Monday Morning, November 15, 2004

Nanometer-scale Science and Technology
Room 213D - Session NS-MoM

Carbon Nanotubes-Electrical Properties

Moderator: M.C. Hersam, Northwestern University

8:40am **NS-MoM2 Quantitative Analysis of Electronic Properties of Carbon Nanotubes by Scanning Probe Microscopy: from Atomic to Mesoscopic Length Scales***, **V. Meunier**, S.V. Kalinin, J. Shin, A.P. Baddorf, R.J. Harrison,* Oak Ridge National Laboratory

Scanning Probe Microscopy techniques are the key to real space imaging of electronic transport properties, including the electrostatic potential distribution and local field effects, in low-dimensional systems. The interpretation of SPM data in terms of the local electronic properties of 1D systems such as carbon nanotubes requires quantitative analysis of the tip-nanotube interactions. Here, the electrostatic interactions between a point charge and a carbon nanotube are studied using a combination of first principles density functional calculations and continuum electrostatics modeling. The atomistic first principles investigation is extended to mesoscopic length scales by matching to a continuum electrostatic approach. Furthermore, realistic tip shape effects are included using an image charge model. An approach for the measurement of tip radius of curvature from the electrostatic SPM data is presented. Within this approach, we can quantitatively describe, for the first time, the capacitive tip-surface interactions and predict the magnitude of the tip gate effect in nanoscale systems, such as carbon nanotubes and semiconductor nanowires.

9:00am **NS-MoM3 Electronics and Optoelectronics with Single Carbon Nanotubes***, **P. Avouris**,* IBM T.J. Watson Research Center **INVITED**

Carbon nanotubes (CNTs) are 1D nanostructures with unique properties that recommend them for applications in future nanoelectronics and optoelectronics. I will discuss the electronic structure and electrical properties of semiconducting carbon nanotubes and the fabrication and performance of nanotube devices. Transport experiments and simulations will be used to determine the switching mechanism of nanotube transistors, the nanotube-metal interactions and the role of the ambient environment on the transistor properties. I will then discuss how these findings can be utilized to produce high performance p-, n- and ambipolar nanotube field-effect transistors (CNTFETs) and logic circuits. Semiconducting CNTs are direct gap materials. This, plus their 1D character have important implications for their optical properties. I will first discuss the nature of the excited states of CNTs. I will show that CNTs form strongly bound 1D-exciton states and discuss the scaling properties of these excitons. Spectra obtained by recording the photocurrent of single CNTs employed as channels of CNTFETs will be presented. I will then show that an ambipolar nanotube field-effect transistor can act as a single molecule, electrically-driven light source. The spectra, polarization and the dependence of the light intensity on applied bias will be used to prove that the light is generated through radiative e-h recombination in the CNT. Spatially-resolved studies of the emission as a function of applied bias will be used to map the boundaries of the electron and hole currents and to determine the recombination lengths. These results show that a CNTFET is a particularly versatile molecular device that can be used, depending on the bias conditions, as a high performance electrical switch, a light detector or a light source.

9:40am **NS-MoM5 Ballistic Transport of Hole in 4µm Carbon Nanotube Channel Transistor with Coulomb Blockade Effect***, **K. Matsumoto**,* Osaka University, Japan

We have succeeded in observing the coexistence of the ballistic transport and Coulomb blockade effects of hole in the carbon nanotube channel transistor. The carbon nanotube was grown by the thermal chemical vapor deposition. After the growth of carbon nanotube, the source, drain, gate electrodes were formed. The distance between the source and drain electrode is 4µmm, that means the effective channel length of carbon nanotube is 4µmm. The sample was measured at 8.6K. The dependence of the drain current on the gate bias shows the periodic Coulomb oscillation and Coulomb diamond characteristics with the periods of 150mV. The drain current decrease with the increase of the gate bias, which means the carrier is hole. From the size of the Coulomb gap, the total charging energy was estimated to be as small as 3.1meV. From this charging energy, the length of the island was estimated to be about 4µmm, which coincides with the carbon nanotube channel length. This fact means that the entire carbon nanotube works as one island for the Coulomb blockade effect for the hole. At the outside of the Coulomb blockade regions, the drain current shows the negative differential conductance with the periods of as small as 400µmV. This negative differential conductance is attributed to the resonant tunneling of the hole through the quantum confinement state formed inside the carbon nanotube. From the periods of the negative differential conductance, the length of the quantum well formed inside the nanotube was calculated to be as large as about 4µmm, which again coincides with the entire carbon nanotube channel length. This result means the quite important facts that the quantum confinement state is formed in the entire carbon nanotube and tunneling barrier is formed at the source and drain electrodes. Therefore, hole can transport ballistically through entire carbon nanotube channel of 4µmm by keeping the coherency of the hole wave.

10:00am **NS-MoM6 Carbon Nanotube Photo-detectors***, **M.S. Marcus**, O.M. Castellini, J.M. Simmons, M.A. Eriksson,* University of Wisconsin-Madison

We demonstrate two different nanotube device structures for use as photo-detectors: Bundle devices on quartz using photo-generated currents in the bundle, and transistor devices on Si/SiO@sub 2@ substrates that use photo-generated voltages in the substrate to provide a gating effect. The transistor devices are fabricated on SiO@sub 2@/p-Si substrates, where the p-Si is used as a gate for the nanotube channel. Light is absorbed by not only the carbon nanotube producing photocurrents, but also in the silicon gate that produces a photo-voltage at the interface between the Si/SiO@sub 2@. We observe that photo-voltages of ~15mV change the channel current by up to 1nA in the transistor. The small addition of the photo-voltage when the nanotube is illuminated by a modulated light source acts to probe the derivative of the channel current with respect to the gate voltage. When the laser illuminates at large distances from the nanotube we find that there are smaller but still measurable changes in the channel current, indicating that the carriers responsible for photo-gating are mobile. In order to isolate the nanotube-light interaction from the silicon gate, we have fabricated nanotube bundle devices on transparent quartz substrates. We measure a variety of response times, some of which are surprisingly slow sometimes taking ~8ms to transition from a light off to on state. We propose that inter-tube coupling plays a role in the long response times, and present a model of why it can take photo-generated carriers a long time to be extracted as photocurrent.

10:20am **NS-MoM7 Field Electron Emission from Aligned Carbon Nanotube Bundles at an Ultra-Low Threshold of 1 V/µm***, **K.-Y. Lee**, M. Katayama, N. Hayashi, Y. Terao, T. Miyake, K. Himuro, S. Honda, J.-G. Lee,* Osaka University, Japan*; T. Hirao,* Kochi University of Technology, Japan*; H. Mori, K. Oura,* Osaka University, Japan

To realize a practically applicable field electron emitter made of carbon nanotubes (CNTs), it is desirable to enhance the electric field concentration determined by the aspect ratio and number density of the individual CNT. As predicted theoretically, the field emission from an aligned CNT array becomes maximum when the ratio of intertube distance to the height of each individual CNT is about 2. We have succeeded in fabricating an architecture that satisfies such an optimal condition by using pillars of aligned CNT bundles. This provides a promising method of obtaining the optimal ratio of interpillar distance (R) to pillar height (H). Patterns of 50 µm diameter and 250 µm pitch of the Fe(5 nm)/Al(10 nm) multilayer catalyst were fabricated on a Si substrate by photolithography and sputtering. The pillars of aligned CNT bundles were grown on the patterns at 700°C by thermal chemical vapor deposition with C@sub 2@H@sub 2@ under a pressure of 600 Pa. Each pillar was composed of CNTs with a number density of about 10@super 10@ cm@super -2@. To obtain the optimal R/H of 2, the pillar height of about 125 µm was adopted. The pillar array exhibited a striking field emission characteristic. The threshold field needed to produce a current density of 10 mA/cm@super 2@, E@sub th@, was 1.0 V/µm. The obtained E@sub th@ is extremely low compared with those for other materials that have been reported so far. Monitoring the electron field emission by means of a fluorescent screen demonstrated the emission uniformity. More details of the results on field emission characteristics, and SEM, TEM observations of the carbon nonotube bundles will be presented.@footnote 1@ This work was partly supported by the Handai Frontier Research Center, and a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science, and Technology. @FootnoteText@ @footnote 1@M. Katayama, K.-Y. Lee, S. Honda, T. Hirao, and K. Oura, Jpn. J. Appl. Phys. (in press).

10:40am **NS-MoM8 Modeling of Gas-modulated Carbon Nanotube Schottky Barrier***, **T. Yamada,*** NASA Ames Research Center

It is reported that the Schottky barrier between a semiconducting carbon nanotube (NT) and a metallic electrode is sometimes modified in the gaseous environment. There are three different cases: (1) there is no charge transfer between the gas and the NT/electrode (gas not charged) and the gas does not have a dipole moment (not polarized), (2) the gas is not charged, but is polarized, and (3) there is a charge transfer between the gas and the NT/electrode and the gas is charged. Case 1 will cause no Schottky barrier modulation. Case 2 will result in the Schottky barrier modulation through the modified work function in either the NT or the electrode due to the dipole moment in the gas. This is understood within the usual Schottky theory. Case 3 will also result in the Schottky barrier modulation, but depending on whether the NT and electrode are connected (closed) or not (open), the modulation is significantly different. The charged gas will attract the opposite charges in the NT and electrode. In the open circuit condition, the gas-NT and the gas-electrode interactions determine how much opposite charges are induced in the NT and electrode, respectively. However, in the closed-circuit condition, which is the usual condition in electronics applications, the induced opposite charges will move around the system and keep the Fermi level constant everywhere. This means that the induced opposite charges are redistributed in the NT and electrode. We have solved this redistribution problem and shown that the Schottky barrier modulation is large when the NT is in the depletion mode, while the modulation is negligible when the NT is consistently in the accumulation mode.

11:00am **NS-MoM9 Environmental Effects on Double Wall Carbon Nanotube Field Effect Transistors***, **D. Kang**, W. Park,* Samsung Advanced Institute of Technology, Korea*; J.R. Kim,* Chonbuk National University, Korea*; C.J. Lee,* Hanyang University, Korea*; J.J. Kim,* Chonbuk National University, Korea

With the rise of nanotechnology, there are many new interesting properties induced by their dimensions and geometries. One of the these is large surface area due to their unique geometric shapes such as nanotube and nanowires. For device applications harnessing these materials, large surface area effects on electrical properties should be investigated for a better understanding of nano devices. Double Wall Carbon Nanotube(DWCNT)s could be the best material to investigate the effects because their small band gap should enhance the response to their environments. In this letter, we fabricate DW-CNTFETs in a back-gated structure and investigate environment effects on the electrical properties of DW-CNTFETs in comparison to SW-CNTFETs. Purified double wall CNTs (DWCNT) were suspended in a solvent and spin coated on SiO2 grown on a heavily doped Si substrate. Scanning Probe Microscopy (SPM) located the position of the wires on the substrate. After the pattern for metals contacts were generated by electron beam lithography, metal electrodes were defined by lift-off process after 100nm Pd metal evaporation. We find that DW-CNTFET shows conversion from unipolar to bipolar in vacuum. However, the SW-CNTFET does not show the conversion in the measurement conditions we used in this study. In ambient air, both CNTFETs shows large hysteresis by electron trapping at slow states. We believe that water adsorption on the tube plays an important role for ambipolar conversion.

11:20am **NS-MoM10 Electrical Characterization of Carbon Welds between Multiwalled Carbon Nanotubes***, **P. Rice**, S.E. Russek, P. Kabos, R.H. Geiss,* NIST

Nanometer scale electronics based on carbon nanotubes have the potential to revolutionize the electronics industry by reducing circuit sizes dramatically and by increasing operational speed due to inherent properties of the nanotubes. Currently there are very few methods of connecting carbon nanotubes to electronics. The most prevalent so far is using the scanning electron microscope (SEM) focused at a junction between the nanotube and the circuit and growing a carbon contamination buildup we call a weld. This buildup, typical in most SEMs, is caused when the electron beam cracks carbon compounds commonly found on the surface of the sample and in the SEM atmosphere. The subsequent free and chemically active carbon quickly attaches itself to nearby surfaces and builds into mounds securely bonding the nanotube to the surface. Using microlithographic test structures we have measured the electrical characteristics of the nanotube and the welds from dc to MHz frequencies. These measurements have shown a semiconductor behavior of the nanotube and weld combination. To separate the weld electrical properties from the nanotube electrical properties we have built test structures that measure contact resistance between unwelded nanotubes and the same nanotubes after welding. Also, the molecular characteristics of the welds are very dependent on SEM parameters such as electron beam energy, alignment of the electron beam, vacuum pressure inside the SEM chamber, and molecular species near the beam impingement on the sample. We will correlate the structure of these welds to electrical properties as influenced by the SEM deposition parameters using transmission electron microscopy.

11:40am **NS-MoM11 Stiffness and Nonlinear Mechanical Properties of Single-Walled Carbon Nanotube Bundles***, **P. Jaroenapibal**, D.E. Luzzi, S. Evoy,* University of Pennsylvania

Nanoscale cantilevered resonators offer great potential as sensing devices due to their high sensitivity to added masses or external forces. Highly-sensitive resonators can be accomplished by using long, thin, stiff, low density, and high quality cantilevers. Hybrid carbon nanotubes represent a powerful platform for the development of tunable nanoresonator-based devices that would provide both high quality resonance and sensing specificity. We have studied the mechanical properties of single-walled carbon nanotube (SWNT) bundles through in-situ transmission electron microscope (TEM) observation of mechanical resonance. The observed resonant frequencies of SWNT bundles ranged from 0.2 - 9 MHz, with resonance qualities Q ranging from 77 to 800. An effective Young's modulus of E* = 76 ± 4 GPa is extracted from the resonance data. This relatively low value indicates that the individual SWNTs are weakly interacting within the bundle, where slippage can occur due to the low sliding resistance between the atomically smooth surfaces of neighboring tubes. Departure from Lorentzian responses, an onset of non-linear behavior was observed under large actuation amplitudes. Specifically, bi-stable responses were observed in 4 µm long and 30 nm wide bundles when their end-point displacement approached a critical amplitude of x@sub c@ = 800 nm. Such non-linear behavior reveals the onset of inter-tube interactions within the bundle when sufficiently large bending is applied. We will discuss this non-linear data with respect to an effective Poisson ratio that results from inter-tube interactions, and describe the impact of beam irradiation on such interactions. Mechanical properties of hybrid carbon nanotubes in which fullerenes or other molecules are encapsulated will also be discussed.

Nanometer-scale Science and Technology
Room 213D - Session NS-MoA

Magnetic Imaging and Spectroscopy

Moderator: B.D. Terris, Hitachi Global Storage Technologies

2:00pm **NS-MoA1 Spin-Polarized Scanning Tunneling Microscopy: Achievements and Perspectives***, **M. Bode**, K. Von Bergmann, O. Pietzsch, A. Kubetzka, R. Wiesendanger,* University of Hamburg, Germany **INVITED**

Within the past decade spin-polarized scanning tunneling microscopy (SP-STM) was developed to a mature technique which not only allows for ultra-high spatial resolution studies of magnetic nanostructures, but also enables the direct correation with the sample`s topography and spin-resolved electronic structure. By reviewing the main achievements of SP-STM, which include the observation of size-dependent reorientation transitions @footnote 1@, the impact of strong external fields on magnetic nanowires @footnote 2@, atomic resolution of antiferromagnetic monolayers @footnote 3@, and the direct observation of thermal switching events of indivitual superparamagnetic entities @footnote 4@, we will discuss the strength and limitations of the technique. Possible future developments will be sketched and evaluated. @FootnoteText@ @footnote 1@ A. Kubetzka et al., Phys. Rev. B 63, 140407 (2001). @footnote 2@ O. Pietzsch et al., Science 292, 2053 (2001). @footnote 3@ S. Heinze et al., Science 288, 1805 (2000). @footnote 4@ M. Bode et al., Phys. Rev. Lett. 067201 (2004).

2:40pm **NS-MoA3 Atomic-Scale Spin-Polarized Scanning Tunneling Microscopy of Magnetic Transition Metal Nitride Surfaces***, **A.R. Smith**, R. Yang,* Ohio University*; H.Q. Yang,* Texas A&M University*; W.R.L. Lambrecht,* Case Western Reserve University*; A. Dick, J. Neugebauer,* Fritz-Haber-Institut der MPG, Germany **INVITED**

Spin-polarized scanning tunneling microscopy (SP-STM) can achieve ultimate magnetic resolution on surfaces, even down to the atomic scale.@footnote 1@@footnote ,@@footnote 2@@footnote ,@@footnote 3@ In earlier work, we have shown the resolution of the spin structure of a novel antiferromagnetic (aFM) surface, Mn@sub 3@N@sub 2@ (010), with a model row-wise aFM structure.@footnote 3@ The surface is prepared using molecular beam epitaxy with a Mn effusion cell and radio frequency N plasma. The magnetic information appears as an additional component which is added to the non-magnetic component in the STM line scan. Furthermore, the magnetic information is bias-dependent; both the amplitude and polarity of the magnetic profile vary with the STM bias. The bias-dependence is understood as energy-dependent variations of the spin density of states of tip and sample. Both the magnetic and non-magnetic information can be extracted from the total STM image and compared with simulations based on theoretical calculations. Using first principles density functional theory, the local density of states for the surface is calculated for Mn@sub 3@N@sub 2@ (010). Two methods of simulation have been investigated for SP-STM. First, we have applied the atom superposition method (ASM). Second, we have simulated the images using the full Tersoff-Hamann (T-H) approach.@footnote 4@ We find that the T-H method is, in general, necessary for a correct simulation of the data due to the spin-dependent orbital lobes of the surface atoms. We furthermore apply the full T-H theory with different numbers of tip atoms to best model the STM data with good success. @FootnoteText@ @footnote 1@S. Heinze {\it et al.}, Science {\bf 288}, 1805 (2000). @footnote 2@D. Wortmann {\it et al.}, Phys. Rev. Lett. {\bf 86}, 4132 (2001). @footnote 3@H. Yang {\it et al.}, Phys. Rev. Lett. {\bf 89}, 226101 (2002). @footnote 4@J. Tersoff et al., Phys. Rev. Lett 50(25), 1998 (1983).

3:20pm **NS-MoA5 Spin-Polarized Scanning Tunneling Microscopy Study of Single-Crystallized Nanodot Arrays***, **T.-H. Kim,*** Seoul National University, South Korea, S. Korea*; J.H. Choi, J. Seo, Y. Kuk,* Seoul National University, South Korea

We have developed a method to grow regularly patterned Fe nanodot arrays with in situ deposition. A self-sustained porous alumina mask was fabricated with an aluminum-coated Si substrate. Using the alumina shadow mask with perfectly ordered pores, we fabricated well-ordered Fe nanodot arrays.@footnote 1@ Fe nanodot arrays with 0.2-10 nm thicknesses, 50-120 nm diameters, and 100-200 nm periods were successfully grown on a W(110) substrate in ultra-high vacuum. Fe nanodots were single-crystallized by mild annealing. Our shadow mask technique can be the simple and fast method to obtain high-density arrays over a macroscopic area. Spin-polarized scanning tunneling microscopy (SP-STM), one of the most powerful techniques to study magnetic nanostructures, can image surface domain structures with a lateral resolution reaching the atomic scale.@footnote 2@ Well-ordered Fe nanodot arrays showed a stronger magnetic interaction between dots than randomly distributed Fe islands. We have performed micromagnetic simulation@footnote 3@ to study interaction between dots. @FootnoteText@ @footnote 1@ J. H. Choi, T.-H. Kim, J. Seo, and Y. Kuk (submitted to APL).@footnote 2@ S. Heinze, M. Bode, A. Kubetzka, O. Pietzsch, X. Nie, S. Blugel, and R. Wiesendanger, Science 288, 1805 (2000).@footnote 3@ We used the OOMMF program (http://math.nist.gov/oommf/). .

3:40pm **NS-MoA6 Spin-Resolved Core Level Photoemission of Ferromagnetic Thin Films***, **G.D. Waddill**, T. Komesu,* University of Missouri-Rolla*; S.A. Morton,* Lawrence Berkeley National Laboratory*; J.G. Tobin,* Lawrence Livermore National Laboratory

We present spin-resolved 2p core level photoemission results for thin films of Fe, Co, and Ni. The films are bcc Fe on a Ag(100) substrate, fcc Co on Cu(001), and fcc Ni/Co/Cu(001). All films have an in-plane magnetic easy axis. We observe spin polarization in the main photoemission peaks consistent with trends in the bulk magnetic moments of the transition metals. In addition, Ni and Co have satellite peaks due to electron correlation effects and we see spin polarization in the Ni 6 eV satellite peak and much weaker spin polarization in the 4 eV Co peak. The existence of a satellite peak in the Co 2p spectrum is somewhat controversial and this data marks the first observation of spin-polarization in that peak. In addition, in the Ni/Co/Cu(001) system we have preliminary results for very thin films of Ni where charge transfer from the Co to the Ni will effect the electronic and magnetic properties of both films. For a 3 monolayer Ni film on Co we see differences in the photoelectron spin polarization of both Co and Ni compared to results for thicker Ni and Co films. These results emphasize the importance of spin-resolved photoemission in understanding the combined Coulomb, spin-orbit, and exchange interactions in the presence of interatomic electron correlation effects and configuration mixing that effect the photoemission process.

4:00pm **NS-MoA7 Spin Polarized Electron Energy Loss Spectroscopy on Ferromagnetic Thin Films***, **T. Komesu**, G.D. Waddill,* University of Missouri-Rolla*; J.G. Tobin,* Lawrence Livermore National Laboratory

Spin-polarized electron energy loss spectroscopy (SPEELS) developed in the 1980s and has become a valuable technique for probing Stoner excitations and spin waves. SPEELS is sensitive to the occupied and unoccupied parts of the spin-split electronic structure of materials, and consequently SPEELS is a complementary technique to spin-resolved photoemission and inverse photoemission that more directly probe the occupied and unoccupied spin-split band structure respectively. Our results, using an unpolarized electron source with spin analysis shows sharp spin-dependent energy loss features in electron scattering from ferromagnetic thin films of Fe, Ni, and Co grown on Ag(100) and Cu(001). This is in contrast to most previous SPEELS studies (primarily using spin-polarized sources and spin analysis) where very broad featureless spectra are observed. We attribute the majority spin peaks we observe to spin-flip exchange scattering from the magnetic films, with the lowest energy feature corresponding to the exchange splitting for the films. The observed minority spin peaks are attributed non-flip exchange scattering.

4:20pm **NS-MoA8 High-Resolution Imaging of Magnetization Dynamics Using X-PEEM***, **A. Scholl**,* Lawrence Berkeley National Laboratory **INVITED**

Ultrafast x-ray pulses (p-sec to f-sec) promise to be an ideal tool to probe the dynamics of magnetic materials. X-rays are sensitive to both ferromagnetic and antiferromagnetic order. Sum rules allow us to quantify spin moment, orbital moment and magnetic anisotropy specific for each element in a sample. High spatial resolution on the order of nanometers can be obtained using x-ray microscopy techniques using zone-plates or electron microscopes. As an example, a study of the precessional dynamics of magnetic vortices, 3-dimensional magnetic curls, will be presented [1]. The dynamics is probed at 100 nm spatial resolution and 70 ps temporal resolution using the PEEM-2 Photoemission Electron Microscope at the Advanced Light Source. It will be demonstrated that the vortex chirality or handedness, which is determined by the out-of-plane magnetization of the vortex core, governs the sub-ns dynamics of the structure, leading to a precessional motion of the vortex center. The dynamics is initiated by a sub-ns field pulse triggered by a laser, which is synchronized to the x-ray source. In contrast, on longer time scales it is known that damping dominates and the dynamics is governed by the in-plane domain structure. The measured vortex speed and the internal magnetic field at the core will be compared with the result of micromagnetic simulations and with the static susceptibility of the magnetic structure. The potential of studying processes beyond the Landau-Lifshitz-Gilbert dynamics using currently developed ultrafast x-ray techniques will also be discussed. [1] S.B. Choe et al., Science 304, 420 (2004).

5:00pm **NS-MoA10 Magnetic Interaction between a Ferromagnetic Substrate and Adsorbed Manganese Porphyrin Molecules***, A. Scheybal,* ***T. Ramsvik,*** Paul Scherrer Institute, Switzerland*; R. Bertschinger,* Paul Scherrer Institut, Switzerland*; M. Putero-Vuaroqueaux,* L2MP-CNRS, France*; T.A. Jung,* Paul Scherrer Institute, Switzerland

The magnetic interaction between a magnetized thin film cobalt substrate and adsorbed manganese(III)-tetraphenylporphyrin chloride (MnTPPCl) molecules has been studied using X-ray magnetic circular dichroism (XMCD). In the regime of submonolayer coverage a clear circular dichroism is observed at the Mn L@sub 32@-edge, verifying that a net magnetization is set up by the manganese ions in the adsorbed molecules. An element specific hysteresis study shows that the magnetic properties of the molecules mirror those of the cobalt substrate. From this and from temperature dependent studies it is concluded that exchange interaction between the cobalt film and the molecules is the dominant cause for this induced magnetism. To our knowledge, this is the first time that an exchange coupling between adsorbed organic molecules and a ferromagnetic substrate has been demonstrated by XMCD at 3d-transition metal L@sub 32@-edges, thereby allowing direct information about both orbital and spin magnetic moments@footnote 1@. As MnTPPCl is the parent compound of the [Mn(III)-porphyrin][TCNE] family of molecular magnets (TCNE = tetracyanoethylene)@footnote 2@, the here presented molecular system and experiment provides a model system for the study of the magnetic interaction at the interface between a conventional ferromagnet and a molecular magnet. Furthermore, an organic semiconductor like tris(8-hydroxyquinoline) aluminium (Alq@sub 3@) can be used to prepare an organic spin-valve exhibiting giant magnetoresistance, as it has been demonstrated recently.@footnote 3@ Thus, the understanding of local magnetic coupling in molecular materials is of utmost importance for the application of magnetic materials in ever smaller dimensions. @FootnoteText@ @footnote 1@ G. Schütz et al., Phys. Rev. Lett. 58 (1987) 737@footnote 2@ J.S. Miller et al., Adv. Mat. 4 (1992) 498@footnote 3@ Z.H. Xiong et al., Nature 427 (2004) 821.

