts to tungsten tip apex in ultra high vacuum. Therefore it is necessary to prepare high voltage power supply and expensive vacuum pumps like ion pumps. Then the aim of our research is to realize the MWNT electron emitter, by which electrons can be extracted at voltages lower than 500V in low vacuum around 10<sup>-3</sup> to 10<sup>-5</sup> Pa. MWNT electron emitters are fabricated as follows. Tungsten wire and tungsten loop were spot-welded, the wire was electrochemically etched. Then metal nano particles were smeared on the etched tip. Using a specially designed nano-manipulator combined with SEM (Tiny-SEM (W380mmxD350mmxH600mm) by Technex in Japan), a MWNT was attached on the tip apex, at first by the electron beam induced carbon deposition, and, to further assure the bonding between the MWNT and the tip, smeared metal nano particles were melted by heating tungsten loop. Typical length and diameter of the fabricated emitters are about 5 $\mu$ m and 20nm, respectively. Furthermore, in the SEM, the field emission can be carried out and the emitter-anode plane distance can be easily controlled on a micrometer scale, which is typically about 20 $\mu$ m. We measured turn-on field of 5 V/ $\mu$ m which is lower than conventional tungsten emitter in UHV. The emission current of 0.1 to 0.3 $\mu$ A can be attained at applied voltage of 70 to 160V on the same low vacuum condition. The stability of emission current about 1.5% at 0.3 $\mu$ A can be gained. The new way of high stability and the brightness and lifetime evaluation can be discussed in

detail in the presentation. @FootnoteText@ hiroshi-suga@@aist.go.jp, tetsuo-shimizu@@aist.go.jp

9:20am **NS-ThM4 Carbon Nanotubes as Ballistic Phonon Waveguides and Electro-Mechanical Switches**, *V. Deshpande, H.-Y. Chiu, H. Postma, M. Bockrath*, California Institute of Technology

PART I: Carbon nanotubes' exceptional thermal conductivity suggests that they may serve as efficient heat conduits to aid in the cooling of nanoscale circuits. Here, we report ballistic phonon transport, which provides the ultimate limit for heat dissipation. Upon heating freestanding nanotube devices with an electrical current, we find that the power required for the nanotube to reach a particular temperature is independent of nanotube length for devices shorter than  $\sim$ 500 nm, and follows a universal scaling law in the tube radius. This provides evidence for ballistic phonon propagation and suggests that, over such length scales, the heat carrying capacity of nanotubes has only fundamental limits imposed by their 1D nature. From our data, we obtain an estimate for the quantum of thermal conductance that is in good agreement with the Landauer picture of phonon transport. We then present a coherent picture of nanotube breakdown based on the thermal activation of bond-weakening electronic transitions. Finally, we find that the efficient propagation of heat to the electrical contacts enables the contacts to be annealed and improved in-situ. PART II: NEMS devices are competitive in switching speed with electronic devices, because of their low mass and small size. We are developing relay devices using multi-walled nanotubes (MWNTs) that exploit the ability of concentric nanotube shells to act as low-friction linear bearings. Analysis of our data yields a measurement of the retraction force on the inner nanotube shells from the outer shells, which agrees with theoretically expected value. We are able to electrostatically telescope shells of a MWNT to establish electrical contact and turn the device to a conducting "on" state. The device can be turned "off" again by applying a sufficiently large gate voltage to bend the nanotube segments until the connection is broken. Possible applications include memories, logic gates, and high-gain nanomechanical amplifiers.

9:40am **NS-ThM5 Carbon Nanotube Transistors and How They Are Different**, *J. Appenzeller*, IBM Research Division, US **INVITED**

Over the last few years carbon nanotubes (CNs) have attracted an increasing interest as building blocks for electronics applications. While metallic nanotubes are considered as interconnects in integrated circuits, semiconducting tubes are evaluated as field-effect transistor (FET) components. Since the first CNFET operation has been demonstrated in 1998, @footnote 1,2@ device performance has been significantly improved. @footnote 3,4,5@ Among other things it has been shown that CNFETs operate in the ballistic regime even at room-temperature, provided that not too large drain and gate voltages are applied and that their channel length does not exceed a couple of hundred nanometers. @footnote 6,7,8@ One of the more unexpected findings in the context of CNFETs was that they cannot be described within a conventional MOSFET model. The most critical observation has been that carbon nanotube transistors in fact behave as Schottky barrier devices. @footnote 9,10@ It was found that switching in nanometer size semiconductors, such as carbon nanotubes, contacted with source/drain metal electrodes is determined entirely by the metal/semiconductor interfaces and their field-dependence, provided that transport in the semiconductor is ballistic. Making use of this particular type of nanotube property, we have been able to gain important insights into the topic of multi-mode transport in CNFETs @footnote 11@ and, most importantly, have recently successfully fabricated the first band-to-band tunneling CNFET with a much more abrupt switching behavior than can be obtained with any conventional transistor approach. @footnote 12@ @FootnoteText@ @footnote 1@ S.J. Tans A. Verschueren, and C. Dekker, Nature 393, 49 (1998). @footnote 2@ R. Martel T. Schmidt, H.R. Shea, T. Hertel, and Ph. Avouris, Appl. Phys. Lett. 73, 2447 (1998). @footnote 3@ A. Bachtold, P. Hadley, T. Nakanishi, and C. Dekker, Science 294, 1317 (2001). @footnote 4@ A. Javey, H. Kim, M. Brink, Q. Wang, A. Ural, J. Guo, P. McIntyre, P. McEuen, M. Lundstrom, and H. Dai, Nature Materials 1, 241 (2002). @footnote 5@ S. Wind, J. Appenzeller, R. Martel, V. Derycke, and Ph. Avouris, Appl. Phys. Lett. 80, 3817 (2002). @footnote 6@ M. Fuhrer, H. Park, and P.L. McEuen, IEEE Trans. on Nanotech. 1, 78 (2002). @footnote 7@ A. Javey, J. Guo, Q. Wang, M. Lundstrom, and H. Dai, Nature 424, 654 (2003). @footnote 8@ S. Wind, J. Appenzeller, Ph. Avouris, Phys. Rev. Lett. 91, 058301 (2003). @footnote 9@ S. Heinze, J. Tersoff, R. Martel, V. Derycke, J. Appenzeller, and Ph. Avouris, Phys. Rev. Lett. 89, 106801 (2002). @footnote 10@ J. Appenzeller, J. Knoch, V. Derycke, R. Martel, S. Wind, and Ph. Avouris, Phys. Rev. Lett. 89, 126801 (2002). @footnote 11@ J. Appenzeller, J. Knoch, M. Radosavljevic, and Ph.

