Thursday Morning, November 7, 2002

Processing at the Nanoscale
Room: C-109 - Session PN+SS-ThM

Patterning and Functionalization
Moderator: W.N. Unertl, University of Maine

8:20am **PN+SS-ThM1 Carbon Nanotube Synthesis and Non-Covalent Surface Chemistry**, ***H. Dai***, Stanford University **INVITED**

This presentation will cover our latest results on, (1) Patterned growth of carbon nanotubes architectures on surfaces. Strategies for assembling nanotubes at their synthesis stage by self-assembly or external forces to orient nanotubes will be shown. (2) (2) Charge transfer interactions between small molecules and polymers with nanotube surfaces and the influence to the physical properties of nanotubes will be discussed. Charge transfer and photochemical effects will be presented. (3) Various non-covalent functionalization schemes for nanotubes will be described. Molecular and metal species can be attached to nanotube sidewalls by pi-stacking, van der Waals and hydrophobic interactions, electroless deposition, metal coordination chemistry. Functionalization by biological molecules will also be presented. The implications of controlled chemical synthesis and functionalization to future nano-electronics for chemical and biological applications will be discussed.

9:00am **PN+SS-ThM3 Thiol Diffusion in Dip Pen Nanolithography**, ***P.E. Sheehan***, *S.E. Kooi, L.J. Whitman*, Naval Research Laboratory

Interest in the properties of nanometer scale objects has greatly increased in recent years and with it the desire for tools to create these objects. Dip Pen Nanolithography (DPN) is one promising tool because it is widely accessible, flexible in choice of materials, and capable of creating structures as small as 10 nm. Our research has expanded the range of molecules used in DPN and has calibrated the rate of their deposition and spread. Calibration of the deposition was performed by developing a model of the diffusive spread of thiols from an AFM tip.[1] To our knowledge, this model allowed the first direct determination of a diffusion coefficient for an alkanethiol on gold. The effect of alkane chain length and terminal on the diffusion coefficient was also studied, and we find that the length of the alkane chain significantly affects deposition. For instance, hexadecanethiol (16 carbons) deposits much more rapidly than the slightly longer octadecanethiol (18 carbons), indicating that chain-chain interactions strongly influence the deposition rate. A fundamental insight into the DPN deposition mechanism was also gained during these studies. It had been proposed that the water meniscus that naturally forms between an AFM tip and the scanned surface enables deposition. When we examined the effect of humidity on thiol diffusion, no correlation was found. Moreover, we find that deposition persists even after two days under dry nitrogen. For this reason, we propose that ODT is deposited directly onto the surface and does not require water as a medium.

[1] P. E. Sheehan and L. J. Whitman, Phys. Rev. Lett. 88 (2002) 156104.

9:20am **PN+SS-ThM4 Reversible Layer Phase Transition Controlled by the Scanning Tunneling Microscope Tip**, ***S. Berner***, *M. de Wild, L. Ramoino, S. Schintke*, University of Basel, Switzerland, *H. Suzuki*, Kansai Adv. Res. Center, Japan, *A. Baratoff, H.-J. Guentherodt*, University of Basel, Switzerland, *T.A. Jung*, Paul Scherrer Institute, Switzerland

Sub-phthalocyanine (SubPc) on Ag(111) shows a complex phase behaviour of the growing first molecular monolayer. With increasing layer coverage, 2D lattice gas, condensed honeycomb superstructure and hexagonal close packed layers are observed. A previous study of SubPc on Ag(111) dealt with the coexistence of the honeycomb superstructure and the 2D lattige gas and showed the high mobility of individual SubPc molecules at room temperature.[1] The complex phase behaviour is a general consequence of the repulsive nearest neighbour interaction between individual molecules and the diffusion at room temperature. In this work we studied SubPc layers with a coverage in the order of 0.7 monolayers on Ag(111) with room temperature scanning tunneling microscopy (STM). On large terraces the SubPc molecules form a hexagonal close packed (hcp) superstructure. However, experimental sequences on confined terrace areas (vacancy islands with diameters of 30-80 nm introduced by sputter defects) reveal interesting details about the condensation and evaporation of molecular islands on a nanometer scale. In such vacancy islands reversible phase transitions between 2D mobile and 2D condensed (hcp) phases could be controlled by the STM tip. In addition, rotational flipping of the orientation of condensed islands between two different substrate lattice registries occurred. Different microscopic mechanisms are discussed in the context of this newly observed complex behaviour. .

[1] S. Berner, M. Brunner, L. Ramoino, H. Suzuki, H.-J. Guentherodt, and T.A. Jung, Chem. Phys. Lett. 348 (2001) 175.