Biomaterial Interfaces
Room 210D - Session BI+NS-TuM

The Nano-Bio Interface

Moderators: G.J. Leggett, University of Sheffield, UK, M. Textor, ETH Zurich, Switzerland

8:20am **BI+NS-TuM1 Programmed Macromolecular Synthesis***, **D.A. Tirrell**,* Caltech **INVITED**

We have developed three approaches to the synthesis of proteins and protein-like macromolecules containing novel amino acids. In the first approach, we replace every copy of one of the natural amino acids by an analogue, in effect building proteins from an altered set of twenty starting materials. This approach is most useful when one is interested in changing the overall physical properties of the protein, or in de novo design of protein-based biomaterials. A second method, which has also been implemented successfully by Schultz and coworkers, allows site-specific incorporation of a single copy of an amino acid analogue in response to a stop codon. Such methods are useful in probing protein structure and function. The third approach, developed most recently, uses mutant transfer RNAs to break the degeneracy of the genetic code, and offers the prospect of a protein chemistry based on a substantially expanded set of amino acid building blocks. This lecture will describe the most important elements of each of these strategies as well as some thoughts on the design of wholly artificial proteins with potential application in biotechnology and materials science.

9:00am **BI+NS-TuM3 The Art of Mechano-Transduction within the Extracellular Matrix***, **V. Vogel**,* Swiss Federal Institute of Technology (ETH), Switzerland **INVITED**

While engineered matrices allow asking well defined questions of how cells interact and respond to their environment, it remains unclear whether a minimal set of cues exists by which synthetic matrices can be engineered that mimics biological matrices in their essential functions. Here we address how mechanical force can alter the conformation of extracellular matrix proteins and consequently regulate the display of the protein's functional states. The function of cells is tightly controlled by their interaction with the surrounding extracellular matrix to which they are coupled via the transmembrane integrins. Using intramolecular fluorescence resonance energy transfer (FRET), we studied the extent to which fibronectin is stretched and partially unfolded by the traction forces generated by fibroblasts in 2d and 3d matrices. We then derive structural models of the unfolding pathways of ECM proteins by computational techniques (steered molecular dynamics simulations), and gain insight how tension applied to extracellular matrix proteins affects the exposure of their molecular recognition sites. The consequences of our findings to the field of biomaterials and tissue engineering will be discussed. @FootnoteText@ V. Vogel, G. Baneyx, The tissue engineering puzzle: a molecular perspective, Annual Review Biomed. Eng., 5 (2003) 441-463. G. Baneyx, L. Baugh, V. Vogel, Co-existing conformations of fibronectin imaged in cell culture by fluorescence resonance energy transfer, Proc. Natl. Acad. Sci. USA, 98 (2001) 14464-14468. G. Baneyx, L. Baugh, V. Vogel, Fibronectin extension and unfolding within cell matrix fibrils controlled by cytoskeletal tension, Proc. Natl. Acad. Sci. USA, 99 (2002) 5139-5143. D. Craig, M. Gao, K. Schulten, V. Vogel, Structural insights how sequence variations tune the mechanical stability of fibronectin type III modules, Structure, 12 (2004) 21-30.

9:40am **BI+NS-TuM5 Capture and Release of Proteins on the Nanoscale by Surface-Confined Biomolecular Switches***, J. Hyun,* Seoul National University, Korea*; W.K. Lee, N. Nath, A. Chilkoti, **S. Zauscher**,* Duke University

In this paper we describe the fabrication and characterization of stimulus-responsive elastin-like polypeptide (ELP) nanostructures grafted onto ï⍰·-substituted thiolates that were patterned onto gold surfaces by dip-pen nanolithography (DPN). We exploited the hydrophilic-hydrophobic phase transition of ELP in response to a change in ionic strength as a switch in order to reversibly immobilize a thioredoxin-ELP fusion protein onto the ELP nanopattern above the lower critical solution temperature. We demonstrated the biological activity of the Trx-ELP nanoarray by binding an anti-thioredoxin monoclonal antibody. Furthermore, we showed that the resulting Trx-ELP/anti Trx-mAb complex could be released below the LCST. Our research demonstrates proof-of-principle that "smart," surface-confined biomolecular switches can be built at the nanoscale. Our method of fabricating switchable surfaces is attractive because it is entirely modular and generic, in that it only requires an ELP-modified or patterned surface and a protein that can be appended with an ELP tag. ELP synthesis is easily achieved through genetic engineering techniques. The nanoscale miniaturization of on-chip separation and the presentation and triggered release of the captured proteins made possible by this methodology should be integrable into nanoscale bioanalytical devices that are currently under development.

10:00am **BI+NS-TuM6 Micro- and Nanopatterns of DNA-Tagged Vesicles***, **B. Städler**, D. Falconnet,* Laboratory for Surface Science and Technology, Switzerland*; F Höök, I Pfeiffer,* Chalmers University of Technology, Sweden*; H Solak,* Paul Scherrer Institute, Switzerland*; J. Vörös,* Laboratory for Surface Science and Technology, Switzerland

A new approach for the creation of vesicular micro-and nanoarrays is presented based on a novel patterning approach termed Molecular Assembly Patterning by Lift-off (MAPL) in combination with the immobilization of DNA-tagged intact vesicles. This technique is shown to be a promising platform for future studies of enzyme and membrane protein activity in a controlled, native nanoenvironment. Fabrication of DNA microarrays by spotting is state-of-the-art today. This arraying technology, however, cannot be directly applied to membrane-based microarrays because the contact with the ambient environment damages the membranes. Our approach starts with conventional single stranded DNA arrays, which are subsequently converted into a membrane protein array by using phospholipidic vesicles tagged with the complementary DNAs. These functionalized vesicles specifically couple to the surface through hybridization of the DNA strands. The MAPL process was used to provide a surface with a background resistant to the nonspecific adsorption of vesicles and active spots (diameter between 1 and 200 µm) for the immobilization of the single stranded DNAs. The surface chemistry of the active spots and background consisted of biotinylated PEG and non-functionalized PEG, respectively. Complexes of biotin-terminated DNA and neutrAvidin, preformed in solution, were immobilized to the biotinylated, active spots. POPC vesicles tagged with complementary cholesterol-terminated DNA could then be specifically coupled to the surface through the hybridization of the DNA strands. Quartz crystal microbalance and optical waveguide technique were used to monitor in situ and optimize the multistep surface modification process. The micropatterns of DNA-tagged, fluorescently labeled vesicles were investigated by fluorescence microscopy. X-ray Interference Lithography was successfully used to downscale the patterning process to the nanometer scale in order to produce single vesicle arrays.

10:20am **BI+NS-TuM7 Label-Free Biosensor Based on the Surface Plasmon Resonance of Gold Nanoparticles***, **S.M. Marinakos**, N. Nath, A. Chilkoti,* Duke University

The optical properties of gold nanoparticles immobilized on a surface were used in a label-free biosensing scheme. The sensing modality is based on the change in the local refractive index associated with receptor-ligand binding at the particle surface which shifts the surface plasmon resonance (SPR) peak in the absorbance spectra of the nanoparticles. In previous work, we have shown that solid, spherical gold nanoparticles with a size in the range of 13-50 nm could be self-assembled on amine-functionalized glass. These chemisorbed nanoparticles were then functionalized with a biotin derivative. We showed that this scheme enabled single wavelength monitoring of streptavidin binding at the surface by single wavelength measurements of the change in intensity that was caused by binding of streptavidin at the nanoparticle-solution interface. In this study, we extend these measurements to anisotropic gold nanorods, in an effort to further improve the analytical sensitivity and detection limits of this label-free transmission optical sensor. Results will be presented that compare streptavidin-biotin binding with sensors fabricated from gold nanorods with previous results on spherical gold nanoparticles.

10:40am **BI+NS-TuM8 Activation of Integrin Function by Nanopatterned Adhesive Interfaces***, J.P. Spatz, **M. Arnold**,* University of Heidelberg, Germany **INVITED**

To study the function behind molecular arrangement of single integrins in cell adhesion, we designed a hexagonally close-packed rigid template of cell adhesive gold nano-dots coated with cyclic RGDfK peptide by lithographic means of diblock copolymer self-assembly. The diameter of the adhesive dots is = 73nm between the adhesive dots results in limited cell attachment and spreading and dramatically reduces the formation of focal adhesion and actin stress fibers. We attribute these cellular responses to restricted integrin clustering rather than insufficient number of ligand molecules in cell-matrix interface since "omicro-nanopatterned" substrates consisting of alternating fields with dense and no nano-dots support cell adhesion. We propose that the range between 58-73 nm is a universal length scale for integrin clustering and activation, since these properties are shared by a variety of cultured cells.

11:20am **BI+NS-TuM10 Lifetime of Biomolecules in Hybrid Nanodevices: The Aging Process of Motor Protein-based Molecular Shuttles***, H. Hess,* University of Washington*; C. Brunner,* ETH Zurich, Switzerland*; K.-H. Ernst,* EMPA Duebendorf, Switzerland*;* ***V. Vogel****,* University of Washington and ETH Zurich, Switzerland

Prolonging the lifetime of biomolecules in their functional states is critical for applications where biomolecules are integrated into synthetic materials or nanodevices. A simplified molecular shuttle system, which consists of fluorescently labeled microtubules propelled by kinesin motor proteins bound to the surface of a flow cell, served here as a model system for such a hybrid device. In this system, the functional decay can easily be assayed by utilizing optical microscopy to detect motility and disintegration of microtubules (MTs). We found that the lifetimes of these hybrid systems were mainly limited by the stability of MTs, rather than of kinesin. To determine the biocompatibility of polymers widely used in microfabrication, we assembled flow cells with glass bottom surfaces and covers fabricated from glass, poly(urethane) (PU), poly(methyl-metacrylate) (PMMA), poly(dimethylsiloxane) (PDMS), and ethylene-vinyl alcohol copolymer (EVOH). Without illumination, only PU had a substantial negative impact on MT stability, while PMMA, PDMS and EVOH showed stabilities comparable to glass. Under the influence of light, however, the MTs degraded rapidly on PDMS or PMMA. A similar effect was observed on glass if oxygen scavengers were not added to the medium. Strong bleaching of the fluorophores was again only found on the polymer substrates and photobleaching coincided with an accelerated depolymerization of the MTs. The presented data provide a benchmark for the lifetime of motor protein-based bionanodevices which utilize glass as the primary synthetic material, and test the impact of a variety of polymer materials on the longevity of microtubules, the most fragile biological structure in the device. This study demonstrates that our definition of biocompatibility evolves, as we progress towards architectures engineered on a molecular level, which integrate multimeric proteins and protein assemblies.

11:40am **BI+NS-TuM11 Analysis of Collision Events of Self-Propelled Biomolecular Shuttles Carrying Cargo***,* ***B.C. Bunker****, A.K. Boal, S.B. Rivera, G.D. Bachand,* Sandia National Laboratories

Collision events between cargo carrying biotinylated microtubules (MTs) laden with 0.56 mm diameter streptavidin coated polystyrene beads (SBs) while being transported across kinesin coated surfaces were observed. Six distinct actions resulted from such collisions: no interaction, SB transfer between MTs, one MT deforming as a result of the collision, co-joining of the two MTs through mutual attachment to the SB, the SB being dislodged from the MT, or one of the MTs being severed. Interactions were studied both as a function of percent biotin-tubulin used to prepare the MTs and temperature. While biotin percent was observed to have a negligible effect of the percent chance of the various outcomes, heating the system from 24ËsC to 30ËsC decreased the likelihood of a SB transfer event while increasing the rate of MT bending and dragging events. Two important factors are proposed to determine the outcome of these collisions: the geometry of the collision event and the nature of the binding site that the SB is originally attached to.

Nanometer-scale Science and Technology
Room 213D - Session NS-TuM

Nanotube Processing and Composite Materials

Moderator: S. Evoy, The University of Pennsylvania

8:20am **NS-TuM1 Controlled Fabrication and Modification of Organized Carbon Nanotube Architectures***,* ***Y.J. Jung****,* Rensselaer Polytechnic Institute, U.S.A*; R. Vajtai, N. Chakrapani, G. Meng, P.M. Ajayan,* Rensselaer Polytechnic Institute*; Y. Homma, Y. Kobayashi,* NTT Basic Research Laboratories*; T. Ogino,* Yokohama National University, Japan

An overview of our results on the controlled fabrication and modification of organized carbon nanotube architectures will be presented. The talk includes strategies for building suspended single-walled carbon nanotubes (SWNTs) forming self-directed networks on nano-scale patterned substrate using chemical vapor deposition (CVD). We elaborate the straightening process of nanotubes in the networks suspended on Si pillars by Ga ion irradiation in a Focused Ion Beam (FIB). Beyond the morphological changes of the nanotubes and nanotube bundles we will present our conclusions for carbon atom ejection and compare with previous electron beam and ion beam irradiation experiments. Although ion irradiation induces defective structures into the nanotube lattice, as micro-Raman mapping shows, the form and dimensions of the nanotubes remain close to that of the original grown morphology. To demonstrate another nanostructure modification we will discuss the formation of intriguing two-dimensional cellular foams from capillarity-induced perturbations during the drying of vertically aligned multi-walled carbon nanotubes (MWNT) architectures with the mechanisms giving rise to pattern formation and methods of controlling the structure and orientation. Similarly, we will briefly present our latest results for organized assembly of multiwalled nanotubes into various 2-D and 3-D structures on planar substrates as well as within anodic porous aluminum oxide templates.

8:40am **NS-TuM2 Growth of Arrays of mm Long, Straight Single-Walled Carbon Nanotubes***,* ***Z. Yu****, S. Li, P. Burke,* UC Irvine

In this work, we demonstrate the growth of arrays of 1.5 mm long, straight single walled nanotubes fabricated using a single furnace with methane and H2 as the feedstock. Recently Huang et al[1] have fabricated 3.7 mm long single walled carbon nanotubes using a two-furnace, dual temperature growth system with CO and H2 as the feedstock. Our work shows arrays of long, straight nanotubes can be grown in a single furnace system. Using a home-built CVD system based on a 3 inch Lindberg furnace, we have synthesized long, straight nanotubes using CVD. The catalysts were prepared as follows: First, a lithographically patterned Ti(50 nm)/Au(200 nm) metallization layer is deposited and patterned using e-beam evaporation onto a Si wafer. Next, an aqueous solution containing nanoparticle catalyst is deposited and lifted off onto only the patterned Au. The growth procedure was as follows: First, the sample was heated to 900 C in Ar. Next, H2 was flowed for 10 minutes. Next, methane/H2 mixture was flowed for 15 minutes to activate the growth.Post-growth characterization was carried out with SEM. AFM growth from nanotubes grown under similar conditions in our lab yielded diameters of 1.5 nm. The growth results indicate an aligned array of nanotubes (6) with pitch of 50 microns and length of at least 200 microns. 3 of the 6 nanotubes were 1.5 mm in length. The growth of the longer nanotubes was terminated only by the presence of a neighboring catalyst site. With properly designed catalyst geometries with room to grow, cm long single walled nanotube growth should be possible. In the future it should be possible to grow 2d arrays by rotating the wafer and carrying out a second growth run. By engineering the nanotube pitch, ultra-dense electrical circuitry could be fabricated. @FootnoteText@ [1] S. Huang, B. Maynor, X. Cai, J. Liu, â?oUltralong Well-Aligned Single-Walled Carbon Nanotube Architectures on Surfacesâ?�, Advanced Materials, vol. 15, pp. 1651-1655, 2003.

9:00am **NS-TuM3 Low-temperature Synthesis of Aligned Carbon Nanotubes by Hot-Filament Assisted DC Plasma CVD***,* ***Y. Watanabe****, Y. Hayashi, S. Nishino,* Kyoto Institute of Technology, Japan

Carbon nanotubes (CNTs) are expected to be used for the field emitters of field emission display (FED) because their high aspect ratio and small radius of curvature lead to large electric-field enhancement at their tips resulting in low operating voltage for electron emission. The synthesis method of vertically aligned CNTs in low temperature below the softening point of a glass substrate should be developed to apply CNTs to field emitters of FED. Motivated by such a background, we carried out experiments of synthesis of CNTs in low temperature by hot-filament assisted DC plasma chemical vapor deposition (HF/DC-PCVD)@super 1@. The growth method and conditions were as follow. First a Co foil substrate was heated by hot tungsten filaments in H@sub 2@ atmosphere. Then after 10 min pretreatment in a H@sub 2@ plasma, CH@sub 4@ gas was added for the growth of nanotubes. DC voltage of -450V was applied to the substrate with the hot-filaments grounded. During the growth, substrate temperature was controlled about 500°c, the gas pressure was 20Torr, and growth time was 10 min. Well-aligned CNTs about 60 nm in diameter were observed by scanning electron microscopy in the density of about 10@super 9@ cm@super -2@ on the surface of the substrate. We have succeeded to synthesize well-aligned and high density carbon nanotubes on Co substrate at 500°c. @super 1@Y.Hayashi, T.Negishi, and S.Nishino, J. Vac. Sci. Technol. A 19(2001) 1796.

9:20am **NS-TuM4 Theoretical Study of Catalytic Growth Single-Walled Carbon Nanotubes**, *F. Ding, K. Bolton,* ***A. Rosen**,* Goteborg University and Chalmers, Sweden

Molecular dynamics (MD) simulations based on an empirical potential energy surface (PES) were used to study iron catalyzed nucleation and growth of single-walled carbon nanotubes (SWNTs). The simulations show that SWNTs grow from the iron-carbide particle at temperatures between 800 and 1400 K, whereas graphene sheets encapsulate the particle at temperatures below 600 K and a three-dimensional (3D) soot-like structure is formed above 1600 K. The simulations also reveal other details of the growth mechanism. For example, it is seen that the growing SWNT maintains an open end on the FeC particle due to the strong bonding between the SWNT end atoms and the particle. The SWNT-particle enthalpy is minimized when the SWNT and FeC cluster have similar diameters. This leads to the growth of SWNTs that have similar diameters to the metal clusters, as has been seen experimentally.

9:40am **NS-TuM5 Controlling and Modeling the Interphase in Polymeric Nanocomposites**, ***L.C. Brinson**, H. Liu, T. Ramanathan,* Northwestern University **INVITED**

Polymeric nanocomposites made by incorporating small amount of nanoscale inclusions into polymer matrices exhibit dramatic changes in thermomechanical properties over the pure polymers. Because the properties of the nanoscale fillers can be extraordinary, even small volume fractions can result in significant changes.. Enhancing the effect is the extremely significant role that the interphase plays in these systems. Given the enormous surface to volume ratio for nanoparticles, the interphase volume fraction can dwarf that of the inclusions themselves. In this paper, experimental evidences of the existence of this interphase region are presented. We show that by properly-controlled functionalization of the nanoscale inclusions, we can impact the properties of the interphase region and consequently control the properties of the nanocomposites. In conjunction with the experimental results, the viscoelastic behavior of multi-phase polymeric nanocomposites is modeled using a novel hybrid numerical-analytical modeling method that can effectively take into account the existence of the interphase region. This hierarchical modeling approach couples the finite element technique and micromechanical approach and operates at low computational cost. Comparison between experimental and modeling results is reported.

10:20am **NS-TuM7 Wetting of Individual Carbon Nanotubes with Organic Liquids**, ***A.H. Barber**, S.R. Cohen, H.D. Wagner,* Weizmann Institute of Science, Israel

Carbon nanotubes show promise as reinforcements in polymer composites. For effective reinforcement, good adhesion between the nanotube and polymer is necessary. Adhesion at a polymer-nanotube interface involves many different types of bonding mechanisms, with wetting of fibers by the liquid polymer regarded as a necessary, but not a sufficient prerequisite for adhesion. Here we present a new experimental method to investigate the wetting behavior of single carbon nanotubes under ambient conditions. Carbon nanotubes, bound to probe tips in a scanning probe microscope are controllably dipped into various organic probe liquids. The changes in force due to the wetting of single carbon nanotubes thus can be accurately measured, giving insights on the interaction between liquid and nanotube. In particular, liquid-carbon nanotube contact angles are measured, which can be interpreted with respect to the nanotube surface characteristics. Using an Owens and Wendt analysis, the polar and dispersive components of the interaction can be separated. Our results show that the surface of the carbon nanotube displays hydrophilic behavior, in contrast to hydrophobic graphite surfaces. This project was supported by the (CNT) Thematic European network on 'Carbon Nanotubes for Future Industrial Composites' (EU), the Minerva Foundation, the G. M. J. Schmidt Minerva Centre of Supramolecular Architectures, and by the Israeli Academy of Science. H.D. Wagner is the recipient of the Livio Norzi Professorial Chair.

10:40am **NS-TuM8 Impregnation of Osmium Dioxide to MWCNTs and Improvement of the Electron Emission Characteristics**, ***T. Noguchi**, M. Shimamoto, M. Nishiwaki,* KEK, Japan; *K. Tatenuma,* KAKEN Inc., Japan; *S. Kato,* KEK, Japan

Osmium dioxide impregnation to MWCNTs was attempted in order to improve the electron emission characteristics. OsO@sub 2@ similar to RuO@sub 2@ has desirable properties including high conductivity (6x10@super -5@ @ohm@cm at 300K), high catalytic performance, and good chemical and physical stabilities. In this study, OsO@sub 2@ impregnation to MWCNTs was conducted by utilizing osmium tetraoxide in a solvent at ambient temperatures and pressures. When compared to MWNTs without impregnation treatment, those MWCNTs impregnated with OsO@sub 2@ have superior and more efficient electrical characteristics with stable emission at a lower electric field as observed for RuO2 impregnated MWCNTs.

11:00am **NS-TuM9 Electron Emission Property from MWCNTs with Subnano Ruthenium Dioxide Clusters and with High Adhesivity on Substrate - High Current Endurance Test in UHV and Influence of H@sub 2@O or CO -**, *M. Shimamoto, T. Noguchi, M. Nishiwaki,* KEK, Japan; *K. Tatenuma,* KAKEN Inc., Japan; ***S. Kato**,* KEK, Japan

Applications of MWCNTs to FEDs, electron sources of electron accelerators and surface analytical tools, and vacuum tubes for microwave amplifier, X-ray, light tube and so on require a high current density of its electron beams, a low threshold of electric field staring the field emission and a long life time with the emission. We reported the achievement of a remarkalbly high DC current density close to 300mA/cm@super 2@ with a threshold electric field of 2V/µm using new technologies of subnano RuO@sub 2@ clusters on MWCNTs surface and of high CNT adhesivity on metalic substrate. An outstanding electron emission property achieved after those treatments would be explainable based on both further increase emission points due to the subnano clusters not only from MWCNT ends but also from strongly bent wall and better thermal conductivity resulted from the heat treatment. Reduction of work function of CNT owing impregnation of RuO@sub 2@ might contribute higher field emission current density as well. Base pressure of XHV should be also big help to make sure reasonable MWCNT life at very high emission current to drastically reduce physical and chemical ion sputtering. In this paper, endurance running tests of MWCNTs in UHV up to 700 hours with a relatively high DC current of 50 mA/cm@super 2@ and degradation of the field emission characteristics due to residual gas such as H@sub 2@O or CO are focused.

11:20am **NS-TuM10 Synthesis of Y-Junction Singlewall Carbon Nanotubes**, ***Y.C. Choi**, W. Choi,* Florida International University

Y-junction singlewall carbon nanotubes were synthesized on thermally oxidized silicon substrates by chemical vapor deposition. Molybdenum, titanium, or zirconium-doped iron nanoparticles supported by aluminum oxide were used as catalysts for the synthesis. Most of singlewall carbon nanotubes have branches, forming Y-junctions. Transmission electron microscopy confirmed the formation of singlewalled structures of Y-junctions with diameters ranging from 2 nm to 4 nm. The density of Y-junctions could be controlled simply by variation of spinning rate when spin coating of catalyst soultion was carried out. It was found from radial breathing mode peaks in Raman spectra that our sample has both metallic and semiconducting nanotubes, indicating the possible formation of Y-junctions with different electrical properties. The growth mechanism based on experimental results will be further proposed.

11:40am **NS-TuM11 Surface-Programmed Assembly Process of Large-Size Multi-Wall Carbon Nanotubes and Its Mechanism**, ***J. Im**, M. Lee, S. Hong,* Seoul National University, South Korea

Recently, the surface-programmed assembly (SPA) process that utilizes surface molecular patterns to guide the assembly of single wall carbon nanotubes (SWCNT) has been reported (Nature 425, 36 (2003)). Herein, we show that the SPA method can be utilized to assemble even large-size multi-walled carbon nanotube (MWNT) which is as large as 30nm in diameter. In addition, we studied the mechanism of the SPA process for both SWNTs and MWNTs by measuring 1) the adsorption probability distribution as a function of CNT size (diameter, length, etc.) and 2) interaction energy between molecular patterns and CNTs. This result implies that SPA method can be applied for electronic applications based on relatively large-size nanowires.

Nanometer-scale Science and Technology
Room 213D - Session NS-TuA

Nanostructures and Biology

Moderator: H.G. Craighead, Applied & Engineering Physics

1:20pm **NS-TuA1 Virus & Biomolecule Detection Using Nanoelectromechanical Devices***, **B. Ilic**, Y. Yang, H.G. Craighead,* Cornell University

We have used resonating mechanical cantilevers to detect binding of viruses and biomolecules captured from liquid. As a model virus, we used a nonpathogenic insect baculovirus to test the ability to immunospecifically bind and detect small numbers of virus particles. Arrays of surface micromachined antibody-coated polycrystalline silicon nanomechanical cantilever beams were used to detect binding from various concentrations of baculoviruses in a buffer solution, by observing the resonant frequency shift of the oscillators. Because of their small mass, the 0.5µm x 6µm cantilevers have mass sensitivities on the order of 10@super -19@ g/Hz, enabling the detection of an immobilized AcV1 antibody monolayer corresponding to a mass of about 3 x 10@super -15@g. With these devices we can detect the mass of a single virus to the cantilever. Resonant frequency shift, resulting from the adsorbed mass of the virus particles, distinguished solutions of virus concentrations varying between 10@super 5@ and 10@super 7@ pfu/ml. Single crystal silicon nanomechanical oscillators with spatially-defined chemical binding sites, with greater mass sensitivity, have similarly been used to detect the binding of specifically bound biomolecules at the attogram level. In both experiments careful controls were done to assure the detected mass resulted from the intended specifically bound biomaterial.

1:40pm **NS-TuA2 Electrokinetic Molecular Separation in Nanoscale Fluidic Channels***, **A.L. Garcia**,* The University of New Mexico

We have developed an interferometric lithography technique to manufacture an integrated micro-nano-fluidic chip for use in bioseparations and sensing. Transport behavior of two dyes, one charged and one neutral, in these silica/silica oxide/Pyrex chips has been quantified. A mixture of the dyes was introduced into an array of nanoscale channels using electroosmosis through the microfluidic channels. Electrokinetic separations of the dyes in these nanochannels at various applied biases were examined in different chips with nanochannel widths ranging from 50-200 nm. Confocal laser scanning microscopy was used to observe the average velocities of the dyes in the array of nanochannels. The resulting velocities were in good agreement with theoretical predictions that take into account the wall surface potential overlap and electrolyte concentrations across the individual nanofluidic channels. Separations were also achieved in these channels by the application of pressure, utilizing the Poiseuille velocity distribution of fluid within the channels.