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Avouris, Phys. Rev. Lett. 92, 226802 (2004).@footnote 12@ J. Appenzeller, Y.-M. Lin, J. Knoch, and Ph. Avouris, Phys. Rev. Lett. 93, 196805 (2004).

10:20am **NS-ThM7 Carbon Nanotube Schottky Diodes for High Frequency Applications, E.W. Wong, H.M. Manohara, E. Schlecht, B.D. Hunt, P.H. Siegel**, Jet Propulsion Laboratory, California Institute of Technology

We have demonstrated Schottky diodes using semiconducting single-walled nanotubes (s-SWNTs) with titanium Schottky and platinum Ohmic contacts for high frequency applications. The devices demonstrate rectifying behavior with large reverse bias breakdown voltages of greater than -15 V. In order to decrease the series resistance, multiple SWNTs are grown in parallel in a single device, and the metallic tubes are burnt-out selectively. At low biases these diodes showed ideality factors in the range of 1.5 to 1.9. Results from devices containing multiple nanotubes suggest that these diodes can act as direct detectors at room temperature at 2.5 terahertz (THz) frequency with noise equivalent powers (NEP) potentially comparable to that of the state-of-the-art gallium arsenide solid-state Schottky diodes, in the range of  $10^{\text{super}} -13^{\text{super}} \text{W/Hz}$  at  $1/2^{\text{super}}$ . In essence, the SWNT Schottky diodes with multiple parallel tubes per device with individually reduced resistances to the order of a few  $k^{\text{OMEGA}}$  promise superior performance compared to that of the state-of-the-art solid-state Schottky diodes for applications at high frequencies.

10:40am **NS-ThM8 Study of High-Field Electron Transport in Multi-Wall Carbon Nanotubes by MCBJ Technique, M. Tsutsui, Y. Taninouchi, S. Kurokawa, A. Sakai**, Kyoto University, Japan

Multi-wall carbon nanotubes are foreseen to be a promising candidate for interconnects within atomic and molecular transistors owing to their high current carrying capacity. However, there still remain some controversies on high-field electron transport in MWNTs, in particular the conductance versus bias voltage (G-V) characteristics. In the present study, we have investigated high-field electron transport in MWNTs utilizing mechanically controllable break junction (MCBJ) technique. One of the advantages in this technique is that electrode gap distance can be manipulated with picometer resolutions after MWNTs being suspended between the electrodes. Bridging of MWNTs over Au electrodes is accomplished by repeatedly breaking Au contacts in a nanotube-dispersed solution. Measured G-V characteristics show that the conductance of MWNTs linearly increases with the bias up to 3 V. An important role of the nanotube/electrode contact resistance on the electron transport through MWNTs is suggested from G-V characteristics acquired at various electrode separations. Bias-polarity asymmetry is observed in Joule heating effects on nanotube/electrode contacts at high biases, and its implications will be discussed in the presentation.

11:00am **NS-ThM9 Enhancement on Field Emission Performance of MWNTs Impregnated with RuO@sub 2@ and Rooted into Metal Substrate, H. Liu**, The Graduate University for Advanced Studies, Japan; T. Noguchi, K. Tatenuma, KAKEN Inc., Japan; S. Kato, The Graduate University for Advanced Studies, Japan

We have shown that field emission characteristics of MWNTs are drastically enhanced by RuO@sub 2@ impregnation and MWNT rooting into a metal substrate. These new key technologies improve both increase of field enhancement factor due to a proper surface density of subnano and nano sized RuO@sub 2@ particles on MWNT surfaces and increase of electrical conductivity, thermal conductivity, high-temperature resistance and tensile strength due to their high adhesivity between MWNTs and the metal substrate. In this paper, we demonstrate that the electron emission current from bulky MWNTs could reach  $1.2\text{A/cm}^{\text{super}} 2^{\text{super}}$  at  $6.0\text{V}/\mu\text{m}$  and reach the maximum of  $1.9\text{A/cm}^{\text{super}} 2^{\text{super}}$  at  $7.5\text{V}/\mu\text{m}$  even in the continuous DC mode in optimization processes for the impregnation and the rooting. According to analysis of microscope images of the substrate, the results above can be corrected by a factor of 2.5 times considering that an area of 40% on the substrate was only covered with MWNTs because surface density of MWNTs on the substrate has not yet fully controlled in the process of the rooting. In the presentation, the detail of these results and discussions will be given with results of endurance running tests at the high current density.

11:20am **NS-ThM10 Topologically Induced Localized States in Single Wall Carbon Nanotubes, S.-J. Kahng**, Korea University, Korea; S. Lee, H. Kim, J. Lee, Y. Kuk, Seoul National University, Korea

The local electronic structures of semiconducting single wall carbon nanotubes was studied with scanning tunneling microscopy. We performed scanning tunneling spectroscopy measurement at selected locations on the center axis of carbon nanotubes, acquiring a map of the electronic density

of states. Spatial oscillation was observed in the electronic density of states with the period of atomic lattice. Defect induced interface states were found at the junctions of the two semiconducting nanotubes, which are well-understood in analogy with the interface states of bulk semiconductor heterostructures. The electronic leak of the van Hove singularity peaks was observed across the junction, due to inefficient charge screening in a one-dimensional structure. Several paired, localized gap states were observed in semiconducting single-wall carbon nanotubes. A pair of gap states is found far from the band edges, forming deep levels. Another pair is located near the band edges, forming shallow levels. The deep levels are explained by a vacancy-atom complex while the shallow levels are explained by a pentagon-heptagon structure. Our experimental observation indicates that the presence of the gap states provides a means to perform local band-gap engineering as well as doping without impurity substitution.

11:40am **NS-ThM11 Optimization of Impregnation of Subnano RuO@sub 2@ Clusters on MWCNT for Field Emission Displays, T. Noguchi, K. Tatenuma**, KAKEN Inc., Japan; S. Kato, High Energy Accelerator Research Organization (KEK), Japan

For applications of MWNTs to FEDs and the other electron sources, we reported the achievement of a remarkably high DC current density close to  $300\text{mA/cm}^{\text{super}} 2^{\text{super}}$  with a threshold electric field of  $2\text{V}/\mu\text{m}$  using a new technology of impregnation of subnano RuO@sub 2@ clusters on MWCNT surfaces and of MWNT rooting into a metal substrate. Here we focus on optimization of the impregnation for better electron emission property of MWNTs on ITO glass substrates. Preliminary investigation showed that two orders of magnitude less quantity of the impregnation was sufficient for MWNTs of high purity than MWNTs of low purity to obtain the same emission property. The quite different quantity of the impregnation for proper emission would be explainable based on possible absorption of RuO@sub 2@ particles into the impurities of MWNTs.