9:40am **PN+SS-ThM5 Covalent Nanopatterning of Liquid Phase Organic Molecules to Silicon Surfaces using Conductive Atomic Force Microscopy**, *M.W. Such, C.R. Kinser*, ***M.C. Hersam***, Northwestern University

Electron stimulated desorption (ESD) with ultra-high vacuum (UHV) scanning tunneling microscopy (STM) is a well-established technique for creating reactive patterns of dangling bonds on predominantly hydrogen passivated silicon surfaces. Gas phase surface chemistry occurs selectively with these nanopatterns, allowing for controlled deposition of materials down to the single molecule level. Although this approach is effective in UHV, it has not yet been utilized for the patterning of non-UHV-compatible materials. This paper describes an analogous means of creating reactive nanopatterns on hydrogen passivated Si(111) surfaces using conductive atomic force microscopy (cAFM) in liquid environments. Unlike cAFM patterning in air that induces oxidation on silicon surfaces, this approach suppresses oxidation through encapsulation of the tip-sample junction in an anhydrous organic solvent (e.g., toluene or dimethyl sulfoxide). Following ESD induced with cAFM, olefinic organic molecules suspended in the organic solvent environment spontaneously bind to the dangling bond patterns. To demonstrate this technique, exo-5-norbornene-2-ol has been patterned with 50 nm resolution on Si(111):H. Lateral force microscopy and force-distance spectroscopy confirm the hydrophilic nature of this molecule compared to the hydrophobic Si(111):H surface. Following deposition, these nanopatterned molecules have been subjected to a subsequent nucleophilic acyl substitution reaction with Lauroyl Chloride at 50°C for 24 hours. Consistent with the expected dodecyl ester modification of the adsorbed norbornene molecule, the resulting nanopattern appears hydrophobic in LFM analysis. The stability of these nanopatterns to subsequent chemistry suggests that the adsorbed molecules are covalently bonded to the silicon substrate. Further applications of this lithography for covalently nanopatterning polymers and biological molecules to silicon surfaces will also be discussed.

10:00am **PN+SS-ThM6 High Resolution Chemo-Mechanical Functionalization of Silicon Surfaces by Atomic Force Microscope**, ***R.C. Davis***, *B.A. Wacaser, T.L. Niederhauser*, Brigham Young University, *I.A. Mowat*, Charles Evans & Associates, *M.R. Linford*, Brigham Young University

We describe a versatile high-resolution method for chemical functionalization of silicon surfaces. An atomic force microscope (AFM) probe is used to mechanically induce chemical functionalization thereby simultaneously patterning and functionalizing the hydrogen-terminated silicon. A 20 nm radius of curvature probe is used to scribe the hydrogen-terminated silicon. When the Si-H and Si-Si bonds are broken in the presence of unsaturated hydrocarbons a reaction occurs in which the hydrocarbon chain is covalently bonded to the Si surface. Using this technique we have produced patches and patterned lines of alkene molecules on a Si (111) substrate with line widths down to 100 nm. Time of flight secondary ion mass spectroscopy measurements verifying the high-resolution chemical functionalization will be presented.

10:20am **PN+SS-ThM7 Fabrication of Si Nanostructures by Scanning Probe Oxidation and Tetra-Methyl Ammonium Hydroxide Etching**, ***F.S.-S. Chien***, Center for Measurement Standards, Taiwan, *W.-F. Hsieh*, National Chiao-Tung University, Taiwan, *S. Gwo*, National Tsing-Hua University, Taiwan, *A.E. Vladar, J.A. Dagata*, National Institute of Standards and Technology

We demonstrated that the process of scanning probe microscope (SPM) oxidation and anisotropic tetra-methyl ammonium hydroxide (TMAH) etching is a low-cost and reliable method to produce smooth and uniform silicon nanostructures on a variety of silicon substrates. Etched structures with a pitch of 100 nm, positive- and negative-contrast structures, and features height greater than 100 nm have been produced on bare silicon, Si_3N_4-coated and silicon-on-insulator wafers. Evolution of hexagonal pits on two-dimensional grid structures were shown to depend on the pattern spacing and orientation with respect to Si(110) crystal directions. We successfully combined SPM oxidation with traditional optical lithography in a mixed, multilevel patterning method for realizing micrometer- and nanometer-scale feature sizes, as required for photonic device designs. The combination of SPM oxidation and TMAH etching is a promising approach to rapid prototyping of functional nano-photonic devices.