2:00pm **NS-TuA3 Fabrication of Nano-Structured Polymeric Surfaces for Bio-Sensing Devices***, A. Valsesia, **P. Colpo**, T. Meziani, M. Manso, D. Gilliland, G. Ceccone, F. Rossi,* EU-JRC-IHCP, Italy

The interaction between material surfaces with specific chemical functionalities and bio-molecules has been widely investigated in order to modulate the performances of bio-sensors and medical devices. When the dimensions of the interacting surface structures are comparable with those of the single protein molecules or small clusters of proteins, the bio-molecules absorption is considerably influenced both from the morphological and chemical point of view. This can be exploited for the orientation of specific binding sites between antigens and antibodies. In this work we develop a reliable technique to produce chemical contrast at sub-micrometric level through the fabrication of nano-island from Poly Acrylic Acid (PAA) film deposited onto anti-fouling substrates. First, a thin layer of PAA is deposited on the substrate by PE-CVD. Then, a layer of polystyrene colloidal nano-particles (200-500 nm) is deposited by spin coating. The nano-particles are then partially removed by oxygen plasma etching of the surface. The etching process is stopped before the complete etching of the nano-particles and the residual ones are removed by ultrasonic bath. Whereas unmasked PAA film is completely etched, nano-domes of as deposited-PAA (located under the nano-mask) are created evenly on the surface. The shape and the 2-D geometry of the resulting PAA nano-domes (lateral distribution, surface density) is controlled by the parameters of the spin casting process and by the wetting characteristic of deposited PAA. The chemistry of the PAA films was characterized by XPS, whilst the resulting nano-structured surfaces have been studied using AFM, SEM, SPM and SIMS in imaging mode. Then protein absorption test have been performed on the nanostrucured surfaces: the SEM and AFM characterization revealed that nanometric proteins clusters are selectively bond on the top of the domes, and not between them where the anti-fouling matrix repels the biomolecules.

2:20pm **NS-TuA4 Hairy Peptide Nanotubes***, **M. Biesalski**, J. Couet, J.D. Jeyaprakash S. Samuel, S. Santer,* Institute for Microsystem Technology (IMTEK), Germany

A general theme in Nanotechnology is the development of novel materials with well-defined composition and nanometer scale structures. To this, materials scientists are increasingly deriving new lessons from naturally occurring "nanomaterials" about useful composition-structure property relationships that might be mimicked with synthetic materials.@footnote 1@ An interesting example constitutes the bottom-up formation of hollow tubular structures by a spontaneous self-assembly of cyclic peptides. Cyclic peptides consisting of alternating D- and L-amino acids posses a flat conformation that allows the build-up of beta-sheet type assemblies, where the cyclic peptides are stacked onto each other forming a hollow tubular structure with a precisely defined inner diameter and all amino acid residues pointing outwards.@footnote 2@ In order to construct functional polymeric nanotubes we have synthesized cyclic peptides that are modified with an ATRP initiator at distinct side groups ("CP-ini"). The CP-ini self-assembles into nanotubes that present these initiator moieties on the surface. The peptide nanotubes are subsequently coated with different functional polymers by using (living) radical polymerization initiated from the surface of the tubes. The so prepared functional nanotubes are characterized with respect to the dimensions, morphology and higher order assemblies using AFM, TEM and X-ray diffraction. The size of the polymeric shell of the nanotubes can be controlled by adjusting the graft density and the molecular mass of the surface-attached polymer chains. The concept of grafting polymer chains from cyclic peptide assemblies is highly modular with respect to the incorporation of a wide range of different functions. @FootnoteText@ @footnote 1@ M. Tirrell, E. Kokkoli, M. Biesalski, Surface Science 500, 2002, p61-83.@footnote 2@ M.R. Ghadiri, J.R. Granja, R.A. Milligan, D.E. McRee, N. Khazanovich, Nature 366, 1993, p324-327.

2:40pm **NS-TuA5 Atomic Force Microscope Conductivity Measurements of Single Ferritin Molecules***, **D. Xu**, G.D. Watt, J.N. Harb, R.C. Davis,* Brigham Young University

We will present electrical measurements on the conductivity of ferritin molecules by conductive atomic force microscope (c-AFM). The high structural stability of ferritin molecules, relative to other proteins, makes them attractive for nanotechnology applications such as nanoscale batteries. Ferritin is an iron-storage protein that functions as an iron reservoir in animals, plants, fungi and bacteria. Ferritin consists of 24 protein subunits that are arranged to form a spherical molecule with an external diameter of 12nm. The hollow ferritin interior with a diameter of ~8nm can hold up to 4500 iron atoms as Fe(OH)@sub 3@. For battery applications the electron transfer rate through the ferritins is a critically important parameter; it will affect the internal resistance and limit the maximum current. Ferritin molecules were self-assembled on gold surfaces to form sub-monolayer films and characterized by AFM prior to electrical measurements. Electrical conductivity measurements were performed on both single apoferritin and holoferritin molecules by c-AFM. The conductivity of monolayer films (~ 1 µm@super 2@) of ferritin molecules on atomically flat gold surfaces was measured for comparison. Holoferritin was 5-15 times more conductive than apoferritin, indicating that for holoferritin most electron transfer occurs through the ferrihydrite core. With 1 volt applied, the average electrical current through single holoferritins and single apoferritins was 2.58 pA and 0.188 pA respectively.

3:00pm **NS-TuA6 Friction Measurements of DMPC Phospholipidic Bilayers***, **G. Oncins**, S. Garcia-Manyes, F. Sanz,* Universitat de Barcelona, Spain

Self-assembled phospholipid layers have been a matter of extensive research during last decades. The high content of these structures in cellular membranes has led to their use as models for the study of a wide bunch of biological, biochemical, biophysical and medical issues. Besides, the Supported Planar Bilayers (SPBs) have been very useful in the study of interaction and adhesion forces between cells, in the modelling of the diffusion kinetics of phospholipids and in the insertion of proteins in membranes. AFM has proved to be the most suitable technique to obtain molecular topographic resolution of these systems and to study the morphology of SPBs under various conditions. We have recently worked with such structures at a nanometric level, mostly performing studies based on AFM force spectroscopy measurements of 1,2-Dimyristoyl-sn-glycero-3-phosphocholine (DMPC) bilayers@footnote 1@. The present work has used Lateral Force Microscopy (LFM) to mechanically test DMPC bilayers supported on mica, performing a series of experiments with laterally and vertically calibrated tips in aqueous environment and in which NaCl concentration has been ramped from 0M to 0.1M. Obtained friction results have been complemented with AFM height images of the same tested bilayer area, being able to relate each friction signal with its corresponding topography. Results have shown that the presence of NaCl modifies drastically the mechanical response of the DMPC bilayer, and, consequently, of the cellular phospholipidic membrane. @FootnoteText@ @footnote 1@Garcia-Manyes, S. ;Oncins, G.; Sanz, F.; Effect of ionic solutions on the nanomechanics of a model lipid bilayer: a quantitative Force Spectroscopy contribution, submitted to JACS Communications.).

Thin Films
Room 303C - Session TF+NS-TuA
Focused Beam Processing & Fabrication

Moderator: J.M. Fitz-Gerald, University of Virginia

2:20pm **TF+NS-TuA4 Localized Heating Effects During Electron Beam-Induced Deposition of Nanostructures***, **S. Randolph**, J.D. Fowlkes, P.D. Rack,* University of Tennessee, Knoxville

In recent years, electron beam-induced deposition (EBID) has shown promise for use in next-generation lithography applications and nanostructure fabrication. While many materials have been successfully deposited on various substrates by EBID, control of feature size and geometry has been lacking. One possible mechanism that makes process control problematic is the localized heating that occurs in the nanostructure while undergoing constant electron bombardment. While the electron beam-induced heating of a bulk sample in the typical SEM is negligible, a focused beam projected onto a raised high aspect ratio feature can cause significant temperature rises in the feature. As the sticking coefficient and residence time of the impinging precursor gas are strong functions of the substrate temperature, it is expected that the deposition rate will vary with the surface temperature of the nanostructure if the process is mass transport limited. Assuming that there are no radiative and convective heat losses through the surface of the sample, the nanostructure growth creates a quasi one dimensional structure that does not dissipate heat as well as a bulk film. Consequently, as the nanostructure grows the surface temperature increases thereby reducing the sticking coefficient and residence time of the impinging gas. In this presentation, a Monte-Carlo electron-solid model will be illustrated which calculates the energy deposition profiles in the bulk and nanostructured features. Using these profiles, a finite element model is used to calculate the temperature profiles. Bulk and nanostructured features will be compared and discussed in context with experimentally observed growth rates.

2:40pm **TF+NS-TuA5 Electron Beam Micromachining***, **P.E. Russell**, D.P. Griffis, A. Garetto,* NC State University **INVITED**

While chemically enhanced focused ion beam micromachining (CE-FIBM) or other ion based micromachining techniques have many practical applications, any ion beam based micromachining technique typically results in some degree of sample damage as well as residual implanted ions. In many cases, these implanted ions cause deleterious effects such as staining in the case of mask repair, alteration of the electrical characteristics of semiconductor and optoelectronic samples and/or surface damage in samples prepared for high resolution electron microscopy or microanalysis. In order to avoid ion staining and following up on our earlier efforts in electron beam induced deposition and material removal, our efforts are currently focused on gaining increased understanding of and development of chemically enhanced electron beam micromachining (CE-EBM) of technologically important materials. The interaction of incident and emitted (secondary and backscattered) electrons with surfaces in the presence of a suitable chemical precursor can induce useful chemical reactions. Electron beam energies from a few hundred eV to 30 keV are routinely available on scanning electron microscopes, and a few systems allow much lower beam energy. The magnitude of the emission of secondary electrons peaks in the range of a few eV to tens of eV's while backscattered electrons are emitted over a broad, albeit higher range of energies up to the full primary energy. This wide range of electron energies coupled with the richness of possible beam/sample/precursor interactions makes available a wide range of possibilities for both deposition and etching with, when compared to damage resulting from ion beam exposure, a dramatically reduced probability of damage and/or unintentional alteration of samples. This talk will review recent developments in both the application and understanding of CE-EBM.

3:20pm **TF+NS-TuA7 Nanoscale Structures and Devices Produced Using Energetic Atomic Beams***, **E.A. Akhadov**,* Los Alamos National Laboratory*; D. Read,* Florida State University*; A.S. Cavanagh, A.H. Mueller,* Los Alamos National Laboratory*; J.C. Gregory, G.P. Nordin,* University of Alabama in Huntsville*; M.A. Hoffbauer,* Los Alamos National Laboratory

Nanoscale patterning of polymeric materials and low temperature thin film growth become possible using atomic species with kinetic energies similar to chemical bond strengths. We have developed a technique exclusive to LANL, called Energetic Neutral Beam Lithography/Epitaxy (ENABLE), that utilizes energetic neutral atoms for materials processing at the nanoscale. In this presentation, we demonstrate the use of atomic oxygen for nanoscale polymer etching and atomic nitrogen for templated nitride thin film growth. High-precision nanoscale formations (<50nm) with aspect ratios exceeding 35:1 were fabricated in polymer films. Taking advantage of the low temperature thin film growth afforded by ENABLE, we have fabricated AlN-based structures using pre-etched polymeric templates for potential electronic, photonic, and nanofluidic applications.

3:40pm **TF+NS-TuA8 A Three - Dimensional Computer Simulation of Electron - Beam Induced Deposition (EBID)***, **J.D. Fowlkes**, P.D. Rack, S. Randolph,* University of Tennessee, Knoxville

A simulation will be presented of the electron - beam induced deposition (EBID) process that was coded using the Matlab(R) program. The simulation has a Monte Carlo component to predict electron trajectories as well as elastic and inelastic electron â?" substrate interactons. A discretization scheme projects each electron scattering event onto a three dimensional matrix to provide a reference point to test for a host of possible events per matrix node including secondary electron generation and/or EBID. Three phases coexist in the matrix including the precursor gas, the deposited phase and the substrate phase. A dynamic model tracks the gas - surface interaction including precursor adsorption, deposition and desorption under thecontext of a Langmuir type surface coverage. Primary, backscattered, and secondary electrons that escape the gas - pillar and gas - substrate interface may induce deposition based on their trajectory, energy and precursor surface coverage. The probability of EBID is based on a "shifted and scaled" ionization cross-section for the precursor gas molecule to be roughly applied as a dissociation cross - section. Primary (PE) and secondary electrons (SE) contribute most signficantly to the EBID growth of high-aspect ratio nanopillars while backscattered electrons (BSE) play more of a feature coarsening role. Two regimes of pillar growth are observed; a region characterized by linear a growth rate where the electron interaction volume interacts with both the growing pillar and the substrate and a second regime, again linear in growth rate, whereby the penetrating electrons interact solely with the high aspect pillar.

Nanometer-scale Science and Technology
Room Exhibit Hall B - Session NS-TuP

Poster Session

NS-TuP1 Electrostatic Potential and Charge Domain Mapping of Samples by a Large Range Scanning Probe Microscope.*, **Y.D. Park**,* Seoul National University, South Korea, Korea*; J. Lee, S. Lee, Y.S. Cho, H. Shin, Y. Kuk,* Seoul National University, South Korea

A large range scanning probe microscope was constructed, with a new beam reflection structure. Z scanner was separated from X-Y scanner for fast scanning of massive samples. A high precision (~100 nm) X-Y stepper was used to scan samples over a large area. Double reflection mirrors are used to avoid z positional errors caused by laser beam path. The nanowires and carbon nanotubes are imaged without any distortion on electrode-patterned Si wafer. The scanning range can be varied from tens of nanometer to tens of micrometer with this microscope. The electrostatic potential mapping over many nanowires and the surface charge domain of ferroelectric samples will be given for examples.

NS-TuP2 Fabrication of High Performance NSOM Probe For Optical Trapping*, S.S. Choi, D.W. Kim, C.K. Chun, **M.S. Song**,* SunMoon University, Korea*; M.J. Park,* Korean Military Academy, Korea

There have been tremendous interests about the optical trapping of the biomolecule in the microdevice with optical spectroscopic capablities. For microdevice application purposes, the optical trapping with nearfield optical probe array seems quite promising. Though, the weak nearfield intensity has been major obstacle for its application. The nearfield optical intensity through the nanosize aperture is dependent upon the aperture size, the grain size of the deposited metallic film, and other factors influencing the surface plasmon excitation. The surface plasmon excitation can be accomplished with periodic texturing of the metal surface around the nanoszie aperture. The enhancement of the nearfield optical intensity can be utilized for the nearfield optical trapping. In this report, the two adjacent metal aperture was fabricated using microfabrication technique including stress-dependent oxidation, isotropic wet etching of silicon oxide and bulk etching of Si, and bimetallic metal deposition. The adjacent nanosize metal aperture with distance less than the input wavelength can improve the output optical intensity. The bimetallic deposition of Ti/Al layer has been performed in order to provide better uniformity of the coated metal film. The buffer layer of Ti thin film would reduce grain size during the reflow process. The reduced grain size of the deposited thin film is supposed to improve throughput of nearfield optical intensity. The fabricated probe array will be utilized for near field optical trapping of the biomolecule. The optical characterization of the fabricated nearfield probe array will be investigated and the biomolecule trapping be tested.

NS-TuP3 Visualization of Two-Dimensional Doping Profile in Si for the Fabrication of Resistive AFM Probe*, **H. Shin**, B. Lee,* Kookmin University, Korea

In recent, scanning resistive probe microscopy (SRPM)@footnote 1@, as a variant of SPM-based techniques, which has a semiconductor resistor at the apex of the tip and can observe surface charges directly, was newly proposed and demonstrated. Spatial resolution of SRPM is dependent upon the size of the prepared resistor at the apex. The size of the resistor can be determined by width of the SiO2 implant mask, where both sides of the mask were open and implanted with As+ ions, and the diffusion length of the ions underneath. Using Kelvin Force Microscopy (KFM), we investigated the area of the resistor or equivalently underneath of the mask and determined the diffusion length of implanted As+ ions. For the first time, the depletion regions in the graded junction between implanted n+ and p-type Si substrate were observed. Furthermore, we proposed the mechanism of the SRPM by the observation of the overlapping depletion regions in the narrow resistor, which results the lowering barrier height for charge carriers. @FootnoteText@ @footnote 1@ H. Park, J. Jung, D.-K. Min, S. Kim, S. Hong, and H. Shin, Scanning Resistive Probe Microscopy: Imaging Ferroelectric Domains, Appl. Phys. Lett., 84, 1734-1736 (2004).

NS-TuP4 Nanoscale Current Mapping of Indium Zinc Oxide Thin Films Investigated by Conducting Atomic Force Microscopy*, **C.Y. Su**,* National Science Council, Taiwan*; H.C. Pan,* National Science Council, Taiwan, Taiwan, ROC*; M.H. Shiao,* National Science Council, Taiwan*; C.N. Hsiao,* National Science Council, Taiwan, R.O.C.

Transparent conducting oxide (TCO) films such as impurity-doped indium oxide systems have been widely applied for opto-electronic devices. Recently, several advantages of ZnO doped indium oxide (IZO) thin film has been reported. Since the photon emissive layer thickness of a device is typically in the range around 100 nm, understanding of the microscopic evidences for improving device performance is required. We have used the technique of conducting atomic force microscopy (CAFM) to investigate the relations between local surface electrical properties and morphologies of IZO thin films treated by different cleaning methods. The conducting regions are attributed to zinc oxide distributed randomly in the average size of 35 nm. Microscopic current mapping indicates ultraviolet-ozone (UV-ozone) treatment is contributed to produce nonconductive region due to generation of stable oxide as reported previously. By applying a tip bias of over -9 V on the nonconducting region, UV-ozone treated sample showed resistance against decomposition while the others failed. This stable oxide acts as a hole transport layer between the photon emissive layer and IZO thin film, which improves stability of devices by decreasing degradation rate of device performance. The surface oxide layer is generally attributed to increasing the work function after UV-ozone treatment, and higher efficiency is achieved as a result of reduction in energy barrier by improving interfacial conditions. Similarly, an additional ultra-thin SiO@sub 2@ layer deposited over IZO thin film would optimize electrical properties for improvement of device performance.

NS-TuP5 A Combined Vapor and Electrochemical Deposition Approach to the Controlled Growth of Nanoscale Metal Dendritic Islands, Beaded Wires, and Continuous Wires*, **C.E. Cross**, J.C. Hemminger, R.M. Penner,* University of California Irvine

Under conditions of careful control of the experimental parameters of substrate temperature and metal atom flux, conventional vapor deposition can be used to grow a variety of useful metal nanostructures. We use this approach to grow dendritic islands as well as beaded nanowires of gold on graphite substrates. Combining this approach with electrochemical deposition allows us to convert beaded nanowires into continuous nanowires (diameters as small as 20nm) that are many microns in length. Low flux vapor deposition of sub-monolayer amounts of gold on a graphite substrate that is held at or near room temperature generates dendritic islands of gold. The islands are fairly monodispersed in lateral dimensions (~100nm across). If the graphite substrate is held at higher temperature (@>=@300°C) "beaded wires" can be grown by decorating the graphite steps. The "beaded wires" are composed of gold "dots" that are 10-20nm diameter. Once again the "beaded wires" consist of gold dots that are highly monodispersed. The "beaded wires" provide excellent nuclei for electrochemical growth of very narrow, long, continuous wires of gold on graphite, where the wires are several microns in length. Each of these classes of structures have potentially interesting uses. The dendritic islands of gold are of interest in studies of the catalytic properties of gold nanostructures. The theoretically expected one dimensional electronic structure and optical properties of linear chains of gold dots that are tens of nanometers in diameter spaced by 10nm are of interest and the long nanometer scale continuous wires of gold are under development for sensor applications.

NS-TuP6 Electrochemically Grown Single Nanowires for Gas and Biochemical Detection*, **C. Lee**, M. Yun, R.P. Vasquez,* Jet Propulsion Laboratory (JPL)*; N.V. Myung,* University of California at Riverside*; E. Menke, R.M. Penner,* University of California at Irvine

We have developed an electrochemical nanowire growth technique which allows the use of a wide variety of sensing materials such as metals, alloys, metal oxides, semiconductors, and conducting polymers. Using this technique, we have grown single 3 micron long Pd nanowires with a diameter of 75 nm. We have also grown single polypyrrole nanowires of 500 nm diameter. The Pd nanowires grown by this technique have been used to sense hydrogen gas and the polypyrrole nanowires have been used as a pH sensor. The Pd nanowire hydrogen sensor operates under ultra low power (~ 25 nW) conditions and exhibits a fast response (<300 ms) due to the small sensor volume. Our hydrogen sensors can detect hydrogen over a wide range of concentrations from 0.02 % hydrogen gas to 10 % hydrongen gas and can be used for monitoring explosive concentrations of hydrogen gas. In the case of single nanowire pH sensor, the current change observed upon the change in the conductivity of polypyrrole is 2 nA when 1 microliter of buffered solution at pH 12.45 is placed on top of the single polypyrrole nanowire sensor.

NS-TuP7 Phase Transformation of Copper Oxide Nanowires*, H.-Y. Chen,* National Tsing Hua University, Taiwan*; S. Han,* National Taichung Institute of Technology, Taiwan*; **Y.-B. Chu,*** National Chung Hsing University, Taiwan*; H.C. Shih,* National Tsing Hua University, Taiwan

The phase transformation of Cu@sub 2@O to CuO nanowires has been investigated by x-ray diffraction, transmission electron microscopy, and field emission electron microscopy. The Cu nanowires were firstly electrodeposited into anodic aluminum oxide templates with the pore size of 100 nm. After that, the specimens were annealed in air at 250°C to 900°C. The Cu completely transformed into Cu@sub 2@O above 250°C, meanwhile the CuO phase appeared above 350°C. The CuO phase increased with temperatures, whereas Cu@sub 2@O decreased significantly with annealing temperature increasing. Additionally, the Cu@sub 2@O phase completely transformed into CuO while the specimen annealed at 900°C. The phase transformation is accounted for the changes of Gibbs free energy with temperatures, and the consideration of thermodynamics is further discussed.

NS-TuP8 Polyaniline Nanofiber Chemical Sensors*, **S. Virji,** J. Huang, R.B. Kaner,* University of California, Los Angeles*; B.H. Weiller,* The Aerospace Corporation

Using a new interfacial polymerization method for the synthesis of conducting polyaniline nanofibers, we have developed nanofiber sensors and compared them to conventional polyaniline sensors. Polyaniline nanofiber films give high sensitivity and fast time responses due to their large surface area that allow for easy diffusion of gases into and out of the film. Conventional polyaniline thin films, chemically synthesized by oxidative polymerization and cast from organic solvents, exhibit strong but relatively slow, diffusion-controlled, doping characteristics when exposed to acid or base. In addition to doping and dedoping, polyaniline can also be reduced in the presence of a reducing gas such as hydrazine and swelling effects occur in the presence of organic solvents. This latter process can involve vapor-induced chain alignment of polyaniline in the presence of small alcohols. With a large range of detection capabilities, high sensitivity and time response, polyaniline nanofibers are a promising sensor material.

NS-TuP9 Growth of CNT and Tungsten Nanowires Deposited in HFCVD System*, **M. Passacantando,** L. Lozzi, R. Rastelli, S. Santucci,* University of L'Aquila, Italy

Oplay an important role in testing and understanding fundamental physical concepts, for example, the role of dimensionality and size in optical, electrical, and magnetic properties, but also hold considerable technological promise for new nanodevices applications. Furthermore the growth of these nanostructured materials directly on silicon, silicon oxide and other thin films now used in the microlectronics production process opens new possibilities for a quick application as nanodevices. Multiwalled carbon nanotubes and tungsten nanowires have been directly deposited in a hot filament chemical vapour deposition (HFCVD) system using acetylen (C@sub 2@H@sub 2@) on 3 nm of Nickel film deposited on Pt-Si@sub 3@N@sub 4@ patterned substrate. The CNT have been grown only on Si@sub 3@N@sub 4@ site, with a presence of tungsten wires on the Pt pattern. The as-synthesized products were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM) and X-ray Photoelectron Spectroscopy (XPS) techniques. The tungsten wires, after the extraction from the deposition apparatus showed a partially oxidised status (WO@sub x@, x=1-2), smooth surface with no amorphous sheath, and a sharp-tip end with diameters in the range of 10-100 nm. The proposed growth method can be easily scaled up for the real applications.

NS-TuP10 Numerical Simulation of Nanostructure Growth*, **H.H. Hwang,*** NASA Ames Research Center*; D. Bose,* Ames Center for Nanotechnology*; T.R. Govindan, M. Meyyappan,* NASA Ames Research Center

Nanoscale structures, such as nanowires and carbon nanotubes (CNTs), are often grown in gaseous or plasma environments. Successful growth of these structures is defined by achieving a specified crystallanity or chirality, size or diameter, alignment, etc., which in turn depend on gas mixture ratios, pressure, flow rate, substrate temperature, and other operating conditions. To date, there has not been a rigorous growth model that addresses the specific concerns of crystalline nanowire growth, while demonstrating the correct trends of the processing conditions on growth rates. Most crystal growth models are based on the Burton, Cabrera, and Frank (BCF) method, where adatoms are incorporated into a growing crystal at surface steps or spirals. When the supersaturation of the vapor is high, islands nucleate to form steps, and these steps subsequently spread (grow). The overall bulk growth rate is determined by solving for the evolving motion of the steps. Our approach is to use a phase field model to simulate the growth of finite sized nanowire crystals, linking the free energy equation with the diffusion equation of the adatoms. The phase field method solves for an order parameter that defines the evolving steps in a concentration field. This eliminates the need for explicit front tracking/location, or complicated shadowing routines, both of which can be computationally expensive, particularly in higher dimensions. We will present results demonstrating the effect of process conditions, such as substrate temperature, vapor supersaturation, etc. on the evolving morphologies and overall growth rates of the nanostructures.

NS-TuP11 Metal Catalyzed Carbon Nanotube Synthesis by Chemical Vapor Deposition: A First Principles Study of CNT Nucleation and Growth*, **S.H. Lee,** G.S. Hwang,* The University of Texas at Austin

Carbon nanotubes (CNTs) have numerous potential applications ranging from chemical and biological sensors to future electronic devices. Their shape, atomic configuration, and chemical composition could be tailored by tuning process parameters such as temperature and feed gas composition. Such atomic scale control is essential for the development of viable novel chemical, biological and electronic devices. However, still very little is known about underlying growth mechanisms, due largely to a difficulty in direct measurement of complex physical and chemical phenomena occurring during actual CVD processing. While current experimental techniques are still limited to providing complementary real space information, the interplay between experiment and theory will contribute to uncovering complex CNT growth mechanisms and subsequently achieving precise control of their physical and chemical properties. Using density functional theory calculations, we have investigated the initial stage of Ni-catalyzed CNT growth with a feed gas of C2H2/NH3. In this talk, we will present i) decomposition of C2H2 and NH3 which is a strong function of the surface facet of catalysts, ii) hydrogen etching of carbon, iii) diffusion dynamics of decomposed carbon atoms, and iv) formation mechanisms of ring structures from small hydrocarbon species. We will also discuss when the atomic configuration of CNTs will be determined, such as zigzag and armchair structures.