## Nanometer-Scale Science and Technology Room 210 - Session NS-ThA

### Nano Processing

Moderator: D.M. Tennant, Lucent

2:00pm **NS-ThA1 Control of Germanium Nanocrystal Morphology and Surface Functionalization**, *H. Gerung*, University of New Mexico; *T.J. Boyle*, Sandia National Laboratories; *C.J. Brinker*, *S.M. Han*, University of New Mexico

We have developed a simple synthesis route for Ge nanocrystals (Ge NCs) via reduction of Ge(II) precursor at 300 °C and 1 atm. The synthesis does not require strong reducing agents and does not produce salts or undesirable byproducts. Literature reports on Ge NC syntheses have focused mainly on direct reduction of Ge(IV) to Ge(0), which requires a combination of high temperature (>400 °C), high pressure (>1 atm), and strong reduction agents. Ge[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> is chosen as the Ge(II) precursor due to the ease of its synthesis in high yield, the absence of potential halide contamination, and the labile amido ligand sets. The synthesis involves the injection of Ge[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> dissolved in oleylamine into non-coordinating solvent 1-octadecene at 300 °C and 1 atm Ar. The resulting Ge NCs form quickly and show a high degree of crystallinity with no oxide formation. These NCs are mostly spherical in shape. The Ge(II) precursor's ligands can be tailored to form Ge[TMPP]<sub>2</sub> (TMPP = 2,2,6,6-tetramethyl piperidine) and using identical reaction conditions, cuboid Ge NCs are formed. Another alternative Ge(II) precursor, Ge[DBP]<sub>2</sub> (DBP = 2,6-di-tert-butylphenoxide) can be isolated from an amide alcohol metathesis reaction between Ge[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> and 2 equivalents of DBP-H. The use of Ge[DBP]<sub>2</sub> under identical reaction conditions as discussed above yields Ge nanowires (Ge NWs) instead of Ge NCs. These results suggest that the Ge(II)-ligand bond strength, the steric orientation of ligands, and the subsequent surfactants formed upon decomposition of the various precursors dictate the size and morphology of Ge NCs by controlling the surface kinetics during crystal growth. We will further discuss optical and electrical characterization of Ge nanocrystals and functionalizing Ge NC surface to incorporate them into a silica matrix.

2:20pm **NS-ThA2 White Luminescence from Silica Glass Containing Nanocrystalline Silicon Prepared by RF Sputtering Technique**, *K. Sato*, *Y. Sasaki*, *K. Hirakuri*, Tokyo Denki University, Japan

Nanocrystalline silicon (nc-Si) is one of promising materials for application to light-related devices because it shows the particle size-dependent luminescence. We previously obtained a red/green/blue luminescence from the nc-Si with various particle sizes. The white luminescence can be realized by the mixture of nc-Si which emits the red/green/blue light. In this paper, we report a fabrication technique of the silica glass containing red/green/blue luminescent nc-Si. Moreover, the luminescence property of the silica glass will be discussed. The silica glass containing nc-Si was formed by co-sputtering of Si chips/silicon dioxide (SiO<sub>2</sub>) targets and subsequently annealing at high temperature. The particle size of nc-Si was varied from 1.9 nm up to 3.0 nm by changing the deposition conditions such as radio frequency power and gas pressure in order to obtain red/green/blue luminescence from the nc-Si. The sample was evaluated by using a photoluminescence (PL) measurement. The silica glass containing nc-Si showed a broad PL spectrum with a peak at 460 nm (blue light), 550 nm (green light) and 800 nm (red light). This is due to the existence of nc-Si in which the particle size differs, i.e., the nc-Si with particle size of 1.9 nm, 2.2 nm and 3.0 nm exhibits blue, green and red luminescence, respectively. When the silica glass was irradiated by using a xenon lamp with an optical band-pass filter of 313 nm, the luminescence color from the silica glass was a white light. The white luminescence could be distinctly seen by the naked eye under room illumination.

2:40pm **NS-ThA3 Silicon Quantum Dots and Nanomembranes: Tools for Quantum Information?**, *M.A. Eriksson*, University of Wisconsin-Madison  
**INVITED**

Silicon has certain unusual properties, including a spin-0 nuclear isotope, that make quantum dots in this material excellent candidates for quantum information processing. Silicon can also form spectacular membranes, one hundred nanometers thick and centimeters across. Such silicon nanomembranes bend and flex like plastic sandwich wrap but retain their single crystal electronic properties. I will present results on silicon quantum dots fabricated using both Schottky gates and Atomic-Layer-Deposition

MOS gates on Si/SiGe modulation-doped heterostructures. These dots have excellent charge stability, but their fabrication currently requires special processing. I also will present recent results on silicon nanomembranes, a material that retains the excellent intrinsic properties of silicon, but that can be bent, strained, and rolled into tubes. These properties offer the potential to use strain in a defect-free system, potentially leading to new ways to create quantum dots with few end-processing complexities. X-ray scattering, TEM, and low temperature electronic transport measurements will be presented, and the prospects for meaningful application of such membranes will be discussed. Work performed in collaboration with L.J. Klein, K.L.M. Lewis, K.A. Slinker, L. McGuire, Srijit Goswami, W. Peng, C. Haselby, D.W. van der Weide, R.H. Blick, S.N. Coppersmith, R. Joynt, Mark Friesen, M.M. Roberts, D. Savage, M.G. Lagally (University of Wisconsin-Madison) and J.O. Chu (IBM Watson).

3:20pm **NS-ThA5 Fabrication and Characterization of ZnO Quantum Dots and Nanosheet Structure**, *R. Mu*, Fisk University; *Y.C. Liu*, *H.Y. Xu*, *S.J. Chen*, Northeast Normal University, PRC

ZnO quantum dots and nanosheets have been fabricated via oxygen plasma assisted electron-beam deposition of ZnF<sub>2</sub> and physical vapor transport techniques. Raman measurements of ZnO QDs showed a strong optical phonon confinement effect and the presence of surface phonon mode which does not exist in Raman spectra of ZnO films. A large blueshift in optical absorption and ultraviolet photoluminescence (UV PL) spectra were observed for ZnO QDs due to a strong quantum confinement effect of excitons. ZnO QDs possess an anomalous temperature dependent behavior in UV PL intensity. In the case of nanosheet, temperature dependent study shows a surprisingly strong high temperature (857K) photon emission. A brief discussion is given in an attempt to understand the physical mechanisms.