NS-TuP12 Evolution of Single-wall Carbon Nanotubes under Atomic and Molecular Deuterium Treatments*, **E.G. Keim,*** University of Twente, MESA+ Institute, The Netherlands*; W. Lisowski,* Polish Academy of Sciences, Poland*; A.H.J. Van den Berg, M.A. Smithers,* University of Twente, MESA+ Institute, The Netherlands

Relatively little experimental activity has been devoted to the interaction of atomic hydrogen with single-walled carbon nanotubes (SWNTs). Here we present SEM, TEM and XPS data dealing with the question of how the SWNTs are affected by prolonged interaction with a gas mixture of atomic (D) and molecular deuterium (D@sub 2@) at various temperatures. The material, HiPco, was first dispersed in isopropanol in an ultrasonic bath and was subsequently deposited on Si(100). Both the heating of SWNTs and their interaction with deuterium were performed in situ in a quartz cell, part of a separate UHV glass system@footnote 1@, and maintained at 78 or 273 K. The SWNT samples were exposed to the gas mixture, produced by the thermal dissociation of D@sub 2@ on a hot W filament, its temperature, T@sub f@, being kept at 1020 and 1550 K for a deuterium pressure of 0.005 and 0.5 Torr, respectively. All gas-solid interactions were monitored in situ by Thermal Desorption Mass Spectrometry (TDMS). See Ref.@footnote 2@ for a description. The spectroscopic and microscopic examinations were performed ex situ. Prolonged interaction of the (D + D@sub 2@) gas mixture produced at T@sub f@ = 1020 K leads to a coalescence of bundles of SWNTs forming large diameter carbon ropes of square and triangular cross-section covered by nano-aggregates of graphite material. Both the coalescence of single SWNTs and a massive reconstruction of bundles of SWNTs into multi-walled nanotubes were found to occur after prolonged exposure of the SWNTs to the gas mixture produced at T@sub f@ = 1550 K. Similar evolution phenomena were observed earlier@footnote 3@, however, after annealing the SWNTs under Ar flow above 2000 K. @FootnoteText@ @footnote 1@ W. Lisowski, Vacuum 53, 13 (1999).,@footnote 2@ W. Lisowski, E.G. Keim and M.A. Smithers, J. Vac. Sci. Technol. A21, 545 (2003).,@footnote 3@ K. Méténier, S. Bonnamy, F. Béguin, C. Journet, P. Bernier, M. Lamy de La Chapelle, O. Chauvet, S. Lefrant, Carbon 40, 1765 (2002).

NS-TuP15 Theoretical and Experimental Studies on the Adsorption of Oxidizing Gas on Carbon Nanotubes Thin Films*, **L. Lozzi,*** University of L'Aquila, Italy*; L. Valentini,* University of Perugia, Italy*; S. Picozzi, C. Cantalini, S. Santucci,* University of L'Aquila, Italy

In this work a combined theoretical and experimental study on CNT-based system for gas sensing applications is reported. Carbon nanotubes thin films have been deposited by chemical vapor deposition on Si3N4/Si substrates provided with Pt electrodes. Microstructural features as determined by SEM, TEM and Raman spectroscopy highlight the growth of defective tubular carbon structures. The electrical resistivity of the CNT film shows a temperature dependence semiconducting-like and a p-type response with decreasing electrical resistance upon exposure to NO2 gas and O3. No response has been found by exposing the film to CO gas, while some other concomitan gases may have an interfering behavior [1]. In order to obtain a theoretical validation of the experimental results, the equilibrium position, charge transfer and density of states are calculated from first principles for the CNT+CO and CNT+NO2 and CNT+O3 systems. Our density functional calculations show that Both CO and NO2 and O3 molecules adsorb weakly on a defect free tube wall, with essentially no charge transfer between the tube and the molecules. The electronic properties of CNTs are sensitive to the adsorption of NO2 and O3 due to an acceptor-like peak close to the tube valence band maximum, while they are insensitive to the CO adsorption. According to the experimental findings, our theoretical results suggest that gas-induced modification of the density of states close to the Fermi level might significantly affect the transport properties of nanotubes. The role of the defects on the wall of CNT is also discussed and related to the experimental results. In particular the anomalous adsorption of O3 that produces a consumption of the CNT film also at low temperatures is explained as the effect of the chemisorption of this gas onto defective sites. [1] C.Cantalini, L.Valentini, I.Armentano, L.Lozzi, J.M.Kenny and S.Santucci. Sensors and Actuators B 95, 195 (2003).

NS-TuP16 Oxygen Functionalized MWNT as Active Layer for Gas Sensing: Detection of NO@sub 2@ and NH@sub 3@*, A. Felten,* LISE, Belgium*; R. Ionescu, E. Sotter, E. Llobet, X. Vilanova, X. Correig,* Universitat Rovira i Virgili, Spain*; C. Bittencourt, **J.-J. Pireaux,*** LISE, Belgium

Due to their large surface area, Carbon Nanotubes (CNTs) show the potential to be applied as the active material of gas sensors. However, the presence of a thick graphite-like layer at the surface of the nanotubes can rule out the sensing potentiality of this material. In this work we use inductive RF oxygen plasma to functionalize the surface of nanotubes. The influence of different plasma conditions (power, treatment time and pressure) on the functionalization of the CNT surface was studied by XPS. The analyses showed that when a too high power is applied, a chemical etching occurs at the surface and the metallic precursors used in the CNT syntheseis are exposed. On the other hand, for an optimized range of the parameters, functional groups (hydroxide, carbonyl, carboxyl) are attached to the CNT while a reduction in the amount of graphite at the CNT surface is observed. After characterization, functionalized MWNTs (Nanocyl Â®) were used to form the sensitive layer of micro-hotplate gas sensors, prepared by the drop coating method. Detection of NO@sub 2@ and NH@sub 3@ concentrations as low as 500 ppb and 200 ppm, respectively, was found to be possible at ambient temperature. Plasma treatment showed to improve the sensing potentiality of CNTs by reducing the thickness of the graphite-like layer at their surface. The presence of the residual metallic catalysts at the CNTs surface proved to play an important role in sensitivity.

NS-TuP17 Synthesis and Property of Carbon Nanosheets at Different Deposition Temperatures*, **M.Y. Zhu**, J.J. Wang, X. Zhao, R.A. Outlaw, D.M. Manos, B.C. Holloway,* College of William and Mary

Carbon nanosheets, a novel form of free-standing graphite sheets with thickness less than 1 nanometer, were synthesized by radio-frequency (13.56MHz) plasma enhanced chemical vapor deposition (PECVD) on Silicon, quartz and tungsten foil. Carbon source, methane (CH@sub 4@), was diluted in hydrogen (H@sub 2@) to produce carbon nanosheets at various temperatures 650°C to 900°C. SEM images show that the surface morphology of carbon nanosheets varies a lot with deposition temperature. Lower deposition temperatures produce large, smooth nanosheets while higher temperatures produce small, corrugated nanosheets. Raman spectroscopy indicates that the crystallinity of nanosheets deteriorates with increasing substrate temperature. Diode I-V curves were acquired to study the field emission property of nanosheets grown at different temperatures, and yield a turn on field of as low as 4 V/µm.

NS-TuP18 Modeling, Fabrication and Characterization of Vertically Aligned Carbon Nanofiber (VACNF) Based Triode Field Emission Devices for Use in Massively Parallel Digital E-Beam Array Lithography (DEAL)*, **X. Yang,*** University of Tennessee at Knoxville*; W.L. Gardner, L.R. Baylor, H. Cui, D.K. Hensley, R.J. Kasica, D.K. Thomas,* Oak Ridge National Laboratory*; M.A. Guillorn,* Cornell Nanofabrication Facility*; M.L. Simpson,* Oak Ridge National Laboratory

Field emission triodes have been fabricated for application in massively parallel Digital E-beam Array Lithography (DEAL) at Oak Ridge National Laboratory (ORNL)@footnote 1@. Vertically Aligned Carbon Nanofibers (VACNFs) were individually grown as the field emission cathode elements. Three electrodes are fabricated: the cathode, the extraction electrode and the focus electrode, separated from each other by 1µm SiO@sub 2@. We have demonstrated Fowler-Nordheim emission characteristics and electron beam focusing. The variation of beam diameter with focus aperture potential observed both optically and lithographically agrees well with electron beam simulations. Further modeling indicates that these devices will benefit from thicker (500 nm vs. 100 nm) electrodes in three ways: (1) improved focus effectiveness; (2) decreased optimal-beam size; and (3) increased depth of focus. The capability to realize thicker electrodes using a low-pressure chemical vapor deposition (LPCVD) tool is being implemented based on these results. Effects on beam shape and size due to electrode or field emitter offsets from coaxial geometry were also investigated with a 3D structure simulation. It was shown that a converged electron beam shape of 50nm or less in diameter is still obtained in the presence of small geometrical offsets. Preliminary 3x3 arrays of these devices have been fabricated and are being tested. While the extraction and focus electrodes are individually addressed the cathode is presently common to all devices. Individually addressed cathode designs, important for implementing DEAL with dose control circuits integrated into the device, are being investigated. Details of device modeling, fabrication, and characterization as well as device development to minimize offsets and realize individual cathode addressing will be presented. @FootnoteText@ @footnote 1@ ORNL is managed by UT-Battelle, LLC, for the U.S. Department of Energy under contract No. DE-AC05-00OR22725.

NS-TuP19 Microstructure Modeling of MOCVD Zirconium Oxide Deposition*, **M.O. Bloomfield**,* Rensselaer Polytechnic Institute*; Z. Song, B.R. Rogers,* Vanderbilt University*; T.S. Cale,* Rensselaer Polytechnic Institute

We use PLENTE, a software designed to study the formation and evolution of microstructure in thin films, to evaluate different models of growth for high vacuum MOCVD of zirconium oxide films on a selection of substrates. ZrO2 is a potentially important high-k dielectric material that can be deposited using zirconium tertbutoxide (ZTB). Cross sectional TEM and AFM of films in the early stages of growth show different wetting and island formation behavior as a function of deposition conditions, substrate selection, and history. Using PLENTE, TEM data and XRD data, we develop models of how islands grow during deposition and compare the evolving structures with experiment, primarily through trajectories of instantaneous void fraction measured experimentally via in situ spectroscopic ellipsometry. Models that include highly wetting islands and strong lateral growth show distinctly different voiding behavior from those with preferential growth non-parallel to the substrate, and in some cases, can be directly mapped to observed growth trajectories. Finally, we use the models developed to predict grain structural development for deposition onto rough and featured substrates, as demonstrations of possible use for integration of ZrO2 films into more complicated microelectronic structures.

NS-TuP20 Fabrication and Characterization of Carbon Nano-Cone Electron Emitters*, **K. He**, N. Badi, A. Bensaoula,* University of Houston

R&D on effective field emitter arrays (FEAs) is now concentrated on nano-structured solid materials because of the significant local increase of the electric field on solid tips with a small radius of curvature. This paper reports on the electron field emission behavior from uncoated and boron nitride coated graphite nano-cones. Since nano-cones emit most of their current into a single narrow beam, it is expected that graphite nano-cones electron emitters will lead to a significant improvement in the performance of high-resolution electron-beam instruments as well as for high power microwave amplifiers. Fresh cleaved highly oriented pyrolytic graphite (HOPG) was surface treated with poly-l-lysine for adhesion purpose. By dipping the sample into a colloidal gold solution with particles with a nominal diameter in the range of 30-50 nm, naturally and uniformly dispersed gold nanoparticles are attached to the HOPG surface. These nanoparticles serve as a mask for a subsequent reactive ion etching process to form the graphite nano-cones. Higher etching rates under oxygen plasma were observed at a plasma power above 180 Watts. Depending on the oxygen plasma etching parameters such as power and etching time, nano-cones with different shapes and sizes were fabricated. A sulfur doped boron nitride coating was deposited on the etched HOPG nano-cones using an ion assisted physical vapor deposition technique. Field emission characteristics from different coated and uncoated HOPG nano-cones will be presented along with their thermal and temporal stability measurements under different pressure environments. Acknowledgment: This material is based upon work supported by the National Science Foundation under Grant No. 0010100 and by NASA cooperative agreement to TcSAM. The authors would like to thank Dr. N. Medelci for his valuable help.

NS-TuP21 Epitaxial Growth of Nisi@sub 2@ on (001)Si Inside 50-200 Nm Openings Prepared by Scanning Probe Lithography*, S.-Y. Chen*, *S.D. Tzeng, S. Gwo,* National Tsing Hua University, Taiwan*; L.J. Chen,* National Tsing Hua University, Taiwan, Republic of China

Epitaxial growth of NiSi@sub2@ on (001)Si inside Si@sub3@N@sub4@ openings of 50-200 nm in size prepared by AFM tip-induced local oxidation has been investigated. From TEM and SEM observation, the size of the openings was found to influence significantly on the morphology of epitaxial NiSi@sub2@. As the dimension of the openings decreases, the shape transition of facetted NiSi@sub2@ from irregular polygons to inverse pyramids was found inside openings. NiSi@sub2@ facetted rods would appear as the size of the openings was further decreased. The results are attributed to the increased interface/volume ratio of silicides with decreasing size of openings and the non-uniform stress distribution within the miniature openings. As the thickness of Ni and annealing time are well-controlled, it is possible to obtain the identical NiSi2 pyramids of nano-scale even though the shape of openings is not identical.

NS-TuP22 Nanoscale Patterning by Pulsed Laser Irradiation and Nanoparticle Alignment*, Y.F. Guan*, *A.J. Pedraza,* The University of Tennessee, Knoxville

One- and two-dimensional nanostructure arrays have been generated in silicon by pulsed-laser irradiation, using a Lloyd's mirror configuration. The nanostructures consisted of periodic ripples and protrusions that could reach an amplitude of 20 nm and a height of 80 nm, respectively. The ripple nanostructure was used as a template for the alignment of gold nanoparticles. The gold was first sputter-deposited on the rippled surface at a grazing angle, and subsequently annealed at 700 °C. Atomic force and high resolution scanning electron microscopy studies revealed that the nanoprotrusions are preceded by the formation of extended ripples. The present experiments show that the Lloyd's mirror configuration strongly enhances the formation of ripples and that nanoprotrusions form at the intersection of two mutually orthogonal sets of ripples. On the other hand, when a Lloyd's mirror is not added only 1-D ripple formation was observed, with no protrusions. Interference of the incoming or refracted laser beam and the laser light scattered by the surface undulations has been long recognized as the cause of periodic ripple formation. It is concluded that the gradient of surface tension arising from a temperature gradient is responsible for the formation of the nanoripple structure, and the breakdown of the ripples into aligned nanoprotrusions is due to a second temperature modulation along the ripple lines. The intersection of two mutually perpendicular ripple structures and the very high reflectivity of the nanoprotrusion tips are the causes that promote this secondary laser light modulation.

NS-TuP23 Electronic and Ionic Processes in Local Oxidation of Titanium Nitride Thin Films*, N. Farkas*, *J.R. Comer, G. Zhang, E.A. Evans, R.D. Ramsier,* The University of Akron*; J.A. Dagata,* National Institute of Standards and Technology

We report an apparently unique property of titanium and titanium nitride thin films to undergo local oxidation or vaporization during scanning probe microscope (SPM)-based lithography. Nanometer-scale oxide dots or holes can be produced reliably depending on reversible SPM tip preparation. The presence of an electron-blocking tip oxide results in oxide growth on the substrate, while its absence leads to electronic breakdown. Both tip conditions can be obtained in a sequential and reversible manner. Electron emission is investigated using a variety of metallic and semiconducting SPM tips. Changing the nitrogen content of the deposition plasma over a wide range alters structural and electrical properties of the substrate materials and provides a basis for understanding the underlying processes, which we characterize by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), SPM roughness, and four-point probe measurements. This work contributes to a better understanding of the electronic and ionic components of the total current during SPM-assisted oxidation and demonstrates that this technique can be used to both modify and to characterize materials on the nanometer scale.

NS-TuP24 Synthesis and Characterization of Germanium Nanocrystals*, H. Gerung*, University of New Mexico*; S.D. Bunge, T.J. Boyle,* Sandia National Laboratories*; C.J. Brinker, J. Lee, M. Osinski, S.M. Han,* University of New Mexico

Semiconductor nanocrystals promise numerous potential applications, ranging from phosphors to biosensors. Herein, we focus on synthesis and characterization of Ge nanocrystals (NCs). Compared to group III-V or II-VI compound semiconductor NCs, the synthesis of Ge NCs in solution has been a challenge due to their covalent bond nature. Very few solution-phase syntheses have been reported, and the precursor preparation often involves a relatively high-pressure (>1 atm) process. We have developed a new method of synthesizing Ge NCs. The size of these crystals ranges from 3 to 10 nm. The control over shape and size dispersion of Ge NCs will be discussed in this presentation. We will present the effect of processing temperature and precursor concentration on the size. The synthesis relies on solution reduction of Ge@super 2+@ to Ge@super 0@ with commercially available precursors at relatively low temperature (300 °C) and at 1 atm of Ar ambient. This new synthetic route is scalable for mass production of Ge NCs. Photoluminescence spectra of Ge NCs show emission from 380 to 510 nm, and they demonstrate the quantum confinement effect of Ge NCs. However, ultraviolet-visible (UV-Vis) spectroscopy and attenuated-total-reflection Fourier transform infrared spectroscopy (ATR-FTIRS) show that Ge NCs are sensitive to air exposure, and they degrade over time in the absence of proper surface passivation. We therefore utilize different types of surfactants to encapsulate and stabilize the Ge NCs. The stabilized Ge NCs can be then incorporated into a silica matrix via sol-gel approach to form a self-assembled 3-dimensionally (3-D) ordered matrix.

NS-TuP25 Fabrication of SiGe Nanodot Array by Anodic Aluminum Oxide Templation*, W.J. Huang*, National Nano Devices Laboratories, Taiwan*; F.M. Pan, D.M. Chen,* National Chiao Tung University, Taiwan

Anodic aluminum oxide (AAO) has a highly ordered hexagonal pore array structure, and has been widely used as a template for nanostructured materials fabrication, such as carbon nanotubes and TiO@sub 2@ nanodots. Silicon germanium (SiGe) is an interesting semiconductor, which has a higher carrier mobility as compared with silicon, and has tunable bandgaps depending on the atomic composition of Ge. Moreover, SiGe is process-compatible with existing Si IC technologies. In conjunction with the AAO templation method and simple dry etching, we have prepared SiGe nanodot array with a dot size smaller than 50 nm. Si@sub 0.85@Ge@sub 0.15@ 50 nm in thickness was deposited on the Si wafer by ultrahigh vacuum chemical vapor deposition (UHV-CVD), followed by the sputter-deposition of TiN (20 nm). An Al film 4 µm in thickness was thermally evaporated on the TiN surface for the AAO preparation. The Al film was anodically oxidized in an oxalic acid electrolyte at room temperature, and the finished AAO pore array has a pore diameter about 60 nm. As the Al layer was completely oxidized, the underlying TiN layer was partially oxidized as well resulting in the formation of the TiO@sub 2@ nanostructure array with a pattern in compliance with the AAO pattern. The TiO@sub 2@ array was then used as the hardmask for dry-etching the remaining TiN and the SiGe bottom layer, and the SiGe nanodot array was thereby produced. Various analytical techniques, such as TEM, AFM and AES, have been employed to characterize the process steps of the SiGe nanodot array.

NS-TuP26 Site-selectivity of Chemical Reaction on a Biomimetic Super-hydrophobic/Super-hydrophilic Micropatterned Template*, N. Saito*, *Y. Wu, M. Kouno, Y. Inoue, O. Takai,* Nagoya University, Japan

Recently, the materials fabrication based on biomimetics attract the attention of many researchers due to their green process, high function and novel self-organized structure. In nature, there are super water-repellent plant leaves such as lotus and taro. These surfaces are covered with hydrophobic micropapilla. The presence of hydrophilic group on such a structure leads to ultra water-repellency. Water droplets would be formed on only super-hydrophilic regions when water was spilled over an artificial super-hydrophobic/super-hydrophilic micropattern on substrates. In this study, we focused on the fabrication and application of biomimetic super-hydrophobic/super-hydrophilic micro-pattern using the microwave plasma-enhanced chemical vapor deposition (MPECVD) and vacuum ultra violet (VUV) lithography. Silicon wafer was used as substrates. Raw materials in the MPECVD were trimethylmethoxysilane (TMMOS) and Ar. The super-hydrophobic/super-hydrophilic pattern was fabricated by VUV irradiation thorough a TEM mesh. In order to confirm the pattern, surface water droplet was observed by environmental SEM. We successfully demonstrated site-selective electroless Cu plating on the pattern from the FE-SEM images.

NS-TuP27 Mechanical Property and Nano Texture of Alumina-Silica Ultra Water Repellent Films

M. Bekke*, Y. Wu, N. Saito, M. Koga, Y. Inoue, O. Takai,* Nagoya University, Japan

Ultra water repellent (UWR) films have attracted significant attention due to both fundamental scientific interests and practical applications. It has been known that UWR film requires the surface with two factor, that is, adequate surface roughness and low surface energy. Wenzel and Cassie found a rule between surface roughness and water repellency. The surface roughness can be obtained using various fabrication methods such as sol-gel, plasma enhanced chemical vapor deposition (PECVD) and spray coating. Mechanical property of the film with large roughness is generally inferior to that of the smooth surface film. This is a crucial problem for an industrial application of UWR film. Therefore, it is necessary to improve the mechanical property of UWR film. In this research, we aim to prepare a UWR film with favorable mechanical properties using microwave plasma enhanced chemical vapor deposition (MPECVD). UWR film was fabricated on Si (100) substrate using the microwave plasma-enhanced chemical vapor deposition (MPECVD). Raw materials were trimethylmethoxysilane (TMMOS), CO@sub 2@ and Aluminum(III) diisoproxide ethylacetoacetate(ADE). The flux of the bubbling gas(CO@sub 2@) was changed and the quantity of the ADE was adjusted. The water-repellency of film was evaluated by water contact angle measurements. The surface morphology of UWR film was acquired by atomic force microscopy (AFM) and field emission scanning electron microscopy (FE-SEM). The chemical bonding states were characterized by Fourier transform infrared spectroscopy (FT-IR) and X-ray photoelectron spectroscopy (XPS). The mechanical properties of the film were evaluated by nanoindentation test.

NS-TuP28 Behavior of Water Microdroplets on Nano-textured Surfaces Fabricated by a Focused Ion Beam Technique

M. Kouno, Nagoya University, Japan*; Y. Wu, N. Saito, M. Koga, Y. Inoue, O. Takai,* Nagoya University, Japan

Water repellency emerged on hydrophobic surfaces has attracted much attention due to fundamental and scientific interests. Surface nano-texture is a key factor for water repellency. Water repellency is generally evaluated by water contact angle. The water contact is usually evaluated in macrometer-scale. Environmental scanning electron microscopy (E-SEM) has the potential of the evaluation in micro-meter scale. In this study, we investigated the correlation between the surface structure and the water repellency based on the observation of water droplets in micro-scale using E-SEM. We prepared two types of samples with different nano-textured surface fabricated by a focused ion beam (FIB) technique. One was consisted of a fine array of concave structures with the center distances being 1 µm on Si(100) substrate. The other was composed of a similar array of convex structures. Their diameters were varied from 150 to 800 nm. All the sample surfaces were modified with the formation of a self-assembled monolayer from heptadecafuluoro-1,1,2,2-tetrahydro-decyl-1-trimethoxysilane [a type of fuloroalkylsilane, FAS, F@sub 3@C(CF@sub 2@)@sub 7@(CH@sub 2@)@sub 2@Si(OCH@sub 3@)@sub 3@] through chemical vapor deposition. These samples were observed by ESEM (Nikon, ESEM-2700). Water droplets were in situ formed on each sample surface by cooling the sample down to ca. 2.5 @super o@C, which is lower than the dew point under the condition of observation chamber. E-SEM images of the water droplets revealed that the water repellency of the sample depends on the shape and the array pattern on the surface in nanometer-scale.

NS-TuP29 Formation of Nanometer-scale Gap Electrodes Based on a Plasma Ashing Technique

Y. Lee, Sungkyunkwan University, Korea*;* ***Y. Roh,*** Sungkyunkwan University, Korea, Republic of Korea*; K.-S. Kim,* Sungkyunkwan University, Korea

Realization of nano- and/or bio-electronic devices requires the formation of metal electrodes with a nanometer-scale gap. Recently the fabrications of metal electrodes 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, special techniques such as electromigration-induced break junction, shadow deposition, or electrochemical deposition have to carry out in order to reduce further the nanometer-scale gap between two metal electrodes formed by microlithography as above-mentioned. One of the proposed techniques to overcome a resolution limit of an optical lithography was a photoresist (PR) ashing technique, in which the minimum linewidth can be formed by ashing the PR pattern defined by the optical lithography. In this work, we proposed a noble and reproducible method to fabricate nanometer-scale gaps between two metal electrodes using PR ashing and lift-off techniques. Using this technique, we obtained metallic electrodes with a nano-gap of less than 10 nm. With this technique, the gaps between two electrodes could be easily controlled and reproduced.

NS-TuP30 Fabrication of MOS Structure with NiSi@sub 2@ Nanocrystals Embedded in Silicon Dioxide

P.-H. Yeh*, C.H. Yu,* National Tsing Hua University, Taiwan*; L.J. Chen,* National Tsing Hua University, Taiwan, Republic of China*; H.H. Wu, T.-C. Chang,* National Sun Yat-Sen University, Taiwan*; P.T. Liu,* National Nano Device Laboratory, Taiwan

A metal-oxide-semiconductor (MOS) structure with NiSi@sub 2@ nanocrystals embedded in the SiO@sub 2@ layer has been fabricated. From the TEM micrograph and diffraction pattern, the nanocrystals were identified to be NiSi@sub 2@. The mean size and the aerial density of the NiSi@sub 2@ nanocrstals were estimated to be ~ 7.6 nm and 3.3 x 10@super 11@/cm@super 2@, respectively. A pronounced capacitance-voltage hysteresis is observed with a memory window of 1 V under the 2-V programming voltage. The process of the structure is compatible with the current manufacturing technology of semiconductor industry. The structure represents a viable candidate for low-power sub-100 nm nonvolatile memory devices.