3:40pm **NS-ThA6 Induced Growth of Calcite and Gypsum using an Atomic Force Microscope**, *A.L. McEvoy*, *F. Stevens*, *S.C. Langford*, *J.T. Dickinson*, Washington State University

Bond breaking at surfaces due to stimuli such as exposure to energetic radiation, mechanical stress, or chemical agents is well established. We examine the consequences of combining localized mechanical stress (due to contact with the tip of an atomic force microscope) and exposure to aqueous solutions. We show that we can induce highly localized, nanometer scale growth on single crystal surfaces of calcite (CaCO<sub>3</sub>), an important biomineral, and gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O) through combined exposure to supersaturated solutions and mechanical stress. Growth occurs along step edges in single atomic layers. The growth rates depend strongly on step orientation. Tip induced deposition is shown to produce surfaces free of obvious defects, in contrast with spontaneous growth in highly supersaturated solutions ( $\sigma > 5$ ). Experimental evidence is presented for tip-enhanced transport of ions to deposition sites. Implications concerning deposition and maintenance of atomically smooth surfaces, including mammalian joints, will be discussed. This work was supported by the National Science Foundation.

4:00pm **NS-ThA7 WCx Nanoparticles as Alternate Catalyst for NOx Reduction**, *A. Rumaiz*, *S. Shah*, University of Delaware; *I. Baldytsky*, University of Delaware

WCx nanoparticles were synthesized using Laser Assisted Inert Gas Condensation (LAIGC). In this process either a metal target is ablated in the presence of a reactive gas or a compound target is used. The evaporated flux obtained by laser ablation is condensed by a circulating He gas to form WC nanoparticles. The structural properties of the samples were investigated using X-ray Diffraction (XRD) and X-ray Photo-Electron Spectroscopy (XPS). The feasibility of using nano WCx as an alternative catalyst for Pt is also addressed. A comparative study on two types of samples of WC (as prepared and carburized W) was done. The samples were used to check for the reduction of NO<sub>x</sub> in a simple reactor. The carburized W shows activity at temperatures around 400°C, while the as prepared WC shows activity at a slightly higher temperature. The stability of both the samples was studied by exposing them to a NO<sub>x</sub> environment at a fixed temperature (where the activity is appreciable) for an extended period of time. XPS and XRD confirm the formation of oxide phase after DeNO<sub>x</sub>. In order to study the nature of oxidation the DeNO<sub>x</sub> reaction was carried in a CO/O<sub>2</sub>/Hydrocarbon gas mixture. The results of these will be presented. Valence band measurements were carried out to compare at the Density of States (DOS) for WC and Pt. Theoretical calculations of the DOS were also done using Self Consistent Field approximation using the WIEN2k code.

# Thursday Afternoon, November 3, 2005

4:20pm **NS-ThA8 Photo-Induced Decomposition of Palladium Acetate for Palladium Nanoparticle Production**, *C.E. Allmond, A.T. Sellinger, G. Peman, J.M. Fitz-Gerald*, University of Virginia

Hydrocarbon reactions and rearrangements catalyzed by transition metals trigger chemical processes at the core of the petrochemical and polymer industries. The highly dispersed metal nanoparticles utilized for these reactions are generally prepared by reducing an aqueous solution of a noble metal salt or through the deposition of a precursor on a high surface area support followed by a further reduction step. Palladium acetate, [Pd(OAc)<sub>2</sub>], is a widely favored metallorganic precursor for thin film processing on various substrates because it decomposes under ultraviolet irradiation. In this research, Pd and Pd acetate nanoparticles were deposited using a novel variation of matrix assisted pulsed laser evaporation (MAPLE). Samples were prepared by dissolving Pd(OAc)<sub>2</sub> into chloroform, then flash-frozen in liquid nitrogen. Deposition onto Si (100) wafers, NaCl crystals, and electron microscopy grids at room temperature was performed using a pulsed excimer laser ( $\lambda = 248$  nm, 5 Hz, 25 ns FWHM) in a dynamic Ar atmosphere at 200 mTorr as a function of laser fluence and Pd metal loading. The nanoparticle sizes, distributions, and morphology of Pd and Pd acetate nanoparticles were characterized by high-resolution scanning electron microscopy (HRSEM), high-resolution transmission electron microscopy (HRTEM), X-ray energy dispersion spectroscopy (EDS), Fourier transform infrared spectroscopy (FTIR), and X-ray diffraction (XRD). Jun-Ying Zhang, Hilmar Esrom, Ian W. Boyd (1996). "Decomposition mechanisms of thin palladium excimer UV radiation." *Applied Surface Science*(96-98): 399-404. Zolt Geretovszky, Ian W. Boyd. (1999). "Kinetic study of 222 nm excimer lamp induced decomposition of palladium-acetate films." *Applied Surface Science*(138-139): 401-407.

4:40pm **NS-ThA9 Engineering of Porous, Tin Oxide Nanoparticle Microshells for Chemical Sensor Applications**, *C.J. Martinez, C.B. Montgomery, B. Hockey, S. Semancik*, National Institute of Standards and Technology

Advanced sensors for applications ranging from homeland security to space exploration will require performance characteristics that include high sensitivity and rapid response. We have sought to enhance the sensitivity and speed of conductometric gas microsensors through the design and fabrication of porous, three-dimensional tin oxide nanoparticle (10 nm) films. These films were fabricated via the self-assembly from solution of nanoparticle-decorated latex microspheres, which serve as sacrificial templates. Through heating (10<sup>4</sup> °C/sec), the latex microspheres were removed to reveal a multiscale porous 3-dimensional structure composed of interconnected hollow nanoparticle microshells with ultra-thin walls (50 nm). The multiscale porous architecture promotes analyte diffusion and maximizes available active surface area. Sensor measurements were performed by depositing these films onto MEMS microsensor platforms with inter-digitated electrodes and embedded heaters. We report on film conductance changes measured at different temperatures (300 °C to 450 °C), caused by exposure to test gases at concentrations 100 ppb in a dry air background. An enhancement in sensitivity to CO, H<sub>2</sub>O and MeOH was observed for these nanoparticle microshell films when direct comparisons were made to other nanostructured sensing films. Special attention has been given to understanding the influence that structural factors (film thickness, packing density, microshell diameter and microshell thickness) have on the sensitivity, selectivity, stability and response time of these materials.