NS-TuP31 The Formation of Au-nanowires Using DNA Molecule as a Template

H.-J. Kim*, Y. Lee, I.-S. Yi,* Sungkyunkwan University, Korea*; Y. Roh,* Sungkyunkwan University, Korea, Republic of Korea*; B. Hong, H.-G. Jee, S.-B. Lee, M.-J. Shin, S.-G. Kim,* Sungkyunkwan University, Korea

The formation of metal nanowires via the conjugation of biomaterials (e.g., DNA molecules) and metal nanoparticles has been extensively investigated to obtain highly ordered electronic components for nanocircuitry and/or nanodevices. Metal nanowires were organized by the hybridization of nucleic-acid-functionalized metal or metallic nanoparticles with DNA molecule as a template. For example, Au-nanowires (AuNWs) were formed using the DNA molecules conjugated by aniline- and lysine-capped Au nanoparticles (AuNPs). In this work, we developed a simple technique to form Au-nanowires by the conjugation of 4-aminothiolphenol-capped gold nanoparticles (ATP-AuNPs) and the immobilized DNA molecules on 3-Aminopropyltriethoxysilane (APS) coated Si wafers. In this technique, a metallization process involves three steps: (1) DNA molecules were immobilized on the Si/APS substrate, (2) ATP-capped AuNPs were formed via strong chemical reaction between thiol (-SH) group of ATP and AuNPs, and (3) AuNWs were then formed by the interaction between DNA and ATP-AuNPs. In addition, we investigated the effects of the relative molar quantity (i.e., AuNPs/ATP) on the network formation of Au-nanowires. Our preliminary works indicate that the relative molar quantity may decide the structure of Au-nanowires. These results, as well as further interpretation of the data, will be presented at the conference.

NS-TuP32 Photoluminescent Emission Properties of Porous Nanostructured Y@sub 2@o@sub 3@:eu Thin Films

P.C.P. Hrudey*, M. Taschuk, Y.Y. Tsui, R. Fedosejevs, M.J. Brett,* University of Alberta, Canada

Nanostructured photoluminescent thin films of europium-doped yttrium oxide (Y@sub 2@O@sub 3@:Eu), a well-known luminescent material, were grown using electron beam evaporation, in combination with the Glancing Angle Deposition (GLAD) technique. GLAD makes use of controlled substrate motion during extremely oblique physical vapour deposition (PVD) of a thin film resulting in a high degree of control over the nanostructure of the film. Films were deposited using pre-doped Y@sub 2@O@sub 3@:Eu source material. Scanning electron microscopy and x-ray diffraction were used to characterize film nanostructure, while the light emission properties of these films were characterized by photoluminescence measurements. In order to improve the photoluminescent response of the films a post-deposition annealing treatment was used. By annealing in air at 850°C, the film crystallinity improves leading to increases in the photoluminescent response by greater than three times that of the as-deposited samples. The emission properties of vertical posts, helices, and normally-incidence solid thin films were obtained and compared. In studying the effect of film structure on the emission properties vertical posts films were found to emit two times more light in the direction normal to the substrate surface than solid films that contained an equivalent mass of material. Additionally, optical filter devices incorporating Y@sub 2@O@sub3@:Eu were fabricated and studied for their effects on the emission properties.

Nanometer-scale Science and Technology
Room 213D - Session NS-WeM

Nanoscale Patterning and Lithography

Moderator: D.W. Carr, Sandia National Laboratories

8:20am **NS-WeM1 Massive Self-Assembly for Integrated Carbon Nanotube Circuits***, **S. Hong**,* Seoul National University, Korea, South Korea **INVITED**

Nanoscale electronic devices made of carbon nanotubes (e.g. transistors, sensors) can be much smaller and more versatile than any conventional microelectronic chips, while the lack of a mass-production method has been holding back their practical applications. Inspired by biomolecular self-assembly, we developed a novel self-assembly method for the wafer-scale fabrication of millions of carbon nanotube circuits with a single-nanotube-level precision. This method may enable industrial-level production of nanotube-based devices such as faster electronic circuits and high-density sensor arrays.

9:00am **NS-WeM3 Surface-Programmed Assembly of Carbon Nanotubes on Silicon Oxide Surfaces for Integrated Circuit Applications***, **M. Lee**, J. Im, S. Hong,* Seoul National University, South Korea

As the microelectronics approaches its resolution limit, alternative electronic devices draw the attention of the scientific community. One strong candidate can be carbon nanotube (CNT)-based electronics. We developed a method to selectively assemble carbon nanotubes at a desired location with precise orientations on silicon oxide substrates. In this process, surface molecular patterns guide the assembly of CNTs onto desired locations. Importantly, we utilized only conventional microfabrication process such as photolithography for the entire process, which makes our method completely compatible with microfabrication techniques. This research can be utilized for fabrication of carbon nanotube-based electric circuits.

9:20am **NS-WeM4 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, Knoxville*; R.J. Kasica, D.K. Hensley,* Oak Ridge National Laboratory*; A.V. Melechko,* Univeristy of Tennessee, Knoxville*; D.C. Joy, P.D. Rack, B. Blalock, S. Islam,* University of Tennessee, Knoxville*; M.A. Guillorn,* Cornell Nanofabrication Facility*; M.L. Simpson,* Oak Ridge National Laboratory

The Digital E-beam Array Lithography (DEAL) concept is currently under development at Oak Ridge National Laboratory (ORNL).@footnote 1@ 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@. The first electrode functions as the cathode and contains a single vertically aligned carbon nanofiber as the field emitter. The second is a 2-µm diameter extraction aperture formed using a self-aligning process. The third is a 4-µm diameter aperture functioning as an electrostatic focusing lens and created using standard photolithographic processing. 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 good agreement with device modeling. Our current 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. @FootnoteText@ @footnote 1@ ORNL is managed by UT-Battelle, LLC, for the U.S. Department of Energy under contract No. DE-AC05-00OR22725.

9:40am **NS-WeM5 Monomer Based Thermally Curable Imprinting Lithography***, **H. Lee**,* Korea University, Korea

Nanoimprint lithography is one of the most viable technologies for mass production of devices with nano-patterns such as optical components (polarizer and diffuser), bio and NEMS devices, photonic crystals and patterned magnetic media. With this technology, nano patterns are generated by duplicating the ruggedness of imprinting stamp onto polymer films on the substrate. However, high pressure (>800psi) and high temperature (>150C)operation is required to transfer nano patterns onto polymer film. In this study, a mixture of base monomer, vaporization inhibitor, anti-sticking agent and thermal initiator was used as an imprint resin. Viscosity of mixture was controlled by relative amount of vaporization inhibitor. Compared to the polymer based resin such as PMMA, monomer based resin has several advantages. Since the monomer based imprinting resin is in liquid phase without heating up to the decomposition temperature of thermal initiator, high quality pattern transfer with minimized residual layer can be done at much lower imprinting pressure. The decomposition temperature of thermal initiator is relatively lower than the glass temperature of polymer. Thus, imprinting can be done at lower temperature (below 100C). Thus, time consumption for heating and cooling can be reduced and higher throughput was obtained. In this study, whole 6 inch diameter wafers were patterned by single step imprinting with the same sized stamp.

10:00am **NS-WeM6 Charge Interactions in Ferroelectric Substrates: the Basis of Ferroelectric Nanolithography***, **D.B. Li**, R. Shao, D.A. Bonnell,* The University of Pennsylvania

A new approach to directed assembly has recently been proposed that allows multiple nanostructures of diverse materials to be positioned in predefined locations. Ferroelectric Nanolithography has been demonstrated in the assembly of metal nanoparticle/functional organic molecule/oxide systems for a wide range of materials. The process is based on patterning ferroelectric domain orientation to control surface local electronic structure, which can be accomplished with exposure to electron beams and optical interference patterns. The underlying physics of these processes is not understood. This paper examines the effects of electron injection and electron-hole pair generation on surface ferroelectric polarization and charge compensation. The effects of dose, substrate thickness, and substrate morphology on pattern spatial resolution and stability are quantified for lead zirconate titanate and barium titanate films. For the case of electron-hole pair generation the mobile carriers compensate local atomic polarization at the surface. On high dose electron injection an electric field is established which reorients the polarization vectors. Both processes alter the local electronic structure by influencing surface band bending.

10:20am **NS-WeM7 Nanoscale Patterning in Application to Novel Materials and Device Structures***, **N. Zhitenev**,* Bell Labs, Lucent Technologies **INVITED**

As the size of electronic devices shrinks down to atomic scale, device properties are increasingly dependent on physics and chemistry of interfaces or interfacial networks. The growth, the patterning and the characterization of such systems at nanometer scale present significant challenges and opportunities. Extremely small devices can display useful functionality based on new physical phenomena. On the other hand, direct lithography requiring deposition of resists, exposure to radiation and to wet/dry chemistry can strongly modify the device properties. Possible solutions are to perform the most invasive patterning before the growth or out of a potentially delicate device structure. We study such fabrication schemes in application to the patterning of self-assembled molecular monolayers between metal electrodes. The first approach uses pre-fabricated masks to confine the deposition of materials. The size of the features is controlled by shadow angle evaporation. Another method uses nanoimprinting to deliver patterned metal onto molecular layer. Metal-molecular layer-metal junctions are fabricated with the size down to ~10-100 nm. While certain electrical properties are fairly reproducible, these techniques provide only initial foothold toward the fabrication of nanoscale interfacial devices. The critical issues that determine the overall performance and require further research are control of the surface topography and the grain structure of metals, doping of the molecular layers by the contacts and formation of the chemical bonds at the interfaces.

11:00am **NS-WeM9 Fabrication of Nanopatterned Polymer Brushes by Scanning-Probe and Electron-Beam Lithography***, **W.K. Lee**, M. Kaholek, S.J. Ahn, S. Zauscher,* Duke University

Here we present several lithographic approaches that we have adopted to fabricate nanopatterned polymer brushes. We demonstrate the use of nanoshaving, where an atomic force microscope (AFM) cantilever tip is employed as a nanomechanical tool to selectively remove a thiol resist. The freshly exposed gold surface in the resulting â?onano-trenchesâ?□ was immediately backfilled with a bromo-thiol initiator and enabled patterned surface initiated polymerization. In a complementary approach we prepared oxide nanopatterns on resist-coated silicon surfaces by applying an electric potential between the AFM cantilever tip and the silicon substrate. In this case the nanopatterns were backfilled with a silane initiator SAM. We show that the choice of silane SAM enables both, ring-opening metathesis and atom transfer radical polymerization. We also used lift-off (dissolution) e-beam lithography (EBL) to generate gold nanopatterns that could again be used to immobilize a thiol initiator. We demonstrate that by choosing an appropriate nanolithography technique and combining it with a suitable polymerization technique allows us to fabricate high-density polymer brush arrays with control over chemical functionality, feature dimension, shape, and interfeature spacing on the nanometer length scale. Furthermore we demonstrate that the spatially controlled immobilization of stimuli-responsive macromolecules on solid surfaces at the nanometer-length scale enables fabrication of â?osmartâ? â?"externally switchableâ?" polymer nanoarrays. Such nanostructures can provide sensing functionality within integrated nanoscale bioanalytical devices in which the transport, separation, and detection of biomolecules must be performed in aqueous solutions.

11:20am **NS-WeM10 Thermal Control in Dip Pen Nanolithography***, **P.E. Sheehan,*** Naval Research Laboratory*; W.P. King,* Georgia Tech*; L.J. Whitman,* Naval Research Laboratory

Although it has been widely assumed that Dip Pen Nanolithography (DPN) requires a water meniscus to tranfer ink from an AFM tip to a surface, we have shown that transfer can occur under xeric conditions@footnote 1@ , a method we call "dry deposition". Our recent studies of dry deposition have led to a number of insights into how DPN can be extended beyond "wet" inks. For example, deposition should be possible at high temperatures (i.e., above the boiling point of water) and, thus, temperature could be used to control deposition. We have utilized a heated atomic force microscope (AFM) cantilever tip to control the deposition of a solid organic ink. The ink, octadecylphosphonic acid (OPA), melts at 98°C and self-assembles on mica, the substrate. Evaporation was used to coat OPA onto a cantilever with integrated microheaters. When the cantilever temperature was below 98°C, no deposition was detected. At 98°C slow deposition was seen, but only after raising the temperature to 122° C was deposition robust. Thermal DPN (tDN) enhances traditional DPN in many ways. First, it allows exquisite control over writing--deposition may be turned on or off and the deposition rate changed without breaking contact with the surface. Secondly, the inks used have lower surface mobilities once cooled and so are able to achieve higher spatial resolution. Thirdly, imaging with a cool tip does not appear to contaminate the surface. This allows in situ confirmation of the deposited pattern without fear of contamination. Finally, tDPN expands the range of useable inks--current work with electronically active molecules that have high melting temperatures will be presented. @FootnoteText@ @footnote 1@ PRL 88, 156104 (2002).

11:40am **NS-WeM11 Chemomechanically Scribing Silicon with an AFM in a Read/Write Fashion***, M.V. Lee, K. Gertsch, **R.C. Davis**, M.R. Linford,* Brigham Young University

One of the most important problems in nanotechnology is the precise positioning of molecules on surfaces. One possible method for accomplishing such nanoscale patterning is the chemomechanical modification of silicon with an AFM tip. Using this method ca. 30 nm functionalized lines have been produced by i) wetting hydrogen-terminated silicon with a reactive compound, and ii) scribing with an AFM tip. Scribing activates the silicon so that it reacts with the liquid it is in contact with wherever the AFM tip is pushed against the surface. The width of the functionalized feature can be controlled by changing the force applied to the tip. In this talk we also report advances in chemomechanically depositing a monolayer on silicon using an AFM, and then chemomechanically replacing the monolayer in the scribed region by scribing over the functionalized region. Time-of-flight secondary ion mass spectrometry is used to confirm surface modifications and alterations. This new read-write capability should significantly increase the usefulness and power of the chemomechanical method at nanometer dimensions. @FootnoteText@ Wacaser, B.A.; Maughan, M.J.; Mowat, I.A.; Niederhauser, T.L.; Linford, M.R.; Davis, R.C. Chemomechanical surface patterning and functionalization of silicon surfaces using an atomic force microscope. Applied Physics Letters 2003, 82(5), 808-810.

Nanometer-scale Science and Technology
Room 213D - Session NS-WeA

Nanotribology and Nanomechanics

Moderator: R.W. Carpick, University of Wisconsin-Madison

2:40pm **NS-WeA3 Qcm-Stm Study of the Nanotribology of Metal-Organic Interfaces***, **S.M. Lee**, M. Abdelmaksoud, J. Krim,* North Carolina State University

Energy transfer plays an important role in many surface processes such as surface diffusion, vibrational relaxation and sliding friction in adsorbed molecules.[1] The Quartz Crystal Microbalance has in recent years been employed to reveal much fundamental information on energy dissipation mechanisms associated with the sliding of atomically thin films along surfaces. While in quantitative agreement with theory and computer simulation, the QCM data have not been cross-referenced to scanning probe measurements of sliding friction and diffusive behavior of atoms along surfaces. We have thus combined a Scannning Tunneling Microscope and QCM to allow direct imaging of films adsorbed on the QCM electrode under both stationary and oscillating conditions.[2] In this study, the nano-scale frictional behavior of copper and nickel surfaces covered by various organic adsorbates (ethylene, iodobenzene, and etc.) was studied by means of STM-QCM. During the STM tip indentation, the changes in resonance frequency and amplitude of the quartz crystal were monitored simultaneously , to explore energy storage or loss mechanisms, as well as tribochemical effects, associated with tip-substrate interactions. The dependence of the frequency and the amplitude changes of each interface will be reported and interpreted in terms of the adsorbate-substrate chemical and physical interactions. Work supported by DOE, AFOSR and NSF. Reference: [1] J. Krim, Surf. Sci. 500, 741 (2002) [2] B. Borovsky, B. L. Mason, and J. Krim, J. Appl. Phys. 88, 4017 (2000).

3:00pm **NS-WeA4 Measurement of the Mechanical Adhesion between a Single-Walled Carbon Nanotube and a Silicon Dioxide Substrate***, **J. Whittaker**,* Brigham Young University*; E. Minot,* Cornell University*; D. Tanenbaum,* Pomona College*; P. McEuen,* Cornell University*; R.C. Davis,* Brigham Young University

Nanotubes were grown over a lithographically defined set of trenches, 60 nm deep and 300 nm wide on a pitch of 500 nm. After finding a nanotube that crossed three or more trenches, we used an atomic force microscope (AFM) to measure the amount of force required to make a single-walled carbon nanotube slip along the silicon dioxide trench tops. This measurement was made by pushing down on the tube with the AFM probe until slip was observed in the force-distance curve. The amount of slack in the slipped tube was also measured by looking at neighboring trenches, giving a force per unit length result.

3:20pm **NS-WeA5 Structural, Electronic and Frictional Properties of Gold Nanoclusters in Decane under Constrained Geometries***, **S.H. Kim**, F. Ogletree,* Lawrence Berkeley National Laboratory, University of California, Berkeley*; S. Hwang, Y.-S. Shon,* Western Kentucky University*; M. Salmeron,* Lawrence Berkeley National Laboratory, University of California, Berkeley

We investigated the behavior of gold nanoclusters suspended in decane (C@sub 10@H@sub 22@) when confined in narrow gaps of a few nanometers. The gaps are made by two parallel and atomically smooth mica surfaces in the Surface Force Apparatus (SFA). The diameter of the nanoclusters ranges from 1.8 to 3.2 nm. They are capped with alkanethiolate ligands of different lengths (C@sub 6@S or C@sub 15@S) to prevent metallic contact. Layering transitions of at least 3 layers are observed, indicating that the nanoclusters form ordered layers in the confined geometry. The mechanical and tribological properties (compressibility, shear resistance), and the dielectric properties of these clusters show remarkable variations with size, ligand length and confining pressure.

3:40pm **NS-WeA6 Nanoporous Au: Surface Characterization and Mechanical Properties***, **J. Biener**, A.M. Hodge, K.J.J. Wu, L.L. Hsiung,* Lawrence Livermore National Laboratory

Nanoporous Au prepared by electrochemically-driven dealloying of Ag-Au alloys has attracted considerable interest due to potential sensor and actuator applications. These materials exhibit an open sponge-like structure of interconnecting ligaments with an unimodal pore size distribution on the nanometer length scale. Due to a high surface-area to volume ratio, the properties of nanoporous materials should be influenced strongly by their surface properties. However, little is known about the surface chemistry of these materials. Here we will present our recent results regarding surface characterization and nanomechanical properties of nanoporous Au with a nominal relative density of ~30%. Time-of flight secondary ion mass spectroscopy (TOF-SIMS) was employed to obtain high-resolution, mass-resolved images of as-prepared Au foam surfaces. Our studies reveal the presence of adsorbed species such as chloride and nitrate from the dealloying process. It is well known from single crystal experiments that these species strongly interact with the Au surface, e.g. chlorine lifts the herringbone reconstruction on Au(111). This example demonstrates the necessity of surface science studies to better understand the properties of these nanoscale materials. The mechanical properties such as modulus and hardness of nanoporous gold were studied by nanoindentation combined with scanning electron microscope (SEM) characterization. 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.

4:00pm **NS-WeA7 Nanotribological Properties of Ultrananocrystalline Diamond***, **D.S. Grierson**, A.V. Sumant,* University of Wisconsin-Madison*; J.E. Gerbi,* Argonne National Laboratory*; J.P. Birrell,* Argonne National Laboratory, U.S.*; J.A. Carlisle, O.H. Auciello,* Argonne National Laboratory*; R.W. Carpick,* University of Wisconsin-Madison

The development of micro- and nano-scale devices with moving parts continues to progress rapidly, but the issue of tribological failure remains critical. The high surface-to-volume ratio at small scales requires that nano-scale adhesion and friction be characterized and reduced. Silicon, the main material currently used in micro- and nanodevices, suffers from poor tribological properties. Ultrananocrystalline diamond (UNCD) is a thin film material that may be far superior tribologically. We present the first measurements of nano-scale adhesion and friction of the tribologically relevant underside of UNCD. This surface is far less adhesive than a silicon reference sample. Furthermore, UNCD can be processed to render it chemically identical to single crystal diamond, minimizing the work of adhesion to the van der Waals limit and strongly reducing friction as well. Our methodology is not only applicable to diamond-based devices but could very well be extended to any thin film material.

4:20pm **NS-WeA8 Gas Phase Lubrication of MEMS***, **S.A. Smallwood**,* Universal Technology Corporation*; K.C. Eapen,* University of Dayton Research Institute*; J.S. Zabinski,* Air Force Research Laboratory (AFRL/MLBT)

A number of different MEMS systems have been designed, fabricated and a few have been marketed. Most commercial MEMS designs are void of parts that simultaneously move and undergo contact due to the problems of stiction, friction and wear. Candidate solutions to tribological problems include monolayers and self-lubricating hard materials. The problem with thin film lubricants is that the coating is fairly quickly worn away. Even though hard coatings such as diamond like carbon (DLC) are expected to have a longer life, improvements in durability are still required. A combination of bound and mobile phase lubricants has been used to extend life through flow of the mobile phase. This provides a protective bound coating and a fluid mobile constituent that offers replenishment. Another replenishment scheme is gas phase lubrication, which offers a way to continuously provide a protective coating by constantly replenishing the contact region. Gas phase lubrication results for MEMS are discussed in this talk. Accelerated screening tests have been performed in vacuum with a pin on disk tribometer tester using a range of Hertzian mean normal stress from 180 to 390 MPa. The tribometer includes a 0.25 inch dia. silicon nitride ball against a polysilicon sample. Protective gases were leaked into the vacuum system during friction tests. These gases include low boiling organic compounds with different functional groups. Surface tribochemistry in the wear track and wear debris were examined using x-ray photoelectron spectroscopy (XPS), microRaman spectroscopy, IR spectroscopy and scanning electron microscopy (SEM). In addition, performance tests were run on operational electrostatic MEMS motors. Surface chemical analyses on screening tests and operational devices are used to provide information on friction and wear mechanisms.

4:40pm **NS-WeA9 Novel Tribological Properties of Quasicrystals in Ultra-High Vacuum***, **J.Y. Park**, D.F. Ogletree, M. Salmeron,* Lawrence Berkeley National Laboratory*; C.J. Jenks, P.A. Thiel,* Ames Laboratory, Iowa State University

The structural and tribological properties of the interface between decagonal Al-Ni-Co quasicrystals and conductive TiN-coated cantilevers have been investigated. This was accomplished using a combined atomic force and scanning tunneling microscopy apparatus in ultrahigh vacuum. Atomically resolved STM images of the 2-fold Al-Ni-Co surface were obtained showing a clear periodicity along 10-fold direction, and a quasi-periodicity (following Fibonacci sequences) along the 2-fold direction. To decrease the high adhesion between the atomically clean quasicrystal surface and the metallic AFM tip (with has high adhesion force as large as 1000 nN), the tip or the surface were passivated by hydrocarbon molecules (ethylene and alkylthiol), which made possible the formation of stable contacts. This allowed us to observe an elastic to plastic transition occurring at a threshold load. With alkylthiol passivated tips the friction properties of the highly anisotropic 2-fold surface could be studied. We found a strong dependence of the friction force on the scanning direction, with low friction occurring along the aperiodic direction and high friction in the periodic direction. This result will be discussed in light of friction models of the interface based on existence or not of commensurability between the two contacting surfaces.

5:00pm **NS-WeA10 Quartz Crystal Microbalance Studies of the Friction of Rotating vs. Rigid C60***, **T. Coffey**,* Appalachian State University*; J. Krim,* North Carolina State University

Since C@sub 60@ was first discovered, it has intrigued tribologists. Due to its weak van der Waals interaction with most materials, its round shape, and its rapid rotation within its lattice position, many had hopes that C@sub 60@ would make an excellent lubricant, and drew analogies to nano-scale ball bearings. Although most experiments have shown that C@sub 60@ is a comparatively poor lubricant, the question of how the rotation of C@sub 60@ affects friction is still an interesting one. We have designed a Quartz Crystal Microbalance (QCM) experiment in ultra-high vacuum to determine how the rotation of C@sub 60@affects slip time (friction). In this experiment, we compare the slippage of methanol at room temperature on one monolayer of stationary C@sub 60@ or slowly rotating (~1 Hz) C@sub 60@ and two layers of quickly rotating (~10@super 9@ Hz) C@sub 60@. We found that the stationary monolayer of C@sub 60@ had longer slip times, or lower friction, than the quickly rotating C@sub 60@, defying the ball-bearing analogy.

Nanometer-scale Science and Technology
Room 213C - Session NS1-ThM

Nanoscale Fabrication

Moderator: C.R.K. Marrian, IBM Almaden Research Center

8:20am **NS1-ThM1 Three-Dimensional Nanotechnology by Focused-Ion-Beam Chemical-Vapor-Deposition**, ***S. Matsui,*** Himeji Institute of Technology, CREST-JST, Japan **INVITED**

The deposition rate of focused-ion-beam chemical-vapor-deposition (FIB-CVD) is much higher than that of electron-beam chemical-vapor-deposition (EB-CVD) due to factors such as the difference of mass between electron and ion. Furthermore, FIB-CVD has an advantage over EB-CVD in that it is more easily to make a complicated 3-dimensional nanostructures. Because, a smaller penetration-depth of ion compared to electron allows to make a complicated 3-dimensional nanostructures. For example, when we make a coil nanostructure with 100 nm linewidth, electrons with 10-50 keV pass the ring of coil and reach on the substrate because of large electron-range (over a few µm), so it is very difficult to make a coil nanostructure by EB-CVD. On the other hand, as ion range is less than a few ten-nm, ions stop inside the ring. Three-dimensional nanostructure fabrication using FIB-CVD has following advantages. (1) As a beam diameter of FIB is 5nm, 3 D nanostructures with a few ten nm can be fabricated by FIB. (2) 3D nanostructures made of metal, semiconductor, and insulator etc. can be fabricated by using various source gases. Three-dimensional nanotechnology using FIB can be widely applied to electronics, mechanics, optics, and biology. We have demonstrated the fabrication of free-space-nanowiring, electrostatic nano-actuator, bio-injector and electrostatic nano-manipulator by using FIB-CVD.

9:00am **NS1-ThM3 Integration of Ion Beams with Scanning Probes for Local Doping and Chemical Analysis of Materials**, ***T. Schenkel****, A. Persaud,* E. O. Lawrence Berkeley National Laboratory*; I.W. Rangelow,* University Kassel, Germany*; S.J. Park, F.I. Allen,* E. O. Lawrence Berkeley National Laboratory*; K. Ivanova,* University Kassel, Germany

We describe our newly developed scanning probe instrument which integrates ion beams with imaging and alignment functions of a piezo resistive scanning probe in high vacuum. In the past, Scanning Probe functions have been combined successfully with lasers, excited reactants, as well as neutral beams for surface analysis or materials modification at a nanometer length scale. In our approach, we transport beams of energetic ions (1 to 200 keV) through small (5-30 nm diameters), high aspect ratio holes (>5:1) in the scanning probe tips. Holes are formed by Focused Ion Beam drilling and thin film deposition. Transport of single ions can be monitored through detection of secondary electrons that are emitted when ions impinge on sample surfaces. Secondary electron yield enhancements for highly charged dopant ions (e. g., P15+, or Te36+) allow efficient detection of single ion impacts for single atom device formation. Detection of secondary electrons and ions enables adaptation of a time-of-flight secondary ion mass spectrometry scheme for correlation of scanning probe images with chemical and molecular composition information on a 10 nm length scale. In our presentation we will discuss potential and limits of this approach in ion placement resolution, sensitivity in surface analysis, as well as issues of probe lifetime and effects of ion guiding in dielectric nanoholes. Acknowledgments: We thank the staff of the UC Berkeley Microlab, and the National Center for Electron Microscopy for their technical support. This work was supported by NSA and ARDA under ARO contract number MOD707501, and by the U. S. DOE under contract No. DE-AC03-76SF00098.

9:20am **NS1-ThM4 Fabrication and Electrical Characterization of 2D Dopant Nanoelectronic Devices in Si**, ***J.S. Kline****, S.J. Robinson, J.R. Tucker,* University of Illinois at Urbana-Champaign*; J.-Y. Ji, T.-C. Shen,* Utah State University*; C. Yang, R.-R. Du,* University of Utah

The integration of nanoscale devices with Si-based microelectronics presents a major challenge in nanotechnology. We address this issue by employing STM patterned P donors as the building block for all-epitaxial nanoscale devices on pre-fabricated templates. To preserve the As-implanted contacts, we have developed a low-temperature UHV process using 300eV Ar ion sputtering and sub-700°C annealing to prepare atomically flat and clean surfaces for STM lithography. Differences in surface features and tunneling spectroscopy allow the registration of the STM to the template. After STM nanolithography, P donors are selectively deposited onto the patterned area by phosphine exposure. Subsequent Si low-temperature deposition and 500°C annealing forms an epitaxial overlayer and activates the dopant atoms. Electron transport measurements at 4.2K for several 2-terminal devices including two-dimensional P wires 10-50nm wide and 30-700nm long indicate resistivity of the wires is in the order of 20k@ohm@/sq. Quantum coherence length and the implication of the oscillations in the magnetoresistance at 0.3K will be discussed. In addition, the fabrication and measurement of tunnel junctions is currently in progress and will also be reported. This work is supported by DARPA-QuIST program under ARO contract DAAD 19-01-1-0324.

9:40am **NS1-ThM5 Scanning Tunneling Microscopy Electronic Characterization of a Nano Device for Quantum Computing**, ***M.E. Hawley****, G.W. Brown, H. Grube,* Los Alamos National Laboratory

Quantum computation is a revolutionary new paradigm that has seen tremendous growth since 1994. The quest to build a quantum computer (QC) has been inspired by its recognized formidable computational potential. The long-term goal in this quest is a large scale, fast, parallel and easily fabricated QC. Although a number of ingenious schemes have been proposed, silicon-based solid-state proposals, using nuclear or electron spins of dopants such a phosphorus as qubits, are attractive because of the long spin relaxation times and their scaleability and integratability with existing silicon technology. We have been working on such a device based on a proposal by B. Kane (Nature 393, 133 (1998), in which buried P atoms placed 20 nm apart act as quantum bits entangled through exchange interactions, atomically placed using Scanning tunneling microscope (STM) lithographic techniques on a hydrogen resist layer. This effort requires dosing the Si(100) surface with phosphine molecules and annealing the phosphorus into the silicon surface. STM-based atomic level lithography methods provides us with the added capability of characterizing the local electronic environment of the dopants. In this talk, Iâ?Tll describe our particular effort to fabricate a QC and the charge imaging technique we are using to image buried phosphorus dopants and charged defects that could potentially interfere with the operation of such a QC device as well as any other nano scale device on the silicon surface.}

10:00am **NS1-ThM6 Nanotip Arrays Fabricated by One-step and Self-masked ECR-Plasma Etching and Their Applications for Field Emission, Antireflection and Sensing**, ***L.C. Chen****, J.S. Hsu,* National Taiwan University, Taiwan*; H.C. Lo,* Academia Sinica, Taiwan*; I.F. Huang,* National Taipei University of Technology, Taiwan*; K.H. Chen,* Academia Sinica, Taiwan*; C.R. Lin,* National Taipei University of Technology, Taiwan*; C.F. Chen,* National Chiao-Tung University, Taiwan

Well-aligned nanotip arrays with a nanotip density as high as 10^12 cm^-2 were achieved by a single-step electron cyclotron resonance plasma process using gas mixtures of silane, methane, argon and hydrogen. Formation of SiC cap was observed on each individual nanotip, implying a self-mask etching mechanism. This dry-etching technique was applied to a variety of substrates such as Si, GaN, GaP, Al, sapphire and glass, indicating its general applicability. The nanotip arrays so produced showed superior field emission as well as antireflection properties. The extremely sharp tip geometry provides large field enhancement, therefore a low turn-on field (<1V/micron), while the sub-wavelength nanostrutured surface exhibits an ultra low reflectivity (<0.1%) in visible and IR. The latter property can be explained by a simple gradient index model. Furthermore, the nanotip arrays dispersed with Ag nanoparticles also showed excellent surface enhancement in Raman scattering (SERS). By optimizing the size of Ag nanoparticle and inter-particle distance, SERS of 8-order has been achieved, suggesting potential application of nanoparticle-dispersed nanotip arrays in molecular sensors.

10:20am **NS1-ThM7 Nanoscale Integration of NanoCarbons Based on Ultrananocrystalline Diamond and Carbon Nanotubes**, ***X.C. Xiao****, O.H. Auciello, J.A. Carlisle,* Argonne National Laboratory

Nanostructured carbon materials exhibit excellent physical, chemical, mechanical, tribological, and electrical and thermal transport properties that are dictated by the many different bonding configurations available to carbon. Ultrananocrystalline diamond (UNCD) films, and carbon nanotubes (CNTs) are recently discovered nanocarbons with unique properties, and are of particular research interest and have many potential applications. Novel properties and applications could also be expected from the nanoscale integration of these two materials. We report in this study our approaches to strategically combine and control the carbon nanostructure consisting of UNCD and CNTs. Two approaches to the integration of UNCD and CNTs have been developed and the material properties evaluated. The first type is the self-assembly of carbon nanostructure based on UNCD and

CNTs which were synthesized simultaneously using a single Ar/CH@sub4@ plasma chemistry in a microwave plasma chemical vapor deposition system. The ease to tailor the nanostructure through adjustment of the nucleation conditions (the relative fraction of nanodiamond seeds for growing UNCD and transition metal catalyst for growing CNTs) as well as the growth temperatures offers a new possibility to form carbon based self assembly nanostructures with unique combined mechanical and electronic properties. In the second approach CNTs are grown directly on UNCD thin films, again through the use of transition metal catalyst dispersed on the UNCD surface and the use of Ar/CH@sub4@ plasmas. The robust integration of vertically aligned CNTs on UNCD combined two desirable electrochemical properties of CNTs and UNCD, i.e. the high specific surface area from CNTs and electrochemical stability from UNCD. Preliminary structure characterization and property studies illustrated the potential of this structure to be used as electrochemical electrodes for chemical sensing applications and in supercapacitors.

10:40am **NS1-ThM8 The Role of Hydrogen in Ultrananocrystalline Diamond Thin Film Growth***, **J.P. Birrell**,* Argonne National Laboratory, U.S.*;* *J.E. Gerbi, O.H. Auciello, J.A. Carlisle,* Argonne National Laboratory

A great deal of recent experimental studies and computer simulations have been performed to try to understand the surface stability of diamond nanocrystals. These results have yielded a number of striking conclusions that and the size of the crystallite. This study can help explain the transition of diamond thin film structure from microcrystalline to nanocrystalline with the reduction of hydrogen in the gas phase during microwave plasma enhanced chemical vapor deposition; namely, that the stability of the surface of the diamond nanoparticle is a strong function of both the hydrogen coverage uses TEM, Raman scattering, and XRD to investigate the role of hydrogen in the growth of ultrananocrystalline diamond (UNCD) thin films in two different regimes. First, we add hydrogen to the normal Ar/CH@sub 4@ gas mixture used during growth, and observe that rather than a monotonic increase in the grain size from nanocrystalline to microcrystalline, the films are clearly mixed-phase, with microcrystalline diamond inclusions that become much more prominent with added hydrogen. Second, we remove hydrogen from the plasma by changing the hydrocarbon precursor from CH@sub 4@ to C@sub 2@H@sub 2@. We observe that there is a lower limit to the amount of hydrogen that needed to sustain ultrananocrystalline diamond growth, below which a significant amount of disordered graphitic carbon is nucleated. We suggest that the reasons for these observed changes are that large amounts of hydrogen (in the form of H@super +@) in the plasma enables the more rapid growth of diamond microcrystals, while low concentrations of hydrogen result in unstable diamond nanocrystals and thus the nucleation of disordered carbon material. This work was supported by the DOE-Office of science-Materials Science under Contract No. W-31-109-ENG-38.

11:00am **NS1-ThM9 Surface-Templated Assembly of Nanoparticles on Solid Surfaces for Nano-Optical Applications***, **S. Myung**, N. Cho, J. Kim, D. Kim, S. Hong,* Seoul National University, South Korea

Nanoparticles made of CdSe or Au have been extensively utilized for optical labeling and other nano-optical applications. In this case, one technological challenge can be positioning nanoparticles onto desired locations on solid substrates with a nanometer scale precision. We utilized surface-templated assembly strategy to position Au and CdSe nanoparticles onto specific locations on Au and silicon oxide substrates. In our method, thiol-terminated self-assembled monolayer (e.g. MPTMS) patterns are utilized to capture nanoparticles from the solution, while methyl-terminated SAM (e.g. 1-octadecanethiol) patterns are utilized to avoid any unwanted assembly of nanoparticles. We also explored the possibility of assembling fluorescent nanoparticles onto 3D structures such as AFM tip for nano-optical applications.

Nanometer-scale Science and Technology
Room 213D - Session NS2-ThM

Nanowires I

Moderator: T.S. Mayer, Penn State University

8:20am **NS2-ThM1 MOCVD Synthesis of Group III Nitride Nanowires and Heterostructure Nanowires***, **G.T. Wang**, J.R. Creighton, P.P. Provencio, W. Pan,* Sandia National Laboratories

Nanowires based on the direct bandgap semiconductor Group III nitride (AlGaInN) materials system are attractive due to their potential in novel optoelectronic applications, including LEDs, lasers, high power transistors, and sensors. To date, the primary growth methods used to synthesize GaN nanowires have been thermal evaporation or chemical vapor deposition techniques using Ga metal or GaN powder source materials in hot-wall tube reactors. These evaporation-based techniques suffer from a general lack of control, reproducibility, scalability, and the ability to produce complex heterostructures. Metal-organic chemical vapor deposition (MOCVD) has achieved widespread commercial adoption for the growth of III-nitride films and devices, with the demonstrated ability to produce complex heterostructures and doping. We have employed a MOCVD process to synthesize GaN nanowires in a standard cold-wall rotating disk reactor on 2-inch diameter wafer substrates coated with Ni catalysts. TEM, EDS, and photoluminescence studies indicate that the nanowires are single-crystalline GaN with Ni clusters at the tips, indicating growth via the vapor-liquid-solid (VLS) mechanism. The nanowires have tip diameters typically from 20-100 nm and lengths of up to tens of microns. We have also been able to synthesize core-shell heterostructure nanowires consisting of a GaN cores and various III-nitride shell materials, including AlN, InN, and AlGaN, and InGaN. The growth processes and reactor environment employed in this study are typical of those used to synthesize device-quality III-nitride films and should be scalable to larger commercial reactors and substrates. The optical and electrical properties of single nanowires and heterostructure nanowires along with the challenges of the MOCVD nanowire growth process will also be discussed.

8:40am **NS2-ThM2 Ultralong and Portable Semiconductor Nanowire Arrays***, **Q. Li**, E.C. Walter, W. van der Veer, R.M. Penner,* University of California, Irvine

Long semiconductor nanowires, organized into parallel arrays, are desirable for a variety of nanoelectronic applications. Most of the current synthesis methods produce nanowires that are randomly distributed and effort must be expended to organize the nanowires onto solid surface for electronic applications. Here we propose a hybrid electrochemical/chemical method for the synthesis of millimeter-long semiconductor nanowires that are organized into arrays on solid surface. Our method involves two steps: First, electrochemical step edge decoration was adopted to obtain the precursor nanowires on highly oriented pyrolytic graphite (HOPG). Second, the as-deposited nanowires were chemically converted to semiconductor nanowires. MoS@sub 2@ nanowire arrays, a semiconductor material stable in moist air up to 80@super o@C, were synthesized by heating electrodeposited MoO@sub 2@ nanowires in H@sub 2@S at elevated temperatures. The nanowires were characterized by TEM, SEM and XRD. Two discrete structures were observed depending on the conversion temperature. For nanowires annealed at or below 700@super o@C, the MoS@sub 2@ nanowires were composed of randomly distributed 5-10 atomic layer thick MoS@sub 2@ ribbons. For nanowires annealed at 800@super o@C, MoS@sub 2@ atomic layers oriented parallel to the HOPG basal plane. Their diameters were easily controlled by their precursor MoO@sub 2@ nanowires. The electronic and optical properties were probed by transferring the nanowires onto suitable surfaces. Conductivity in both types of wires was thermally activated and the thermal activation energy was tuned from 125meV (700@super o@C annealing) to 25meV (800@super o@C annealing), lower than the reported MoS@sub 2@ thin films. The optical adsorption spectra showed two excitons, which blueshifted as a function of nanowire thickness due to the quantum confinement. Such organized and portable nanowire arrays are promising for nanoelectronics applications.

9:00am **NS2-ThM3 Fabrication of Gold Nanowires by Non-contact Atomic Force Microscopy***, **M.E. Pumarol**, Y. Miyahara, P. Grutter,* McGill University, Canada

Interfacing nanostructures to the macroscopic world is fundamental for their study and possible electronic applications. SPM-based metal deposition techniques are an attractive approach for this goal: due to their easy implementation and the possibility of a maskless direct modification of the surface. These techniques exploit the very intense electric field that appears when an SPM tip is in close proximity with a surface and a potential difference is applied. Here we use a commercial AFM operated in a dynamic mode and in ambient conditions for direct writing /patterning of gold nanowires. For their fabrication, voltage pulses of 20 â?" 30V are applied to a gold coated AFM tip and an insulating surface with a finite tip-surface gap of several nanometers. This produces gold dots with lateral dimensions from under 10 nm to 100 nm, and by increasing the deposition duty cycle dots are overlapped to form a nanowire. Control of the tip sample separation is critical to ensure the reliability and reproducibility of the deposition process. In this work, we use an innovative non-contact based technique to precisely control this separation and by extension the electric field. An advantage of this method of deposition is the ability of locating the part of the sample to which the nanowire will be contacted / attached. Here, we bridge gold macro-electrodes, deposited by EBL, by forming a nanowire between them. A new way for overcoming proximity effects of the AFM tip with a protruding electrode is presented. In the future, this technique will be useful for attaching contact leads to nanostructures like q-dots, nanodots, nanoparticles, and others.

9:20am **NS2-ThM4 Controlled Polymerization of Substituted Diacetylene Self-assembled Monolayers Confined in Molecule Corrals***, T.P. Beebe, Jr.,* University of Delaware*; A. Schnieders,* ION-TOF USA, Inc.*; **S.P. Sullivan,*** University of Delaware

The ever growing need to further miniaturize integrated circuits has lead to an increase in research on nanoelectronics. We have shown that it is possible to directly polymerize self-assembled 10, 12-tricosadiynoic acid (TCDA) adsorbed on highly oriented pyrolytic graphite (HOPG) at the solid/liquid interface using a Scanning Tunneling Microscope (STM) tip. Polymerized oligomers are formed at a predefined point where a voltage pulse is applied while operating in Scanning Tunneling Spectroscopy (STS) mode. The oligomers can be confined and controlled on the nanometer scale using molecule corrals created on the substrate via ToF-SIMS Cs@super +@ ion bombardment. In over ~ 150 observations polymerized oligomers never extended over domain boundaries or corral edges, providing natural connection points to possibly test the electrical properties of the nanowires. The quasi-infinite supply of diacetylene molecules remaining in the covering solution enables a dynamic exchange of molecules to the surface. This exchange occurred on approximately the same time scale (10@super -1@ s) as it does to collect one image, and depends weakly on the length of the desorbing oligomer. The desorption is thus likely influenced by tip-surface interactions as is often the case in STM experiments. A theoretical model is currently being developed to further our understanding of the effect of oliogmer length on the rate of oligomer desorption from the HOPG surface.

9:40am **NS2-ThM5 Semiconducting Nanowires - Synthesis, Characterization and Novel Properties***, **S.-T. Lee,*** City University of Hong Kong, China **INVITED**

Oxide-assisted growth (OAG) via thermal evaporation is introduced to produce large-quantity, high-purity (no metal contamination) silicon nanowires. OAG is a generic synthetic method that can produce a host of one-dimensional semiconducting nanowires, including those of Group VI (Ge, C, SiC), III-V (GaN, GaAs, GaP) and II-VI (ZnO, ZnS, ZnSe) elements. Silicon nanowires are produced with controlled diameter, desired orientation or pattern, and morphology (wire, chain, ribbon, cable). The structural, optical, electronic, and chemical properties of silicon nanowires have been characterized. Atomically-resolved STM images revealed detailed atomic structure of Si nanowires, while STS measurements demonstrated quantum size effect in the bandgap of Si nanowires. Regular arrays of intramolecular junctions in Si nanowires are shown to exhibit sharp conductivity changes across junctions. Si nanowires give strong polarized green-red emission, and exhibit interesting chemical and sensing properties. We further show properly assembled nanowires possess strong photoluminescence and lasing properties. The results offer exciting opportunities for research and applications in nanoscience and nanotechnology.

10:20am **NS2-ThM7 Strain Mapping in Nanowire Heterostructures***, **J.L. Taraci,*** Arizona State University*; M.J. Hÿtch,* Centre National de Recherche Scientifique, France*; T. Clement, J.W. Dailey, D.J. Smith, P. Peralta, J. Drucker, S.T. Picraux,* Arizona State University

A new method for the detailed strain analysis of nanowires and nanowire heterostructures will be discussed. This technique enables strain mapping of nanowires based on the combination of high resolution electron microscopy and image analysis. The accuracy to which strain may be determined using this method is better than 0.3%, which allows for the accurate strain mapping of core-shell and heterostructure nanowires. The technique is applied to nanowires grown by vapor-liquid-solid CVD using disilane and digermane. We will show how this technique can be used to obtain detailed distributions of @epsilon@@sub xx@, @epsilon@@sub yy@, @epsilon@@sub xy@, mean dilatation, and rotation maps within individual nanowire heterostructures. We first demonstrate the method by analysis of a single Ge nanowire which displayed a linear rotation along the growth axis, with the nanowire in compression and tension on either side of the central axis. The measured results are shown to be in agreement with a nanomechanics description of the nanowire for a bending moment applied at the end of the cantilevered nanowire beam. We then present preliminary results for Si-Ge core-shell and heterointerface nanowires. This technique allows for the direct strain mapping at heterostructure interfaces due to the lattice mismatch. In these studies the Si/Ge growth is carried out at 400°C and below to minimize any chemical interdiffusion effects on the strain profiles. The resulting strain maps of nanowire heterostructures can then be directly compared with Stillinger Weber modeling of the anticipated Si-Ge strain distributions, assuming chemically abrupt interfaces. The large aspect ratio nanowire structures allow rapid lateral relaxation with distance from the interface and thus provide an interesting contrast to conventional strained layer heterostructures.

10:40am **NS2-ThM8 Direct Atomically Resolved Imaging inside a Nanowire***, **A. Mikkelsen**, N. Skold, L. Ouattara, M. Borgstrom, J.N. Andersen, L. Samuelson, W. Seifert, E. Lundgren,* Lund University, Sweden

Semiconductor nanowires are perceived as future components in nanoelectronics and photonics. Applications, such, bio/chemical sensors , n- p- type diode logic and single nanowire lasers have already been realized in the laboratory. Because of the extremely small dimensions of a nanowire, atomic scale structural features can have a significant impact on their properties. The large surface to bulk ratio of tailor-made nano-crystallites and low dimensional systems as compared to usual bulk crystals can result in new crystal structure and morphology not found in bulk equivalents. Therefore, structural methods that address these issues are highly desirable. One such method is Scanning Tunneling Microscopy (STM) that has revolutionized our perception nano-scale objects and low-dimensional systems. In this study we demonstrate a new powerful method to image individual atoms inside freestanding III-V semiconductor nanowires using a combination of Cross-Sectional Scanning Tunneling Microscopy and a novel embedding scheme. We image areas of the nanowire with atomic resolution both along the wire, and through the face of the wire. Utilizing this method we for example image the individual atoms in planar twin segments of the wire and show that individual atomic impurities in a GaAs nanowire can be imaged. Finally we image the GaAs nanowire at the substrate interface revealing intriguing details about the initial growth of the nanowire.

11:00am **NS2-ThM9 Time-Resolved X-Ray Excited Optical Luminescence Studies of Semiconductor Nanowires@footnote 1@***, **R.A. Rosenberg**, G.K. Shenoy,* Argonne National Laboratory*; S.T. Lee,* University of Hong Kong, China*; F. Heigl,* Canadian Synchrotron Radiation Facility*; P.-S.G. Kim, X.-T. Zhou, T.K. Sham,* University of Western Ontario, Canada

Due to quantum confinement effects nanostructures often exhibit unique and intriguing fluorescence behavior. X-ray excited optical luminescence (XEOL) provides the capability to chemically map the sites responsible for producing low energy (1-6 eV) fluorescence. By taking advantage of the time structure of the x-ray pulses at the Advanced Photon Source (APS, ~80 ps wide, 153 ns separation) it also possible to determine the dynamic behavior of the states involved in the luminescence. In this presentation we show how this technique can be utilized to understand the XEOL from silicon nanowires (~14 nm diameter) and show preliminary results from studies of II-VI nanoribbons. Previous XEOL studies of silicon nanowires have revealed luminescence in the 400-700 nm region.@footnote 2@@super ,@@footnote 3@ The lower wavelength part of the spectrum is associated with the oxide shell while longer wavelength emission is due to the silicon core. The present results support these findings. In addition we find that the longer wavelength, silicon core emission has a relatively short lifetime (<10 ns) while the oxide shell fluorescence has a much longer lifetime. These results will be discussed in terms of prior time-resolved work on porous silicon and related systems. In addition we plan to present initial results from studies of ZnS, ZnTe, CdSe and CdS nanoribbons. @FootnoteText@ @footnote 1@Work supported by U.S. Department of Energy, Office of Basic Energy Sciences under Contract No. W-31-109-ENG-38.@footnote 2@X.-H. Sun, Y.-H. Tang, R. Zhang, S.J. Naftel, R. Sammynaiken, T.K. Sham, H. Y. Peng, Y.-F. Zhang, N.B. Wong, and S.T. Lee, J. Appl. Phys. 90, 6379 (2001).@footnote 3@T.K. Sham, S.J. Naftel, P.-S. G. Kim, R. Sammynaiken, Y.H. Tang, I. Coulthard, A. Moewes, J.W. Freeland, Y.-F. Hu, S.T. Lee, Phys. Rev. B, to be published.

11:20am **NS2-ThM10 Mechanical and Electromechanical Behaviour of Li@super +@(Mo@sub 3@Se@sub 3@)@super -@ Nanowires and Nanowire Bundles***, **A. Heidelberg,*** Trinity College Dublin, Ireland*; J.W. Schultze,* Heinrich-Heine-Universität Düsseldorf, Germany*; J.G. Sheridan, B. Wu, J.J. Boland,* Trinity College Dublin, Ireland

Li@super +@(Mo@sub 3@Se@sub 3@)@super -@ forms quasi-1D crystals and is structurally related to the Chevrel phases @footnote 1@. It can be viewed as a condensation polymer of (Mo@sub 3@Se@sub 3@)@super -

@ units. In the crystal the {(Mo@sub 3@Se@sub 3@)@super -@}@sub n@ strands are separated by Li@super +@ counterions. The crystals dissolve in polar solvents with @epsilon@ > 45 yielding conductive polyelectrolytes. From solution conductive single nanowires with a diameter of 0.6 nm and bundles of nanowires were deposited on substrate surfaces. The bundle height is typically between 10 and 100 nm and the length exceeds 5 @micron@ @footnote 2@. Mechanical measurements on Li@super +@(Mo@sub 3@Se@sub 3@)@super -@ nanowire bundles with a height range between 25 and 200 nm have been carried out using a SPM-nanomanipulator. For the experiments nanowires were deposited out of solution across trenches on SiO@sub 2@. The trench depth was typically between 100 and 300 nm and the width between 1 and 3 @micron@. To prevent any slippage of the nanowires 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. The size of the Pt lines varied depending on the size of the wire of interest. Lateral manipulations on nanowire bundles yielded force traces. Taking into account the wire shape and dimensions as well as the AFM cantilever dimensions, the Youngs modulus, the yield strength and the maximum bending strength of the nanowires can be obtained from the force traces. The Youngs modulus for Li@super +@(Mo@sub 3@Se@sub 3@)@super -@ nanowires has been measured to be in the range of 500 to 600 GPa. The electromechanical properties of nanowire bundles under mechanical stress were also measured. @FootnoteText@ @footnote 1@ R. Chevrel, M. Sergent, J. Prigent, J. Solid State Chem 3 (1971) 515 @footnote 2@ A.Heidelberg, J. W. Schultze, C. J. Booth, E. T. Samulski, J. J. Boland, Z. Phys. Chem. 217 (2003) 573.

11:40am **NS2-ThM11 Strong Field Emission of Taper-Like and Rod-like Si Nanowires Grown on Si@sub X@Ge@sub 1-X@ Substrate***, **Y.-L. Chueh**,* National Tsing Hua University, Taiwan*; L.J. Chou,* National Tsing Hua University, Taiwan, Republic of China*; S.L. Cheng, J.H. He, W.W. Wu,* National Tsing Hua University, Taiwan*; L.J. Chen,* National Tsing Hua University, Taiwan, Republic of China

Taper-like and rod-like Si nanowires (SiNWs) have been synthesized on Si and Si@sub 0.8@Ge@sub 0.2@ substrate annealed at 1200 °C in N@sub 2@ ambient. The tip regions of taper-like SiNWs are about 5-10 nm in diameter. The average length of the taper-like SiNWs is about 6 µm with aspect ratios is around 150-170. On the other hand, the rod-like is 5-100 nm in diameter, and 4-5 µm in length. The proposed growth models of there nanowires are oxide-assisted growth (OAG) and vapor-liquid-solid (VLS) growth. The taper-like morphology may be created by the passivation of the SiO@sub 2@ coating layer, and resulted in the different levels of absorption of SiO along the nanowires. The formation of metal-catalyst free rod-like SiNW is due to creation of unstable thin SiO@sub x@ layer, which vaporized easily during the annealing process. The optical and field emission characterization of these SiNWs have been investigated and present. Taper-like Si nanowires exhibit a superior field emission with a turn-on field of 6.3-7.3 V/µm and a threshold field of 9-10 V/µm. The @beta@ value are estimated to be 700 and 1000 at low and high fields, respectively. The excellent field emission characteristics are attributed to the perfect crystalline structure and taper-like geometry of the Si nanowires.