5:00pm **NS-ThA10 Measurement of the Young's Moduli of Individual Electrospun Nanofibers**, *L.M. Bellan*, Cornell University; *J. Kameoka*, Texas A&M University; *H.G. Craighead*, Cornell University

Our measurements of the Young's moduli of individual electrospun polymer nanofibers support previous claims that electrospinning can produce polymer fibers with high degrees of molecular orientation. Electrospinning is a technique for fabricating micro- and nanoscale fibers using a strong electric field to extract a jet from a viscous solution. These fibers may be oriented by depositing them on a rotating substrate. We have used this technique to deposit oriented polyethylene oxide and silica glass nanofibers over trenches etched in silicon. The suspended fibers were depressed using an atomic force microscope, and the resulting force-displacement data was used to determine the Young's moduli of the individual fibers. The Young's moduli of the polyethylene oxide fibers were significantly larger than the reported values for polyethylene oxide bulk and films, which supports previous claims of molecular orientation in the

fibers. The Young's moduli of the glass fibers were consistent with values calculated from previously measured mechanical resonance frequencies of similar fibers. We are currently investigating mechanical properties of individual nanofibers spun from other polymers.

## Nanometer-Scale Science and Technology

### Room 210 - Session NS-FrM

#### Nanotube Processing and Properties

**Moderator:** N.A. Burnham, Worcester Polytechnic Institute

**8:20am NS-FrM1 Precise Placement of a Multi-Wall Carbon Nanotube using Nano Manipulator in SEM, H. Abe, M. Tanaka, M. Horikawa, Y. Naitoh, T. Shimizu, AIST, Japan**

There have been many studies for realizing electric devices using carbon nanotubes (CNTs). Particularly a variety of growth methods have been developed in order to control the diameter and the electric properties. In addition, we have thought that it is important to place precisely a CNT onto the designated position and make electrically and mechanically reliable contacts between CNT and electrodes for the realization electric circuit using CNT. From now, we have manipulated a multi-wall CNT (MWNT) and fabricated a MWNT tip for high-resolution SPM measurement using specially designed SEM manipulator. Then we developed several bonding methods by melting low melting point alloy and TiNi nano particles, whose bonding showed good conductivity of several  $10k\Omega$  and mechanical strength of more than 2GPa. In addition to the techniques, we have tried to fabricate a bridge structure using a MWNT in the SEM manipulator. Then we succeeded in bridging a MWNT between electrodes whose distance is from  $1\mu\text{m}$  to  $4\mu\text{m}$ . This technique enables us to control the attaching position of less than  $50\text{nm}\times 50\text{nm}$  and to float or touch MWNT from the substrate. We could really bridge a MWNT by floating between thermal heater of  $300\text{nm}$  and thermal bath for precise thermal conductivity measurement of a single MWNT. We have thought that this technique could be applied to other nanotubes' bridge structure fabrication and their physical property. The way of fabricating a MWNT bridge structure will be shown using video file in detail in our presentation.

**8:40am NS-FrM2 Hydrogenation of Single Wall Carbon Nanotubes, A.S. Nikitin, H. Ogasawara, Stanford Synchrotron Radiation Laboratory; D. Mann, Z. Zhang, H. Dai, K.J. Cho, Stanford University; A. Nilsson, Stanford Synchrotron Radiation Laboratory**

The hydrogenation of the single wall carbon nanotubes (SWCN) is considered as a mechanism of hydrogen storage in the nanotube materials. We present the hydrogenation of the single wall carbon nanotube films with an atomic hydrogen beam. Using X-ray absorption spectroscopy, we demonstrated that C-C bonds in the walls of SWCN decrease of  $sp^2$  character and increase of  $sp^3$  character simultaneously due to hydrogenation. On the basis of X-ray photoelectron spectroscopy results combined with theoretical calculations, we show  $65\pm 15\%$  hydrogenation of carbon atoms in the SWCN films that corresponds to  $5.1\pm 1.2$  wt % hydrogen weight capacity of the studied sample. The formed C-H bonds are stable at ambient temperature and can be broken in the temperature range from  $300^\circ\text{C}$  to  $600^\circ\text{C}$ . These results clearly demonstrate that a chemical interaction mechanism of hydrogen with SWCN is possible with a large hydrogen storage capacity.

**9:00am NS-FrM3 Well - Aligned Growth of Carbon Nanotubes/Fibers in Anodized Aluminum Oxide Pores by DC Plasma Enhanced Hot Filament Chemical Vapor Deposition, H.W. Yap, B. Ramaker, A.V. Sumant, R.W. Carpick, University of Wisconsin-Madison**

In many carbon nanotube (CNT) or carbon nanofiber (CNF) applications - such as field emission flat panel displays, it is ideal to have an ordered and dense vertically aligned dense CNT/CNF array over a large area. The anodized aluminum oxide (AAO) template is favorable since it offers uniformly spaced pores for isolated and directional growth of these CNT/CNFs. Several research groups have already reported the use of the AAO template to grow CNT/CNFs via thermal chemical vapor deposition (CVD) but they were not successful in obtaining vertical and isolated growth once they emerged from the pores. Thus, etching of the AAO had to be subsequently performed. Microwave plasma enhanced MPECVD has been shown to give better alignment, however it is not cost effective in terms of power requirements and large area deposition. Here we report a cost effective, low power alternative approach: dc plasma enhanced hot filament CVD (dcPEHFCVD). To our knowledge, this is the first successful report to grow well aligned CNTs via AAO pores using dcPEHFCVD. Here, no anodization of the aluminum, pore widening of the AAO, post growth etching of the AAO or pretreatment of the catalyst are needed. Nickel nanowires electrodeposited in the pores act as catalysts. We find that tip growth mode is dominant here. The hot filament plays an important role in

dissociating hydrocarbon species as well as heating the substrate to enhance the catalyst driven CNT/CNF growth. The plasma's electric field aligns the CNT/CNFs and is responsible for most of the growth chemistry. High resolution transmission electron microscopy reveals that both CNTs and CNFs are formed via the tip growth mode and have graphitic walls. The majority of CNTs have hollow interiors but some CNFs exhibit herringbone-like fringes in the interior. AFM images of the tubes are obtained and provide quantitative measurement of the length variations of the tubes.