Organic Films and Devices
Room 304C - Session OF+NS-ThM

Molecular Electronics

Moderator: X.-Y. Zhu, University of Minnesota

8:20am **OF+NS-ThM1 Molecular Engineering to Test the Mechanism of Conductance Switching for a Variety of Conjugated Molecules***, **A.M. Moore**, B.A. Mantooth, A.A. Dameron, Z.J. Donhauser,* The Pennsylvania State University*; J.W. Ciszek, F. Maya, Y. Yao, J.M. Tour,* Rice University*; P.S. Weiss,* The Pennsylvania State University

Phenylene ethynylene oligomers have been studied as candidates for molecular electronic devices using scanning tunneling microscopy.@footnote 1-6@ These molecules were inserted into host alkanethiolate self-assembled monolayers for isolation and individual addressability. Many different hypotheses and theoretical predictions have been put forth to describe conductance switching.3-4 We have tested several of these through variations in the molecular design of our molecular switches and have concluded that the only mechanism consistent with all the switching data are that changes in the molecule-substrate bond hybridization leads to the observed conductance changes. @FootnoteText@ @footnote 1@Donhauser, Z. J.; Mantooth, B. A.; Kelly, K. F.; Bumm, L. A.; Monnell, J. D.; Stapleton, J. J.; Price, D. W.; Rawlett, A. M.; Allara, D. L.; Tour, J. M.; Weiss, P. S. 2001, Science 292, 2303.@footnote 2@Donhauser, Z. J.; Mantooth, B. A.; Pearl, T. P.; Kelly, K. F.; Nanayakkara, S. U.; Weiss, P. S. 2002, Jpn. J. Appl. Phys. 41, 4871.@footnote 3@Mantooth, B. A.; Weiss, P. S. 2003, Proc. IEEE 91, 1785.@footnote 4@Moore, A. M.; Dameron, A. A.; Mantooth, B. A.; Yao, Y.; Ciszek, J. W.; Maya, F.; Tour, J. M.; Weiss, P. S. 2004, Nanotechnology In press.@footnote 5@Lewis, P. A.; Inman, C. E.; Yao, Y. X.; Hutchison, J. E.; Tour, J. M.; Weiss, P. S. In Preparation.@footnote 6@Dameron, A. A.; Ciszek, J. W.; Tour, J. M.; Weiss, P. S. In Preparation.

8:40am **OF+NS-ThM2 Room Temperature Molecular Memory Observed from a Nanowell Device***, N. Gergel, **N. Majumdar**,* University of Virginia*; K. Keyvanfar, N. Swami,* University of Virgina*; L.R. Harriott, J.C. Bean,* University of Virginia

Researchers are debating whether the electrical switching behavior observed from some molecular devices can be attributed exclusively to the molecules@footnote 1@. We tested an OPE molecule with a nitro side group. This molecule showed electrical switching behavior when tested in a nanowell device at room temperature. This behavior was not seen when testing a simple conjugated molecule that lacked the nitro group. The test was performed in a nanowell device that consisted of a monolayer of molecules self-assembled on an area of gold 10-40 nm in diameter and capped with titanium and gold@footnote 2@. The I-V characteristics of the nitro molecule clearly showed two distinct conductivity states with a current ratio of 5 to 1 at room temperature. The experimental data showed that at a particular threshold voltage, the output current changed from a high current state to a low current state. This change in state was reversed with the opposite applied voltage. Hysteresis was not observed when testing a similar conjugated molecule without the nitro group at room temperature. Thus, the switching behavior could be attributed to changes in the conductivity of the nitro molecules due to the applied voltage. Other groups have reported seeing negative differential resistance behavior (NDR) in the I-V characteristics of the nitro molecule@footnote 3@. We saw similar peaks to those reported. However, our investigations indicate that this behavior is not reversible without the application of a negative threshold voltage. For this reason, these molecules may not be suitable for classic NDR circuits (e.g. Goto pairs@footnote 4@). This hysteretic behavior may nevertheless have device potential. @FootnoteText@ @footnote 1@ R.F. Forrest, Science 302, 556 (2003).@footnote 2@N. Majumdar, et al, submitted to J. Vac. Sci. Tech.@footnote 3@ M.A. Reed, et al, Applied Physics Letters 78, 3735 (2001).@footnote 4@ G. Rose, and M. Stan, IEEE NANO, San Fransisco, Aug (2003).

9:00am **OF+NS-ThM3 Metal/Molecule/Metal and Metal/Molecule/Semiconductor Device Structures***, **D. Janes**,* Purdue University **INVITED**

This talk will describe the development and electrical characterization of two classes of molecular electronic components. The first class of structures involves metal-molecule-metal systems with pre-formed metal contacts, primarily lateral break junctions formed either by electromigration or by shadow evaporation. A number of molecular species have been studied using these structures, including short aromatic thiols and short DNA double strands with thiol bonding groups at each end. The electrical characteristics of these devices indicate that strong coupling between the contacts and the molecular species can be realized. The second class of devices involves metal/molecule/semiconductor device structures, which are lithographically defined and fabricated using an indirect evaporation technique for the metal (top) contact and p+ GaAs for the bottom contact. In these structures, the electronic conduction between the metal and semiconductor can be modulated by choice of molecular species. Several alkyl thiol and aromatic thiol molecules have been employed in order to determine the effects of molecular length, conjugation and intrinsic dipole moment. The current-voltage characteristics and conductance versus temperature both indicate that the molecular layers change the transport mechanism, generally involving a lower effective barrier height than that of a metal/semiconductor Schottky barrier. These results reflect previous studies in which nanoscale metal/molecule/semiconductor structures exhibited low resistance contacts, implying that effective coupling and control of the surface electrical properties can be achieved using a molecular layer.@footnote 1@ A simple model for the conduction has been developed, utilizing our prior studies on surface Fermi level unpinning in GaAs structures.@footnote 2@ @FootnoteText@ @footnote 1@ T. Lee, et al., APL 76, 212 (2000). @footnote 2@ S. Lodha, et al., Appl. Phys. Lett. 80, 4452 (2002).

9:40am **OF+NS-ThM5 Room Temperature Negative Differential Resistance Measured through Molecular Monolayers Adsorbed to Silicon Surfaces with Ultra-high Vacuum Scanning Tunneling Microscopy*, N.P. Guisinger,* *R. Basu, M.E. Greene, A.S. Baluch, M.C. Hersam,* Northwestern University

In recent years, substantial progress has been made in the emerging field of molecular electronics. In particular, metal-molecule-metal junctions have been widely studied. In this paper, a continued study of charge transport through molecule-semiconductor junctions is considered. The presence of the energy band gap in semiconductors provides opportunities for resonant tunneling through individual molecules, leading to interesting effects such as room temperature negative differential resistance (NDR).@footnote 1@ In this study, the ultra-high vacuum scanning tunneling microscope was used to probe charge transport through two different molecular monolayers adsorbed to the Si(100) substrate. I-V measurements were taken on monolayers of TEMPO and cyclopentene for both degenerately doped n-type and p-type Si(100) substrates. Initial I-V measurements through the TEMPO monolayer exhibited a suppression of NDR behavior relative to previously reported transport through isolated molecules.@footnote 1@ I-V measurements were also taken on isolated cyclopentene molecules, as well as on cyclopentene monolayers. The cyclopentene monolayers similarly exhibited a suppression of the observed NDR behavior relative to transport through isolated molecules. For both molecular monolayers, the suppression of the peak-to-valley ratio (PVR) has been measured to exceed a 47 percent reduction compared to observed PVRs of isolated molecules. The resulting NDR suppression in both monolayers indicate that the local environment surrounding the molecules strongly influences charge transport. In addition to molecular monolayers, initial studies of transport through isolated TEMPO molecules adsorbed to both degenerate and non-degenerate Si(111) will be discussed. @FootnoteText@ @footnote 1@N. P. Guisinger, M. E. Greene, R. Basu, A. S. Baluch, and M. C. Hersam, "Room temperature negative differential resistance through individual molecules on silicon surfaces," Nano Letters, 4, 55 (2004).

10:00am **OF+NS-ThM6 Two Distinct Types of Switching Behavior in a Single Molecule*, A.S. Blum,*** *J.G. Kushmerick, C.H. Patterson,* Naval Research Laboratory*; J.C. Yang,* Duke University*; J.C. Henderson, Y. Yao, J.M. Tour,* Rice University*; R. Shashidhar,* Geo-Centers, Inc.*; B.R. Ratna,* Naval Research Laboratory

There is recent controversy surrounding the ability of molecules to function as switches in molecular electronic devices. We report the observation of two distinct types of switching in matrix isolated and complete monolayers of bipyridyl-dinitro-oligophenylene-ethynylene (BPDN). Extensive measurements in a scanning tunneling microscope (STM) demonstrate both stochastic and voltage driven switching in this molecule, representing the first description of two distinct types of switching in a single molecule. While stochastic switching has been reported for several molecular systems, we argue that the observed voltage controlled switching is a distinct physical event specific to BPDN. Furthermore, consistent switching behavior measured with both a scanning tunneling microscope and a crossed-wire tunnel junction demonstrates that the switching is intrinsic to the molecule and is not an artifact of the measurement system.

10:20am **OF+NS-ThM7 Electrical and Mechanical Contacts at the Atomic Scale: a Combined UHV STM/AFM Study*, Y. Sun,*** *M. Henrik, S. Schaer, Y. Miyahara, A.-S. Lucier, M.E. Ouali, P. Grutter,* McGill University, Canada*; W. Hofer,* University of Liverpool, United Kingdom

Understanding electrical contacts is widely considered as one of the central issues in molecular electronics. As a first step, we have measured simultaneously at the atomic scale the interaction forces and the currents between a sharp tungsten tip and a Au(111) sample using a combined ultra-high vacuum scanning tunnelling and atomic force microscope (UHV STM/AFM). Close correlation between conductance and interaction forces were observed in the regimes from weak coupling to strong interaction. In particular, the electrical and mechanical points of contact are defined as a result of the observed barrier collapse and adhesive bond formation, respectively. The points of contact as defined by force and current measurements coincide within measurement error. We find experimentally that at contact the very front atoms of the tip apex experience repulsive forces, while the total interaction force remains attractive as a consequence of competing interaction decay lengths. Ab-initio calculations of the current as a function of distance were performed for our experimental tip-sample system. We find that in the weak coupling regime the calculated electrical current as a function of distance is in quantitative agreement with experimental results only if tip and sample relaxation effects are taken into account. The calculated relaxation of the tip apex atoms is 50-100 pm. We conclude that force effects of different decay lengths cannot be excluded if a detailed understanding of atomic scale contacts is to be achieved.

10:40am **OF+NS-ThM8 Structure of Self-Assembled Monolayers on Platinum*, D.Y. Petrovykh,*** University of Maryland, Naval Research Laboratory*; H. Kimura-Suda, A. Opdahl, L.J. Richter, R.D. Van Zee, M.J. Tarlov,* National Institute of Standards and Technology*; L.J. Whitman,* Naval Research Laboratory

We studied formation of self-assembled monolayers (SAMs) on polycrystalline platinum thin films using X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR), spectroscopic ellipsometry, and contact angle measurements. In particular we are interested in properties of SAMs on Pt with respect to their possible use as a substrate for Si-compatible molecular electronics. We find that SAMs formed on piranha-cleaned Pt from ethanoic solutions of n-alkanethiols have initial quality comparable to or better than that achieved under other conditions. The FTIR and XPS data indicate that films are formed with nearly normal orientation of alkane chains, have higher packing density than comparable SAMs/Au, and remain stable in ambient air for 3-5 days. XPS spectra of the S 2p region also show that SAMs/Pt are distinctly multicomponent. The main component, with the lowest binding energy, unambiguously corresponds to alkanethiol molecules adsorbed on Pt in a configuration similar to that for SAMs/Au. The minority higher binding energy components are not affected by exposure to good solvents and thus appear to correspond to different binding configurations related to surface roughness and oxidation (rather than to physisorbed molecules). Our results suggest that the use of oxide-free and atomically smooth Pt substrates may be necessary to attain a single-component, high-quality SAM on Pt.

11:00am **OF+NS-ThM9 Oligomer Length Dependent Study of Metal-Molecule Interactions in Model Molecular Wire Systems*, C.D. Zangmeister,*** NIST, US*; S.W. Robey, R.D. Van Zee,* NIST

Interactions at the molecule-contact interface perturb the molecular orbitals important for electron transport in conjugated systems. These perturbations are particularly important for the nanometer size junctions applicable in molecular-scale electronics. This study looks at the variation of the occupied electronic structure of fully conjugated model molecular wire compounds as a function of molecular length. Specifically, the number of phenyl rings was varied from a single ring to three rings in unsubstituted phenylene ethynylene monolayers chemisorbed on Au using ultraviolet photoemission spectroscopy. This provides a qualitative picture of the extent of perturbation of the electronic structure due to thiol coupling and the variation of the molecular @pi@ levels important for electron transport as a function of the degree of conjugation. These data show a shift towards the Au Fermi levels in the @pi@ levels by more than an eV as the conjugation length is increased. These observations will be discussed in terms of previous electron transport investigations of these compounds adsorbed on Au.

11:40am **OF+NS-ThM11 Electrical Properties of DNA Characterized by Conducting-Atomic Force Microscopy**, *C. Nogues,* ***S.R. Cohen****, S. Daube, R. Naaman,* Weizmann Institute of Science, Israel

DNA has been widely promoted as the key component of future molecular devices, due to its unique assembly and recognition properties. Specifically, the strong interaction between complementary base-pair sequences on interacting DNA strands can be utilized to self-assemble a desired structure in a molecular circuit. The most basic building blocks of such circuits can be formed through the hybridization of two single strands into a double one, and the specific binding of functionalized DNA strands to gold electrodes using the chemical thiol-gold linkage. Such manipulations can exploit the ease in which DNA strands can be synthesized, and modified chemically. Despite these advantages, the electrical properties of individual strands of DNA have yet to be reproducibly characterized, due to the inherent difficulties in reliably accessing and measuring single molecules. We have attacked this problem by developing protocols for reproducible formation and characterization of DNA monolayers, and then probing their electrical functioning using conducting atomic force microscopy (cAFM). The electrical contact to the DNA was made by chemical binding to a gold electrode on one end, and to a gold nanoparticle on the other. Thus, repeatable measurements of the conductivity of individual DNA strands have been performed. Meaningful differences could be detected between conductivity in single- and double-strand DNA. The single strand DNA was found to be insulating over the range of -2 to +2 V, while the double strand DNA passes significant current outside a 3 eV gap.

Nanometer-scale Science and Technology
Room 213C - Session NS1-ThA

Nanoscale Imaging

Moderator: D.M. Tennant, Lucent Technologies, Bell Laboratories

2:00pm **NS1-ThA1 Single Electron Charging in Individual InAs Quantum Dot Observed by Nonconctact Atomic Force Microscopy**, ***Y. Miyahara***, *R. Stomp, S. Schaer, Q. Sun, H. Guo,* McGill University, Canada*; S. Studenikin, P. Poole, A. Sachrajda,* National Research Council, Canada*; P. Grutter,* McGill University, Canada

Understanding the electronic structure of quantum dots (QD) is not only important for application but also of great interest in fundamental physics. Although there have been a number of studies of electronic properties using mainly optical or capacitance spectroscopy techniques, investigating a single QD remains challenging because of the extremely small dot dimensions. Spectroscopic techniques based on scanning probe microscopy have been employed, in particular scanning tunneling spectroscopy (STS). In STS the acquired tunneling spectra feature the Coulomb staircase or/and the discrete energy states of the QD depending on the size of the QD and the tunneling barrier thickness. However, these measurements are limited to substrates with adequate conductivity since a measurable tunneling current of typically 1 pA or more is usually required. Here, we report the first successful observation of the Coulomb blockade effect by electrostatic force measurements. The main experimental features in the electrostatic force vs. the tip-substrate bias voltage curves agree well with a simple theory based on the semi-classical theory of the Coulomb blockade effect. Comparison of the experimental results with the model calculation will be made and the possibility to observe the discrete energy states will also be discussed. One of the important differences to STS is that there is no continuous current flowing in the system. As a consequence, this technique can detect single electron events. Furthermore, this implies that this technique can also be applied to the QDs embedded in other materials.

2:20pm **NS1-ThA2 Nanoelectromechanics of Scanning Probe Microscopies of Ferroelectric Surfaces**, ***S.V. Kalinin***, Oak Ridge National Laboratory*; A. Gruverman,* North Carolina State University*; J. Shin, A.P. Baddorf,* Oak Ridge National Laboratory*; E. Karapetian, M. Kachanov,* Tufts University

Nanoscale applications of ferroelectric materials including MEMS and nonvolatile memory components have motivated a number of studies of ferroelectric behavior on the nanoscale using a wide array of electromechanical Scanning Probe Microscopy techniques including Piezoresponse Force Microscopy, Atomic Force Acoustic Microscopy, Scanning Near-Field Acoustic Microscopy, and Heterodyne Ultrasonic-Electrostatic Force Microscopy. Quantitative interpretation of SPM domain imaging mechanisms and particularly hysteresis loop measurements and tip-induced polarization switching processes requires description of contact mechanics for the ferroelectric surface including electromechanical coupling effects and also the structure of electroelastic fields inside the material. Here, the analytical solution of the coupled electromechanical problem for piezoelectric indentation is used to derive the relationship between indentation force, tip bias and tip displacement. These stiffness relations are utilized for quantitative interpretation of the imaging mechanism of the electromechanical SPM techniques. The structure of the electroelastic fields yields a quantitative measure of the signal generation volume and also provides a quantitative basis for the analysis of tip-induced polarization switching and local hysteresis loop measurements. The early stages of the switching process require the exact structure of the electroelastic fields to be known, while the late stages of switching processes can be adequately described using point charge type models. Tip-induced switching is shown to be possible only above a minimum threshold tip bias, producing a well-defined minimal size of the switched domain. Approaches to reduce minimal written domain size for ferroelectric lithography and data storage are discussed.

2:40pm **NS1-ThA3 High-Resolution Force Microscopy: Observing Atoms at Work**, ***R. Bennewitz***, McGill University, Canada*; L. Nony, E. Gnecco, O. Pfeiffer, A. Socoliuc, S. Maier, A. Wetzel, C. Gerber, E. Meyer, A. Baratoff,* University of Basel, Switzerland **INVITED**

Force microscopy has made progress towards quantitative determination of forces with lateral resolution on atomic scale. One example is the observation of enhanceded interactions at the edge atoms of nanoscale pits in KBr surfaces which are able to trap otherwise mobile molecules. Dynamic modes of force microscopy allow to detect dissipative processes with the same lateral resolution. For the molecules trapped in nanoscale pits, a strongly enhanced dissipation is observed compared to the KBr substrate. Dissipation is also the focus of friction force experiments, which recently have revealed new aspects of atomic friction processes, like a regime of ultra-low friction obtained at low loads. New instrumental developments including the combination of a force microscope with mass spectrometer will be discussed.

3:20pm **NS1-ThA5 Imaging of Radiation Effects on an Active Silicon-On-Insulator (SOI) Device using Scanning Capacitance Microscopy (SCM)**, ***C.Y. Nakakura***, *M.R. Shaneyfelt, R.A. Jones,* Sandia National Laboratories

Two-dimensional (2D) imaging of electrical properties using atomic force microscopy (AFM)-based techniques has attracted considerable attention in the semiconductor industry, primarily for 2D-dopant profiling of cross-sectioned device junctions. Scanning capacitance microscopy (SCM) has been most widely used for this purpose by acquiring nanometer-scale, 2D free carrier images, from which dopant information can be extracted. The bulk of reported dopant profiling studies using SCM, however, have been performed on shorted, inoperable devices that only show the static device as fabricated. In this study, we expand on conventional, cross-sectional carrier profiling: first, the images were acquired using a modified SCM to permit carrier profiling of active devices and, second, the devices were measured before and after radiation exposure to visualize the effects on device operation. Understanding radiation effects in semiconductor devices is critical to the development of radiation-hardened integrated circuits used in harsh environments, such as Earth-orbit and outer space. We will demonstrate that SCM is a promising tool for directly imaging the effects of radiation in cross-sectioned, silicon-on-insulator (SOI) metal-oxide-semiconductor field-effect transistors (MOSFETs). Following exposure to radiation, the impact of the radiation-induced charge buildup at the Si/SiO@sub 2@ interface of the SOI substrate is readily observed in the SCM images. The methodology of the active device measurements, as well as the implications of radiation exposure on the operation of these devices, will be discussed. @FootnoteText@ Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

3:40pm **NS1-ThA6 High Resolution Structural and Chemical Information: A Combined STM, SEM and SAM Analysis of Ag Nanocrystallites on Si**, ***J. Westermann***, *M. Maier, J. Poppensieker, G. Schaefer,* OMICRON NanoTechnology GmbH, Germany

For the analysis of nanostructured materials it is of crucial importance to be able to characterise not only structural properties of the material, but also determine chemical composition, as well as electronic and magnetic properties of individual nanostructures. To accomplish this, we have combined a high resolution SEM column with an STM under true UHV conditions with extension possibilities for AFM, SEMPA, FIB, and EBL. This enables in situ SEM and STM imaging to study the sample topography from mm down to 10 pm scale on the same sample spot. Using the electron column as an excitation source for Auger, chemical analysis is possible with sub 10 nm resolution. STM related techniques like STS allow the characterisation of the electronic structure and magnetic imaging using spin polarised STM. Besides the observation of sample properties, the STM+SEM combination also offers unique possibilities for sample modification on the nanoscale, offering both electron beam lithography and STM manipulation under SEM control. Using Ag nanocrystals on Si(111), we demonstrate the capabilities of this approach. The samples were prepared by evaporation of Ag on a clean Si (111) substrate at elevated temperatures. We show SEM and SAM images with a resolution down to 3 nm (SEM), and 10 nm (SAM) respecively allowing for chemical analysis with ultimate resolution. We demonstrate the importance of SEM to select areas of interest, and subsequently position the STM tip to image these areas. STM images with atomic resolution show the surface structure and reconstructions on both the silver crystals and the silicon substrate. The latter shows a @sr@3x@sr@3 reconstruction induced by the silver.

4:00pm **NS1-ThA7 Atomic Level Analysis of Polythiophene by the Scanning Atom Probe**, ***O. Nishikawa***, *M. Taniguchi, M. Ihara,* Kanazawa Institute of Technology, Japan*; H. Kato, S. Takemura,* Kanto Gakuin University, Japan

Thin films of conductive polythiophene grown by the electrochemical process on silicon and ITO substrates are investigated by utilizing unique capability of the scanning atom probe (SAP). The thickness of the films is 10 to 30 Î¼m and the dopant is BF4-. Since the variation of the field emission current I with the applied voltage V to the polythiophene is related with the work function of the specimen surface, the I-V curves, the F-N plot, were obtained. The slope and intercept of the F-N plots (S-I chart) indicates that the work function does not vary with the synthesizing process and the substrate. The comparison of the S-I chart of CNT, W and Si shows that the work function of the polythiophene is close to that of Si. The variation of the S-I chart with temperature also suggests that the polythiophene films are semi-conductive because the emission current varies with temperature as Si. The SAP analysis was conducted by applying voltage pulses or laser pulses. The mass spectra of the detected ions are closely related with the structure of the polythiophene. The Most abundant ions have the masses 80 to 83 which indicates that these ions are SC4Hn, the basic unit of the polythiophene. The ratio of the number of sulphur atoms to that of carbon atoms is 1 to 4 as expected. The detection of various ions such as C+, C2+ and SC3Hn+ suggests that some areas not polymerized and stay in the graphite like state. All sulphur atoms were found as a clustering atom with carbon and hydrogen such as SC4Hn2+ and SC3Hn+. Since the evaporation field of doubly charged ions is usually higher than that of singly charged ions, the detection of doubly charged cluster ions indicates that the SC4Hn2+ clusters are very stable and the atoms forming the clusters are fairly strongly bound. No oxidation of the polythiophene was noticed.

4:20pm **NS1-ThA8 Probing Ion Transport at the Nanoscale: Time-Domain Electrostatic Force Spectroscopy on Glassy Electrolytes***, **A. Schirmeisen**, A. Taskiran, H. Fuchs, B. Roling, S. Murugavel, H. Bracht, F. Natrup,* University of Muenster, Germany

Ion conducting solid materials play an important role as electrolytes in energy conversion systems, such as batteries and fuel cells, and also in electrochemical sensors. Of particular interest are so-called fast ion conductors with conductivities that are comparable to liquid electrolytes. Currently, a lot of research work is being done in order to find new materials with improved conductivities. For instance, nanostructured materials become more and more technologically relevant. An important prerequisite for further progress in this field is a better understanding of the ion transport mechanisms on microscopic length scales. Up to now, the experimental techniques used for probing the ion transport are mainly macroscopic in nature, e.g. conductivity spectroscopy, tracer diffusion measurements and NMR relaxation techniques. The macroscopic averaging over the motions of all ions in a sample leads to a loss of information making it desirable to develop techniques that are capable of probing the ion transport on nanoscopic length scales. In this contribution, we demonstrate that electrical atomic force microscopy (AFM) techniques yield information about the dynamics of mobile ions in small subvolumes of a sample. In dynamic mode AFM, a voltage is applied between the tip and the sample, at typical tip-sample distances of about 10 nm. In this case, the voltage drop in the sample occurs mainly in a nanoscopic subvolume below the surface. Ionic motions in this subvolume influence the electrostatic forces acting between tip and sample. We record the time dependent evolution of the forces at sample temperatures from 100 K to 600 K, which allows us to extract the activation energy of the ion conduction process. The comparison of macroscopic with our nanoscopic measurements on different solid electrolytes shows that time-domain electrical AFM is capable of probing the ion dynamics and transport in nanoscopic subvolumes of the samples.