**9:20am NS-FrM4 Carbon Nanosheets--A Sub-nanometer Two-dimensional Carbon Nanostructure, M.Y. Zhu, J.J. Wang, X. Zhao, R.A. Outlaw, B. French, D.M. Manos, B.C. Holloway, College of William and Mary**

In this paper, we report a sub-nanometer scaled two-dimensional carbon nanostructure--Carbon nanosheets (CNS) by radio-frequency plasma enhanced chemical vapor deposition (RF-PECVD). CNS were synthesized from mixed gases of methane ( $\text{CH}_4$ ) and hydrogen ( $\text{H}_2$ ) on various substrates, including Si,  $\text{SiO}_2$ , Al,  $\text{TiO}_2$ , Mo, Zr, Ti, Hf, Nb, W, Ta, Cu and 304 stainless steel, without any catalyst or substrate pre-treatment. SEM, HRTEM, SAD, Raman spectroscopy, XRD, XPS and AES, were used to characterize the morphology and structure properties of the CNS. The results showed that CNS consist of graphene layers, oriented nearly vertically to the substrates. Typical CNS are hundreds of nanometers in width and height, but only few nanometers in thickness, sometimes as thin as a single-atomic-layer. Raman spectra of CNS featured D peaks and G peaks for  $sp^2$  bonded carbon, and low energy peaks, similar to RBM mode of single wall carbon nanotubes, were also observed. Analysis indicated that CNS is pure carbon without detectable contamination. BET measurement revealed a specific surface area of  $\sim 1300\text{m}^2/\text{g}$ , which is the theoretical maximum value for a 2-layered graphene sheet. The high surface area makes CNS a potential candidate of catalyst support and hydrogen storage in fuel cell applications. Diode I-V curves, acquired to study the field emission property of nanosheets, showed a turn-on field as low as  $1\text{ V}/\mu\text{m}$  and a current density of  $2.2\text{mA}/\text{mm}^2$  over an area of  $1\text{mm}^2$ . This indicates that CNS is a good cathode material for cold field emission devices.

**9:40am NS-FrM5 Super Growth - Highly Efficient Synthesis of Impurity-Free Single-Walled Carbon Nanotubes and its Applications, K. Hata, AIST, Japan**

**INVITED**

We demonstrate an extremely efficient chemical vapour deposition synthesis of single-walled carbon nanotubes where the activity and lifetime of the catalysts are enhanced by an addition of water into the ambient of the CVD furnace, a growth mode we call "Super Growth". The enhanced catalytic activity of super growth results in massive growth of super-dense and vertically-aligned single-walled nanotubes forests with heights up to 2.5 millimeters. In addition, these SWNT forests were easily separated from the catalysts, producing the most pure SWNT material (over 99.98%) ever made, amazingly through an all-dry process without any purification. Moreover, patterned highly organized intrinsic single-walled nanotube structures were successfully fabricated. Super Growth simultaneously addresses many critical problems such as scalability, purity, and cost, and opens up innumerable opportunities ranging from fundamental research to real applications. @FootnoteText@ @footnote 1@K. Hata, et al., Science 306. 1362 (2004)

**10:20am NS-FrM7 Microstructural Modifications of Multiwalled Carbon Nanotubes by keV Ar<sup>+</sup> Bombardment: a High Resolution TEM Study, D.-Q. Yang, E. Sacher, Ecole Polytechnique of Montreal, Canada**

The surface functionalization and microstructural modification of carbon nanotubes (CNTs) have both attracted great interesting because of their potential applications to microelectronic devices and advanced functional CNT-based materials. One functionalization method is to break C-C bonds with keV Ar<sup>+</sup> treatment, thus producing highly localized amorphous regions containing free radicals capable of further reaction. Such treatment of NTs has recently been found capable of changing the electronic properties and enhancing the field emission of multiwalled CNTs (MWCNTs). To better understand the interaction between the ion beam and CNTs, we have studied their microstructural evolution, under keV Ar<sup>+</sup> beam irradiation, by high resolution TEM. We found that Ar<sup>+</sup> treatment doses from  $10^{13}$  to  $10^{15}$  ions/cm<sup>2</sup> produce free radical defects, an amorphous layer, as well as nanonodules that continue to grow and, on contacting another such growing nodule, crosslink the nanotubes. We discuss the formation mechanism of these microstructural modifications.

# Friday Morning, November 4, 2005

10:40am **NS-FrM8 Structural, Optical, and Electrical Properties of Functionalized SWNTs with DNA and Metal Nanoparticles**, *G.-H. Jeong*, NTT Basic Research Laboratories, Japan; *A. Yamazaki*, Tokyo University of Science, Japan; *S. Suzuki*, *Y. Kobayashi*, *K. Furukawa*, *K. Torimitsu*, NTT Basic Research Laboratories, Japan; *Y. Homma*, Tokyo University of Science, Japan

Because of the outstanding physical, chemical and electrical properties of carbon nanotubes (CNT), a number of applications in various fields are expected. Especially, extensive CNT-functionalization researches have been performed to control electronic property because diameter- or chirality-controlled growth has not realized yet. Recently, we have performed the experimental approach to create CNT-based novel hybrid structures and demonstrate here the results. DNA and Au nanoparticles (NP) are selected to functionalize CNT due to their specific assembling property. By controlled chemical vapor deposition, single-walled carbon nanotubes (SWNTs) were successfully synthesized not only on flat substrate but also on Si-pillar substrate which allows suspending nanotubes. SWNTs-functionalization was performed by covalent coupling between carboxyl and amine groups. DNA/Au hybrids were made using thiolated-DNA and Au NP and confirmed by UV-visible absorption spectroscopy. Finally, SWNTs were modified with Au NP or DNA/Au hybrids. The density of Au NP attached along the suspended SWNTs was controlled by changing treatment time and concentration of the Au colloid. In Raman characterization, we observed new peaks at radial breathing band after Au NP attachment, which may be caused by surface-enhanced Raman scattering. Photoluminescence peaks were also detected from the SWNTs/Au hybrids and will be investigated the effect of Au functionalization. The intensity change of radial breathing band and defect band in Raman spectra was also observed from the SWNTs/DNA/Au hybrid, which implies the different electronic or optical properties are expected. These results show functionalized CNT can be further developed to electronic and optical applications. @FootnoteText@ @footnote 1@NTT Basic Research Laboratories, NTT Corporation, Atsugi, Kanagawa 243-0198, Japan @footnote 2@CREST, JST, c/o Dept. of Physics, Tokyo University of Science, Tokyo 162-8601, Japan

11:00am **NS-FrM9 Nanomechanical Resonance Studies of Carbon Nanotube Peapod Bundles**, *P. Jaroenapibal*, *C.Y. Nam*, *J.E. Fischer*, *D.E. Luzzi*, University of Pennsylvania; *S. Evoy*, University of Alberta, Canada