5:00pm **NS1-ThA10 Novel MEMS Devices for Accurate Lateral and Normal Force Measurement in AFM***, **P.J. Cumpson**,* National Physical Laboratory, UK, United Kingdom*; J. Hedley,* Newcastle University, UK

The uncertainty in the spring constants of AFM cantilevers is a limiting factor in a wide range of measurements of nanoscale quantities (chemical, electrical, mechanical) at a lateral resolution of 30 nm or below. The tip/cantilever fabrication process suggests that manufacturing cantilevers to the exquisite dimensional accuracy required to produce sufficiently repeatable spring constants will always be a challenge; an easy and accurate calibration method is needed. A number of methods have been suggested for calibrating AFM cantilevers@footnote 1@, all of which have limited accuracy or are difficult to perform. We have developed a novel microfabricated device capable of calibrating AFM cantilevers for normal spring constant@footnote 2@ much more easily. The device consists of a surface micromachined silicon resonator, which can be set into resonance at an amplitude of around 10 nm in vacuum. By applying Doppler interferometry and electrical measurement simultaneously, the spring-constant of the MEMS device can be deduced, to an uncertainty of around ±2%, without physical contact. Here we present a new MEMS device for the first time, specifically designed to make lateral force constant calibration easy and accurate. This presented challenging fabrication and interferometry problems. Nevertheless, it is particularly valuable since few other options exist for quantitative measurement of lateral force. @FootnoteText@ @footnote 1@ N A Burnham et al, Nanotechnology 14 (2003) 1-6.@footnote 2@ P J Cumpson and J Hedley, Nanotechnology 14 (2003) 1279-1288.

Nanometer-scale Science and Technology
Room 213D - Session NS2-ThA

Nanowires II

Moderator: S.-T. Lee, City University of Hong Kong, China

2:00pm **NS2-ThA1 Gaede-Langmuir Award Presentation: Ultra-high Vacuum Electron Microscopy for Surface Analysis and Nanomaterials**, **INVITED**

Nanostructures are investigated increasingly by ultra-high vacuum (UHV) electron microscopy in the last decades. In recent years scanning tunneling microscope (STM) and/or atomic force microscope (AFM) is incorporated in UHV electron microscope apparatus to study not only structures but also properties in-situ. Also a great advance in the optics of the electron microscope, aberration free lens, allows us to image individual atoms (or atomic columns) within nanostrucutres. I present recent development of our UHV high-resolution electron microscopy that has an aberration free lens and a scanning probe microscope, and results on conductance quantization of metal nanowires and forces acting on the free-standing nanowire that spans between electrodes

2:40pm **NS2-ThA3 VLS Epitaxy of Si Nanowires: Kinetics and Morphology***, **T. Clement**, J.L. Taraci, J.W. Dailey, D.J. Smith, J. Drucker, S.T. Picraux,* Arizona State University

The high aspect ratios and novel electronic and chemical properties of silicon nanowires have made them increasingly interesting for applications ranging from flexible electronics to chemical sensors to microfluidic surfaces. However the mechanisms behind vapor-liquid-solid (VLS) crystal growth have received only limited attention since the seminal work of Wagner for whisker growth more than 30 years ago.@footnote 1@ Here we study the VLS kinetics and growth modes dominating CVD grown Si nanowires (SiNWs) as a function of growth pressure and temperature. In contrast to our previous studies of Ge nanowires, we observe SiNW growth throughout a wide range of pressures and temperatures. Au nanodots with a nominal thickness of 2.5 nm and average lateral separation of 30 nm are evaporated in UHV on hydrogen terminated Si(111) and Si(100) surfaces; these Au nanodots function as the seeding species for VLS nanowire growth. Subsequent growth using disilane (Si@sub 2@H@sub 6@) gas at pressures ranging from 1x10@super -2@ to 1x10@super -6@ Torr and temperatures ranging between 300°C and 700°C produces highly uniform SiNW structures at low temperatures and unstable structures at higher temperatures, specifically kinks and nonuniformity in SiNW diameter. The initiation of nanowire growth is a nucleation-limited process, and we also report on new in situ optical scattering studies of SiNW nucleation times. Finally, characterization via field-emission SEM, RBS, and TEM will establish the SiNW growth rate dependence on substrate temperatures and pressures. Examples of the dramatic superhydrophobic and superhydrophilic behavior of functionalized SiNW surfaces will be given. @FootnoteText@ @footnote 1@ R.S. Wagner, in Whisker Technology, Levit, A.P. ed, (Wiley-Interscience, New York, 1970) pp 47-119.

3:00pm **NS2-ThA4 Growth Of ZnO Nanowires and Their Applications in Dye Sensitized Solar Cells***, **J.B. Baxter**,* University of California Santa Barbara*; M. Reichman,* University of Texas-Austin*; E.S. Aydil,* University of California Santa Barbara

ZnO is a wide band gap semiconductor (Eg = 3.37 eV) with applications in UV optoelectronics, varistors, piezoelectronics, and photovoltaics. Nanostructured ZnO can enable applications that require high semiconductor surface area such as sensors and dye sensitized solar cells. We have grown single crystal ZnO nanowires ~80 nm in diameter and several microns long by chemical vapor deposition (CVD) using the organometallic precursor zinc acetylacetonate (Zn(acac)@sub2@) in the presence of oxygen. Dense arrays of ZnO nanowires exhibit large surface areas and can be grown on various oxide substrates, making them suitable as the mesoporous semiconductor in dye sensitized solar cells. Single crystal ZnO nanowires offer improved conduction pathways compared to sintered nanoparticles used currently, where electron transport occurs by a hopping mechanism. The surface area for dye adsorption can be increased significantly by extending the growth time to allow for the nucleation and growth of smaller secondary nanowires from the primary nanowires, improving current densities in the cells. We have used these types of nanowires to produce initial solar cells with short circuit current densities of 75 µA/cm@super2@, open circuit voltages of 0.63 V, and fill factors of 39 % when illuminated with 100 mW/cm@super2@ simulated solar light. A limitation of the initial solar cells is poor light harvesting, with less than 10% of incident light absorbed by the dye. We are currently investigating methods for seeding nanowire growth to improve the nucleation density, which will increase nanowire surface area and dye adsorption. Transport properties of the nanowires can be significantly enhanced by treatment in hydrogen plasma at room temperature. H atoms passivate defects and increase conductivity by increasing carrier densities. H exposure improves the UV photoluminescence of the nanowires and both the fill factor and the open circuit voltage of the solar cells.

3:20pm **NS2-ThA5 Progress Towards Silicon Nanowire-based Complementary Logic*****, T.S. Mayer****, Y. Wang, T.-T. Ho, K.-K. Lew, L. Pan, E.C. Dickey, J.M. Redwing,* Penn State University **INVITED**

There has been considerable interest in bottom-up assembly of semiconductor nanowires for their application in future logic, memory, and sensor circuits. In this talk, we will present results of recent research showing that p- and n-type dopants can be intentionally incorporated into silicon nanowires (SiNWs) during template-directed vapor-liquid-solid (VLS) growth to produce complementary field effect devices. In this work, Au metal particles electrodeposited within 80-nm diameter pores of anodized alumina templates serve to catalyze SiNW growth at temperatures of 500° C using 10% silane (SiH@sub 4@) in H@sub 2@ as the silicon gas source, trimethylboron (TMB) as the p-type dopant, and phosphine (PH@sub 3@) as the n-type dopant. Transmission electron microscopy (TEM) studies of individual SiNWs show that approximately two-thirds of the SiNWs are single crystal, while the remaining one-third are bicrystals. Additionally, the surfaces of all of the p- and n-type SiNWs investigated were free of amorphous layers that were observed previously when diborane was used as a p-type dopant gas. Secondary ion mass spectroscopy (SIMS) on bundles of SiNWs indicate that B- and P-concentrations increase with increasing TMB:SiH@sub 4@ or PH@sub 3@:SiH@sub 4@ gas ratios between 10@super -5@ and 10@super -2@, and can exceed 10@super 19@ cm@super -3@ for the highest gas ratios investigated. Gate-dependent conductance measurements of individual B- and P-doped SiNWs show complementary characteristics that are consistent with depletion mode device operation, where the threshold voltage is adjusted by changing the dopant:SiH@sub 4@ gas ratio during VLS growth. Independent measurements of four-point resistivity also show a clear decrease in resistivity with increasing TMB:SiH@sub 4@ or PH@sub 3@:SiH@sub 4@ gas ratios. These results confirm that p- and n-type dopants can be effectively incorporated during SiNW synthesis to produce complementary field effect devices in the same material system.

4:00pm **NS2-ThA7 The Role of Electrodeposited Metal Nanowires in Gas Sensing*****, B.J. Murray****, E.C. Walter, R.M. Penner,* University of California, Irvine

It in unclear what role, if any, metal nanowires have to play in chemical sensing. While the literature is ripe with examples of sensors based on semiconductor nanowires, there have been very few examples using metal nanowires. For these investigations - silver, copper, gold, and platinum nanowires were prepared by Electrochemical Step Edge Decoration (ESED) on a graphite surface. These nanowires were polycrystalline, consisted of a 1-D array of fused particles 50 nm to 950 nm in diameter, and had lengths of 100 µm or more. The resistance of these metal nanowires was probed as a function of the concentration of a chemisorbing gas. Upon exposure to ammonia (NH@sub 3@), arrays of these "fused particle" wires showed a resistance increase, @DELTA@R/R@sub 0@, that was fast, large (up to 1,000%), and reversible. Compared to literature on thin metal film sensors, the response of these nanowire arrays was much larger than expected. We propose that the elements responsible for this response were concentrated at a small minority of locations along axis of the wires. This proposed model, the Chemically Responsive Interparticle Boundary (CRIB) model, will be discussed. Finally, the chemical structure of these elements has been investigated to determine the role, if any, of air oxidation on sensor function.

4:20pm **NS2-ThA8 1-D Metal Oxide Sensor and Catalyst: the Comparative Study of Pristine and Surface Doped Individual Nanowire***, A.A. Kolmakov,* University of California, Santa Barbara*; S.V. Kalinin,* Oak Ridge National Laboratory*; Y. Lilach,* ***M. Moskovits,*** University of California, Santa Barbara

We investigated transport properties of individual metal oxide single crystal nanowires and nanobelts operating in high vacuum and under â?oreal worldâ? conditions for sensing and catalysis applications. Using impedance measurements under different gas environment in conjunction with scanning probe microscopy we were able to determine the major factors contributing to charge transport in nanowire. We found that when nanowire radius is comparable with its Debye length, the adsorption/desorption of donor/acceptor molecules on the surface of the nanowire and in its proximity alters the bulk electron density inside the nanowire what sensitively modulates conductivity of the nanowire. In vivo conductometric measurements on individual nanowire during its surface doping with metal particles reveals the formation of nano-Schottky barriers which drastically enhance of the reactivity/selectivity of the nanowire as gas sensors and catalyst.

4:40pm **NS2-ThA9 Thermoelectric Nanowire Arrays for Waste Heat Conversion*****, E. Menke****, R.M. Penner,* University of California at Irvine

No longer relegated to specialized roles like powering satellites, thermoelectric materials are garnering interest for more mundane uses like solid-state refrigerators and collecting waste heat in automobiles. A number of research groups are currently working on a variety of methods to improve the efficiency of thermoelectric materials. Our attempts to create more efficient thermoelectric devices have focused on fabricating arrays of high aspect ratio nanowires of bismuth telluride, presently the best conventional thermoelectric material for room temperature applications. I will present our method for preparing bismuth telluride and doped bismuth telluride nanowires on highly oriented pyrolytic graphite via electrochemical step-edge decoration. This will be followed by the characterization of these nanowires by scanning electron microscopy, x-ray diffraction, and energy dispersive x-ray analysis. Finally, I will end by briefly discussing our attempts to measure the thermoelectric figure of merit for these nanowires.

5:00pm **NS2-ThA10 Devices Formed Using Deposited Polymeric Nanofibers***, J. Kameoka,* Cornell University*; H. Liu,* Cornell Univeristy*; D. Czaplewski, R. Mathers, S. Verbridge, G. Coates,* ***H.G. Craighead,*** Cornell University

We have used deposited polymer nanofibers for the formation of electrical, optical and mechanical devices. We used a microfabricated tip as a controlled scanning source for electrostatically driven deposition of oriented nanofibers and for interfacing the fibers to lithographically defined surface structures. Because of the ability to deposit these materials as individual oriented fibers with diameters in the range of 50 nm to ~1µ, they can be utilized in new device architectures. In this talk we describe the use of the deposited polymer nanofibers as chemical sensors and as templates for the formation of mechanical and nanofluidic devices composed of inorganic materials. Utilizing the properties of a conducting polyaniline polymer we have formed ammonia sensors comprising a single oriented fiber deposited on gold electrodes. We created mechanical devices such as silicon nitride mechanical oscillators with dimensions on the order of 100 nm, formed using deposited poly(methylmethacrylate) fibers. The oscillators were defined in a silicon nitride layer by using the fiber as a mask for reactive ion etching, followed by removal of a sacrificial underlying layer. After releasing the devices, the frequencies of the modes of oscillation of the beams were determined by laser interference techniques. We fabricated nanofluidic channels of elliptical cross-section, without the use of high resolution lithography. The sacrificial template fiber consisted of a heat-decomposable polycarbonate that was deposited on a substrate and encapsulated by a spin-on glass. The channels were formed by thermal removal of the sacrificial polymer nanofibers. The oriented nanofiber deposition method, used in these experiments, offers an approach for the rapid formation of self-assembled nanoscale devices, connected to microfabricated structures, which would be difficult to form using a completely self-assembled or completely lithographic approach.

Nanometer-scale Science and Technology
Room 213D - Session NS-FrM

Nanometer-scale Structures

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

8:20am **NS-FrM1 Peter Mark Memorial Award Presentation: Nanometer-Scale Fabrication Techniques for Building Semiconductor Devices***, **K. Guarini**[1],* IBM T. J. Watson Research Center **INVITED**

Integrated circuit performance improvements have been achieved largely by aggressive shrinking of the silicon transistor and metal interconnect dimensions. Future technology generations will require even greater innovation to continue the performance trend. New materials, device structures, and integration schemes will all play roles in advancing CMOS technology. Novel nanometer-scale patterning techniques will be critical to this success. This talk will give an overview of nanometer-scale patterning needs of the semiconductor industry and highlight several novel solutions. Direct write scanning probe lithography (SPL) is a high-resolution patterning technique that uses a sharp tip in close proximity to a sample to pattern nanometer-scale features. Low energy electrons field emitted from a probe tip can be used to expose polymer resists with sub-30-nm resolution and nanometer-scale alignment registration. In comparison to electron beam lithography, SPL has wider exposure latitude, improved linearity, and reduced proximity effects. Material self assembly provides an alternative means for pattern formation at the nanometer-scale. With feature sizes defined by fundamental molecular properties, self assembly can access dimensions and densities beyond the capabilities of conventional patterning techniques. Our work has focused on identifying and demonstrating key applications of self assembly. In one example, we enhanced the capacity of thin film metal-oxide-semiconductor devices using nanostructured electrodes patterned by self assembly. We have also demonstrated the use of material self assembly in facilitating continued scaling of non-volatile FLASH memories. These high resolution patterning processes offer innovative solutions to existing challenges in microelectronics and are well suited to enabling enhanced device performance and functionality by augmenting the available tool kit for manufacturing.

9:00am **NS-FrM3 Self-assembled Multilayers Creating Tailored Resists for Nanostructure Fabrication***, **M.E. Anderson**, E.M. Carter, A.R. Kurland, C. Srinivasan, M.W. Horn, P.S. Weiss,* The Pennsylvania State University

Designing and patterning complex hierarchical assemblies by exploiting methods of directed self-assembly in combination with a variety of lithographic techniques has been an active area of research for patterning in the sub-100 nm regime. We have used self-assembled multilayers to create molecular ruler resists to define nanostructures with precise spacing and edge resolution reaching the nanometer-scale.@footnote 1-3@ A molecular ruler resist of self-assembled multilayers, composed of alternating layers of @alpha@,@omega@-mercaptoalkanoic acids and coordinated metal ions, is selectively deposited on initial lithographically defined gold structures. This resist can be tuned based on the number of layers deposited to a desired thickness (routinely between 10-100 nm). Then, metal is deposited on the sample and the resist is removed, yielding spacings between metal structures dependent on the dimensions of the tailored resist. Work is underway to build molecular ruler resists independently either by capping selected regions of growth or by orthogonal growth of two different multilayer systems. A scheme in development is electroless metal deposition of the secondary metal, where the ruler resist both defines the structure spacing and inhibits deposition for selective metal placement. Molecular ruler resists can withstand the rigors of lithographic processing and are being developed to advance this method toward device fabrication. @FootnoteText@ @footnote 1@ A. Hatzor and P.S. Weiss, Science 291, 1019 (2001).@footnote 2@ M. E. Anderson et. al., Journal of Vacuum Science and Technology B 20, 2739 (2002).@footnote 3@ M. E. Anderson et. al., Journal of Vacuum Science and Technology B 21, 3116 (2003).

9:20am **NS-FrM4 Studies of Self-Assembling Bilayers for Layered Nanofabrication (LNF)***, **T.-Y. Shih**, A.A.G. Requicha, M.E. Thompson, B.E. Koel,* 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 we have called layered nanofabrication (LNF). We report on the embedding of gold nanoparticles in several layers of octadecyltrichlorosilane (OTS) deposited on a SiO@sub2@ surface. Atomic force microscopy (AFM) was used in ex-situ studies of the formation of self-replicating bilayers with hydrophobic-hydrophilic properties and hydrogen bonding as triggered by treatments using acetone. Analysis of the Au nanoparticles after several bilayer-by-bilayer growth cycles showed that they decreased in apparent height and roughness according to the number of deposited layers. Ellipsometry was used to monitor the OTS film thickness and characterize the film growth mode. We were able to achieve a controllable, stepwise linear growth of a flat, multilayer film that eventually produced a high-quality, planarized nanoparticle-containing surface.

9:40am **NS-FrM5 Cross-sectional Ballistic Electron Emission Microscopy Studies of Molecular Beam Epitaxy Grown Quantum Wells***, **C. Tivarus**, J.P. Pelz, M.K. Hudait, S.A. Ringel,* The Ohio State University

Schottky diodes formed on GaAs quantum wells grown by Molecular Beam Epitaxy are studied using Cross-sectional Ballistic Electron Emission Microscopy (XBEEM), in order to determine the influence of quantum confinement and pinning effects on Schottky barrier (SB) formation. The diodes were formed by both in-situ and ex-situ gold deposition on cleaved sides of heterostructures composed of a sequence of GaAs quantum wells (QW) separated by AlGaAs barrier layers. Using this technique, we were able to determine the local SB height for each QW. We found that the SB height increases with decreasing the QW thickness d@sub QW@ , varying from ~0.91 eV for d@sub QW@ @>=@ 9 nm to ~1.04eV for d@sub QW@=1 nm. This dependence will be discussed in terms of the QW confinement energy as well as reduced pinning effects at the QW/metal interface. We will also compare XBEEM samples made by in-situ vs. ex-situ metal deposition to clarify the role of chemical treatment and of an interfacial oxide layer on the SB formation. Additionally, the cross sectional configuration offered a direct measure of electron beam spreading due to scattering inside the metal film, as a function of film thickness. This spreading was surprisingly large, with full width at half maximum spreading of ~16 nm (~23 nm) for a 4 nm (7nm) thick Au film. The measurements will be compared with model simulations to quantify inelastic and elastic hot-electron scattering processes in the bulk and at the interfaces of the metal film, and to gain insight into the controversial issue of whether lateral momentum is conserved during hot electron transport over a metal/semiconductor interface. Work was supported by NSF and Office of Naval Research.

10:00am **NS-FrM6 Defect Mediated Transport in Nanostructures by Scanning Impedance Spectroscopy***, **R. Shao**, M.P. Nikiforov, J. Vavro, D.A. Bonnell,* The University of Pennsylvania

Defects and interfaces can dictate the transport properties of macroscopic structures and completely dominate the behavior of nanostructures. We have shown that Scanning Impedance Microscopy (SIM) can be used to determine local electronic structures of scattering centers in nanotubes/wires and the perturbing effect of atomic interfaces on local continuum properties. This talk will combine SIM and low temperature transport measurements to quantify the effect of defects on transport in individual nanofibers and at atomically abrupt oxide interfaces in SrTiO@sub 3@ bicrystals. In the latter case we have found a defect induced phase transition at low temperature.

10:20am **NS-FrM7 Supramolecular [60]Fullerene/Porphyrin Assemblies on Metals***, **H. Spillmann**,* University of Basel, Switzerland*; D. Bonifazi,* ETH Zürich, Switzerland*; A. Kiebele, H.-J. Güntherodt,* University of Basel, Switzerland*; T.A. Jung,* Paul Scherrer Institute, Switzerland*; F. Diederich,* ETH Zürich, Switzerland

The unique electrochemical and photophysical properties of porphyrin and [60]fullerene compounds makes them promising candidates for the construction of two- and three-dimensional organic-based materials. An important question is how pristine C60 and self-assembled monolayer of porphyrin arrays will organize on surfaces. Self-assembly of electron-rich flat aromatic molecules such as porphyrins shall enable the selective formation of electron donating monolayer, which can be covered by pristine C60. The chromophore interaction between the electron donor (porphyrin) and acceptor (C60) should enhance a supramolecular multilayer structure. Herein, we report first Scanning-Tunneling-Microscopy investigations of the behaviour of several porphyrin derivatives on metal surfaces wherein single porphyrin molecules are forcefully arranged in self-assembled monolayer. The specific properties of the single porphyrin derivatives make such molecularly modified surfaces suitable

---

[1] **Peter Mark Memorial Award Winner**

candidates for patterned surfaces to allocate fullerenes. Consequently, first nanostructures based on the interaction of the fabricated porphyrin-based assemblies with fullerene molecules will be presented.

10:40am **NS-FrM8 Synthesis and Optical Characterization of Gold Nanoplates***, C.S. Ah,* ***W.S. Yun****, D.H. Ha, K.J. Kim,* Korea Research Institute of Standards and Science, Korea

We report on a high-yield synthesis and optical characterization of gold nanoplates. The nanoplates were prepared by controlled reduction of hydrogen tetrachloroaurate with reduced amount of sodium citrate in the presence of poly(vinyl pyrrolidone). The plates have a shape of either triangle or truncated-triangle of around 10@super 4@ - 10@super 5@ nm@super 2@ in area with a thickness of about 20 - 30 nm. High-resolution TEM analysis reveals that the individual plate is a single crystal with well-developed flat {111} facets. Optical spectra of the nanoplates show distinctive plasmon absorption bands which can be attributed to their highly-anisotropic shape. The optical characteristics are strongly dependent upon the size of the gold nanoplates. In particular, the absorption band in NIR region, which is believed to originate from the longitudinal dipole plasmon resonance, dramatically shifts to red when the planar size of the plate increases. We hope that this gold nanoplate should serve as an excellent platform for molecular self-assembly and as a useful building-block in developing new-materials and devices.

11:00am **NS-FrM9 Non-Spherical Metal Nanoparticles: Tuning Optical Properties by Controlling Structure***,* ***J.S. Shumaker-Parry****, H. Rochholz, F. Stefani, W. Knoll, M. Kreiter,* Max Planck Institute for Polymer Research, Germany

Gold colloids have been studied extensively due to the dependence of their optical properties on colloid size, interparticle spacing, and local dielectric environment. Recently there have been efforts to prepare non-spherical nanoparticles because of their unique electronic, optical and other physical properties. We have fabricated novel non-spherical metal nanoparticles by combining colloidal lithography, metal film evaporation and ion beam milling. This process produces a large number of metallic nanoparticles on a surface with uniform size and identical orientation in parallel, a major advantage compared to electron beam lithography methods. Gold and silver quartermoon and c-shaped nanoparticles have been fabricated. A finite element method was applied to classical electrodynamics for two-dimensional models of these nanoparticles in order to understand the optical characteristics. These calculations predict large electromagnetic field enhancements that are localized or uniformly distributed, depending on the nanoparticle structure. We have characterized the optical properties of the nanoparticles using extinction scattering cross section spectroscopy and single-particle light scattering spectroscopy. We show that the optical properties of the nanoparticles can be tuned by changing the size of the colloid mask and by controlling the opening of the c-structure.

11:20am **NS-FrM10 Elucidation of the Electronic Properties of Immobilized Alkanethiolate-Stabilized Gold Clusters and Nanoparticles Using Scanning Tunneling Microscopy**, *P.S. Weiss,* ***R.K. Smith****, S.U. Nanayakkara, B.A. Mantooth, G. Woehrle,* The Pennsylvania State University*; J.E. Hutchinson,* University of Oregon

The single electron transport properties of metal nanoparticles have led to great interest in their potential integration into nanoscale electronics. Here, we discuss and compare the electronic characteristics of isolated, solution-derived, and ligand-stabilized gold clusters (Au@sub 11@L@sub 10@) and nanoparticles (Au@sub 101@L@sub 43@), taken in both cryogenic (4 K, UHV) and ambient conditions using scanning tunneling microscopy and spectroscopy. The clusters and particles (d@sub CORE@ = 0.8 nm and 1.5 Â± 0.5 nm, respectively) are immobilized on alkanethiolate self-assembled monolayers with inserted dithiol molecules. We thoroughly characterize the self-assembled monolayer surface to which the nanostructures are attached with both local probes and ensemble measurements. At low temperature, the Au@sub 11@ clusters demonstrate Coulomb blockade behavior, with zero-conductance gaps resulting from quantum size effects.

11:40am **NS-FrM11 Optical Properties of Ordered Arrays of Vanadium Dioxide Nanoparticles***,* ***R. Lopez****, J.Y. Suh, R.F. Haglund Jr., L.C. Feldman,* Vanderbilt University

Arrays of vanadium oxide nanoparticles with long-range order have been fabricated by pulsed laser deposition in an arbitrary pattern defined by focused ion-beam lithography. Interaction of light with the nanoparticles is controlled by the geometrical arrangement as well as by the differing optical properties displayed by the metallic and semiconducting phases of VO@sub 2@. The particle arrays present a previously unknown scattering resonance in the blue region of the spectrum. The scattering is pronounced in the semiconductor phase, but is less intense and slightly blue-shifted in metallic state. This phenomenon is intrinsically interesting, since previous studies of VO@sub 2@ switching have been confined to the IR region, whereas this configuration produces the relevant optical effects of the transition in the visible spectrum. In addition, the transition to the metallic state does not exhibit the usual step function at the critical temperature. Instead, the scattered light begins to increase in intensity at 68°C, the temperature of the bulk phase transition, and reaches a maximum before falling to a lower value in the metallic state resulting in a anomalous double loop hysteresis. This transient scattering enhancement results from the order-disorder transition that occurs as the nanoparticles are transformed by random fluctuations. The disorder or inhomogeneity present during this process enhances the scattering by coherent contributions of length scales longer than the array lattice constant, the necessary additional Fourier components to describe a disordered system. Arrays such as this open up new opportunities to study surface plasmon interactions for nanoparticles in close proximity, with the added advantage that the interaction can be switched on by the thermally driven metal-semiconductor phase transition in VO@sub 2@.

Author Index

Bold page numbers indicate presenter

Author Index

Author Index