The recent development of hybrid carbon nanotube materials, such as supramolecular self-assembled arrays of C60 molecules encapsulated within single-wall carbon nanotubes (C60@SWNT), has opened new possibilities for the development of nanomechanical devices of tunable properties. We studied the mechanical properties of C60-filled SWNT bundles through analysis of their resonance in a transmission electron microscope (TEM). X-Ray diffraction was used to qualitatively study the filling of C60 in the bulk material. The intensity of the (1,0) bundle peak, located at  $Q = 0.45 \text{ \AA}^{-1}$ , was reduced after filling of the tubes with C60. Electron diffraction analysis revealed a C60 spacing periodicity of  $9.97 \text{ \AA}$  within the lumen of the SWNTs. Mechanical resonance measurements were conducted in a TEM by selecting bundles whose extremities were appropriately affixed. An average ratio of  $(E^*/\rho)^{1/2} = 19002 \text{ \AA} \pm 2307 \text{ m/s}$  was extracted from the resonance analysis of the C60-filled bundles, compared to a ratio of  $(E^*/\rho)^{1/2} = 13230 \text{ \AA} \pm 3187$  for the unfilled material. These values correspond to an effective average Young's modulus of  $E^* = 240 \text{ \AA} \pm 105 \text{ GPa}$  for empty bundles, and of up to  $E^* = 650 \text{ \AA} \pm 156 \text{ GPa}$  for the C60-filled materials. These moduli are significantly lower than the  $\sim 1 \text{ TPa}$  usually reported for individual SWNTs due to the weak interaction and sliding effect that are known to exist between tube surfaces. However, the significant increase of stiffness upon filling is believed to be related to an increase of strain energy of the individual SWNTs within the bundle. A dependence of this modulus on bundle diameter was also observed. This dependence is explained by the increased importance of inter-tube slipping in bundles of larger diameter. We will also present recent results on the mechanical resonance properties of single-crystalline GaN nanowires. Preliminary resonant analysis of 30-160 nm wide wires suggest an average effective Young's modulus of  $E^* = 120 \text{ \AA} \pm 20 \text{ GPa}$ .

11:20am **NS-FrM10 Molecular Dynamics Simulation of Irradiation Effects on the Mechanical Failure of Multi-Walled Carbon Nanotubes**, *S.K. Pregler*, *S.B. Sinnott*, University of Florida

Polyatomic ion-beam deposition on advanced materials, such as semiconductors, carbon nanotubes, polymers, and nanocomposites, to induce surface chemical modification is an important process used to achieve thin film growth, surface etching, and nano-texturing of the

surface. Previous atomistic simulations have shown that particle beam deposition can induce crosslinking between the shells of unfunctionalized multiwalled carbon nanotubes. In this work, we investigate the effect of atomic, polyatomic, and electronic irradiation of chiral and armchair multiwalled carbon nanotubes. In particular, Ar and CF<sub>3</sub><sup>+</sup> ions are considered. The innermost shells of the irradiated nanotubes were then pulled at a constant rate of 40 m/s until axial load failure. The approach used is classical molecular dynamics simulations using reactive empirical bond-order potentials and the primary knock-on atom approach to model the effects of electron irradiation. The objectives of this study are to determine the degree to which multi-walled nanotube failure is mitigated by the irradiation-induced cross-links, and how irradiation affects the stability and structural integrity of the nanotubes. In addition, the influence of the irradiating species and nanotube chiral structure on the results is examined. Lastly, the predicted outcomes are compared to new and published experimental studies. This work is supported by the National Science Foundation (CHE-0200838).

11:40am **NS-FrM11 Direct Synthesis of Suspended Single-Walled Carbon Nanotubes Crossing Plasma Sharpened Carbon Nanofiber Tips**, *C.H. Weng*, *K.C. Leou*, *W.Y. Lee*, *Z.Y. Juang*, *C.H. Tsai*, National Tsing Hua University, Taiwan

Single-walled carbon nanotubes are one of the most important quasi-one-dimensional nano-materials but their properties or associated device characteristics are very sensitive to the surroundings, e.g., surfactants or wrapping materials, and ambient gases, etc. It has been shown that such environmental perturbation effects could be minimized by suspending the SWNTs. Here we report a novel method for direct synthesis of suspended single-walled carbon nanotubes (su-SWNTs) using vertically-aligned carbon nanofibers (CNFs) as templates via a three-step fabrication process. Plasma enhanced chemical vapor deposition (PECVD) is first employed to grow vertically aligned CNFs on silicon substrates patterned with coated catalytic nickel film of 10 nm thickness. The CNFs are then post-treated by energetic argon plasma in the same reactor to yield structural transformation of CNFs with sharpening tips embedded with catalytic nanoparticles of a favorable size, presumably below 10 nm. A thermal CVD process then subsequently followed to directly synthesize SWNTs suspended across the tips or sidewalls of post-treated CNFs (PT-CNFs) with a span up to 10  $\mu\text{m}$ , as revealed by the analysis using scanning electron microscopy and resonance micro-Raman spectroscopy. We also demonstrated that one can maximize the yield of su-SWNTs on the tips of PT-CNFs by optimizing the post-treatment conditions to provide a protective coating to suppress the growth of SWNTs from sidewalls. The method of fabricating su-SWNTs described in this letter can be extended to position a single isolated SWNT for the purpose of either minimizing environmental perturbations during SWNT characterization or enhancing performance in nano-device applications.@footnote 1@ @FootnoteText@ @footnote 1@ This work was supported by the National Science Council of the Republic of China and the Center for Nano Science and Technology in the University System of Taiwan.

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 Schlecht, E.: NS-ThM7, 29  
 Schuh, D.: NS+EM-TuM11, 14  
 Schwarz, U.D.: NS1-MoA5, 7  
 Schwen, D.: NS2-MoM2, 4  
 Seifert, W.: NS2-MoM1, 4; NS2-MoM7, 5  
 Sellinger, A.T.: NS-ThA8, 31  
 Semancik, S.: NS-ThA9, 31  
 Senoner, M.: NS-WeM9, 23  
 Seol, K.S.: NS-TuP21, 20  
 Seong, S.Y.: NS-TuP21, 20  
 Shah, S.: MI+NS-TuM2, 12; NS-ThA7, 30  
 Shang, L.: NS2-MoA10, **9**  
 Sheehan, P.E.: NS1-MoM2, 2; NS-WeA4, **25**  
 Sheridan, J.G.: NS2-MoM4, 5  
 Shi, J.: MI+NS-TuM3, **12**  
 Shih, T.Y.: NS2-MoA4, **9**  
 Shimizu, T.: NS-FrM1, 32; NS-ThM3, 28  
 Shin, H.-J.: NS-WeA10, **26**  
 Shin, S.: AS+BI+NS-MoM11, 2  
 Shutthanandan, V.: NS-TuP13, 18  
 Siegel, P.H.: NS-ThM7, 29  
 Simpson, M.L.: NS-TuP5, 17  
 Sinnott, S.B.: NS1-MoA2, 7; NS-FrM10, 33  
 Skold, N.: NS2-MoM1, 4; NS2-MoM7, 5  
 Skuza, J.: MI+MS+NS-ThM7, **27**  
 Slinker, K.A.: NS+EM-TuM3, 13; NS+EM-TuM4, **13**  
 Smith, D.A.: TF+NS-MoA3, **10**  
 Son, J.M.: NS-TuP21, **20**  
 Song, Y.: NS-TuP19, **19**  
 Srinivasan, C.: NS2-MoA6, 9  
 Srivastava, C.: MI+NS-TuM1, 12  
 Stevens, F.: NS-ThA6, 30  
 Stichtenoth, D.: NS2-MoM2, 4  
 Stiévenard, D.: NS+EM-TuM10, 13  
 Stoltz, A.J.: TF+NS-MoA4, 10  
 Streifer, J.: NS2-MoA10, 9  
 Strobel, S.: NS+EM-TuM11, 14  
 Stroschio, J.A.: NS-WeA5, **25**  
 Stucky, G.D.: NS-TuP11, 18  
 Subramanian, S.: NS-WeA1, **25**  
 Suga, H.: NS-ThM3, **28**  
 Sumant, A.V.: NS-FrM3, 32  
 Sung, J.H.: NS-TuP3, **17**  
 Suzuki, M.: NS-ThM1, 28  
 Suzuki, S.: NS-FrM8, 33  
 Swaminathan, P.: NS1-MoM9, 4  
 — T —  
 Tak, Y.: NS1-MoM10, 4; NS-TuP25, 20  
 Takahashi, K.: AS+BI+NS-MoM11, 2  
 Tanaka, M.: NS-FrM1, 32; NS-ThM3, 28  
 Tanaka, Y.: AS+BI+NS-MoM11, 2  
 Taniguchi, M.: AS+BI+NS-MoM7, 1  
 Taninouchi, Y.: NS-ThM8, 29  
 Tatenuma, K.: NS-ThM11, 29; NS-ThM9, 29  
 Terminello, L.J.: NS1-MoM7, 3  
 Thevuthasan, S.: NS-TuP13, **18**  
 Thompson, G.B.: MI+NS-TuM1, **12**; NS-TuP2, 17  
 Tokumoto, H.: NS-ThM3, 28  
 Torimitsu, K.: NS-FrM8, 33  
 Tornow, M.: NS+EM-TuM11, 14  
 Tovar, J.D.: NS-WeA7, 26  
 Trouilloud, P.: MI+MS+NS-ThM9, 27  
 Tsai, C.H.: NS-FrM11, 33  
 Tsai, C.J.: NS-TuP37, 22  
 Tse, K.-Y.: NS+BI-TuA5, **15**  
 Tsutsui, M.: NS-ThM8, **29**  
 Tsuya, D.: NS-ThM1, 28  
 — U —  
 Unger, W.: NS-WeM9, 23  
 Uraoka, U.: NS1-MoM4, 3  
 Urbietta, A.: NS+EM-TuM10, **13**  
 Utker, I.: TF+NS-MoA7, 11  
 — V —  
 Valsesia, A.: NS+BI-TuA1, **15**  
 van Buuren, T.: NS1-MoM7, 3  
 Vasile, M.J.: TF+NS-MoA6, 10  
 Vasquez, R.: NS2-MoM3, 4  
 Vogel, V.: NS2-MoA9, 9  
 Völkel, B.: NS-TuP1, 17  
 Voronko, M.: NS-TuP9, 18  
 — W —  
 Waggoner, P.S.: NS-TuP16, **19**  
 Wahl, K.J.: NS1-MoA1, **7**  
 Wang, C.: NS2-MoM9, **5**  
 Wang, C.M.: NS-TuP13, 18  
 Wang, C.W.: NS-TuP33, **21**  
 Wang, G.-C.: NS1-MoM8, 3  
 Wang, J.: NS2-MoM3, 4  
 Wang, J.H.: NS-TuP34, 21  
 Wang, J.J.: NS-FrM4, 32; NS-TuP14, 19; NS-TuP22, 20  
 Wang, P.-I.: NS1-MoM8, 3  
 Wang, S.C.: NS-TuP29, 20  
 Weaver, J.H.: NS1-MoM9, 4; NS-TuP16, 19  
 Weiss, P.S.: NS2-MoA3, 8; NS2-MoA6, 9; NS-WeM5, 23  
 Welle, A.M.: NS2-MoA7, 9  
 Wells, D.: NS2-MoA5, 9  
 Weng, C.H.: NS-FrM11, 33  
 Westermann, J.: NS-WeM9, 23  
 Whitman, L.J.: NS1-MoM2, 2; NS-WeA4, 25  
 Wiesendanger, R.: NS-WeM10, 23  
 Willey, T.M.: NS1-MoM7, **3**  
 Wise, K.E.: NS-TuP11, 18  
 Wong, E.W.: NS-ThM7, **29**  
 Worledge, D.: MI+MS+NS-ThM9, 27  
 Worthington, E.: NS-TuP11, 18  
 Wu, B.: NS2-MoM10, **6**; NS2-MoM4, 5  
 Wu, G.C.: NS-TuP33, 21  
 Wu, H.W.: NS-TuP37, **22**  
 — X —  
 Xu, H.Y.: NS-ThA5, 30  
 Xue, S.: MI+MS+NS-ThM1, 27  
 — Y —  
 Yabashi, M.: AS+BI+NS-MoM11, 2  
 Yacaman, M.J.: AS+BI+NS-MoM9, 2  
 Yamada, F.: AS+BI+NS-MoM8, 2  
 Yamashita, I.: NS1-MoM4, 3  
 Yamazaki, A.: NS-FrM8, 33  
 Yang, C.: NS2-MoM5, **5**  
 Yang, D.-Q.: NS-FrM7, **32**  
 Yang, H.: NS-TuP31, 21; NS-WeA10, 26  
 Yang, M.: NS1-MoM2, 2; NS-WeA4, 25  
 Yang, X.: NS-TuP8, 18  
 Yap, H.W.: NS-FrM3, **32**  
 Ye, D.-X.: NS1-MoM8, 3  
 Yeh, C.-M.: NS-TuP12, **18**  
 Yeom, G.Y.: NS-TuP9, 18  
 Yong, K.: NS1-MoM10, 4; NS-TuP25, 20  
 Yoo, W.J.: NS-TuP27, **20**  
 Yoon, O.J.: NS-TuP10, 18  
 Yun, M.: NS2-MoM3, **4**  
 Yun, W.S.: NS-TuP23, **20**  
 — Z —  
 Zauscher, S.: NS+BI-TuA3, 15  
 Zhang, F.: NS+EM-TuM11, 14  
 Zhang, Y.: NS-TuP13, 18  
 Zhang, Z.: NS-FrM2, 32  
 Zhao, X.: NS-FrM4, 32; NS-TuP14, 19  
 Zhu, M.Y.: NS-FrM4, **32**  
 Ziberi, B.: NS-WeA8, **26**