10:40am **PN+SS-ThM8 Charge Trapping in Oxide-Nitride-Oxide-Silicon Structures Studied by Electrostatic Force Microscopy**, ***S.-D. Tzeng***, *Y.-C. You, S. Gwo*, National Tsing-Hua University, Taiwan, ROC

A novel approach of fabricating oxide-nitride-oxide-silicon (ONOS) charge storage structures is demonstrated by using the scanning-probe-induced oxidation process under ambient conditions. During the probe oxidation process, both positive and negative charges are injected and trapped inside the ONOS cell. By means of quantitative electrical force microscopy (EFM) measurements, we have investigated the trapping behavior of the probe-oxidation-induced charges. We found that the retention time of the negative charge is much shorter than the positive one. By measuring the decay lifetimes of these trapped charges after annealing at different temperatures, we have determined the trapping energies of both types of charges. We also found that, after high-temperature annealing, these trapped charges can be detrapped. The resulting ONOS cell can be used as a nonvolatile memory element with write/erase capability locally controlled by a biased scanning probe tip.

11:20am **PN+SS-ThM10 Ferroelectric Lithography for Multicomponent Nanofabrication**, ***D.A. Bonnell***, *S.V. Kalinin, R.A. Alvarez, X. Lei, R. Shao, Z. Hu, J.H. Ferris*, University of Pennsylvania

In spite of the variety of approaches to the assembly of nanowires, nanoparticles, and organic/biological molecules, device functionality has been achieved in only a few select systems. The organization of dissimilar molecular or nanostructural constituents into predefined structures necessary to yield functionality remains a challenge. We report here a novel approach that controls atomic polarization of ferroelectric substrates to vary local electronic structure. It will be demonstrated that chemical reactivity involving electron transfer is domain specific due to surface band bending. The minimum feature size is on the order of 3 nm and resolution positioning 10-20 nm. When combined with chemistry associated with self assembly, nanostructure composites consisting of oxide substrates, metal nanoparticles, and organic/biological molecules can be fabricated in predefined configurations. This leads to the potential to make electronic or opto-electronic devices on the 10 nm size scale. The approach will be demonstrated with simple devices.

11:40am **PN+SS-ThM11 Size-Induced Ferroelectric Phase Transitions in $PbTiO_3$ and $PbZrO_3$ Nanotubes Formed by Sol-Gel Template Synthesis**, ***B.A. Hernandez***, *K.-S. Chang, E.R. Fisher, P.K. Dorhout*, Colorado State University

Nanotubes of the perovskite ABO3 (A = Pb, B = Ti,Zr) have been prepared by sol-gel template synthesis. A size-induced ferroelectric phase transition for PbTiO3 and PbZrO3 nanotubes was observed by thermal analysis. The nanotubes were prepared within Whatman Anodisc templates (200 nm pore size) with a sol-gel method using titanium and zirconium alkoxides and lead acetate. Scanning electron microscopy demonstrated that the structures formed within the template were 50 Î¼m long tubes with 200 nm outer diameters. Transmission electron microscopy and electron diffraction revealed that the tubes were polycrystalline. Comparison of the d-spacing between electron and bulk powder X-ray diffraction patterns allowed assignment of the crystalline phase of the nanotubes as tetragonal for PbTiO3. Differential scanning calorimetery was used to monitor the ferroelectric phase transition temperature (Tc). Comparison between the bulk powders and nanotubes showed an anomalous decrease Tc. Values for PbTiO3 Tc were determined to be between 496.5°- 489.7°C for bulk powders with grain sizes of 75 and 35 nm respectively and 234.4°C for the nanotubes having a grain size of 11.2 nm. Preliminary results for PbZrO3 shows that the Tc decreases from 229.9 for bulk powder to 123.6 for nantRoom temperature Raman spectra also indicated structural size effects by monitoring the energies of the E1(TO) soft mode and relative intensities of the E2(TO) mode.

Processing at the Nanoscale
Room: C-109 - Session PN-ThA

Charged Particle Patterning and Emission

2:00pm **PN-ThA1 Nanoscale Electron Beam Stimulated Processing**, ***P.D. Rack***, *R.C. Burns, Y. Deng, Y. Choi, D.C. Joy,* University of Tennessee

The ability to manipulate materials at the nanoscale is critical for the nanotechnology revolution that is occurring. To intelligently design and or repair nanoscale devices requires techniques to selectively and nanoscopically deposit and remove material in a controllable fashion. Current techniques to selectively deposit or etch microscopic features utilize ion beam deposition and etching, laser ablative etching using far field and near field optics, and mechanical abrasion using a fine microtip. In this paper we will discuss electron stimulated nanoscale processing. The experimental set-up for the process will be presented and experimental results for electron stimulated nanoscale processing will be shown. The relevant electron-solid, electron-gas, and gas-solid interactions that are critical for nanoscale electron beam processing will be discussed. The effect that the beam energy has on the reaction rate for stimulated deposition and etching will be illustrated and the growth kinetics will be discussed. To minimize the effective spot size, strategies to control surface diffusion as well as electron-gas scattering will also be discussed.

2:20pm **PN-ThA2 Electron Beam Patterning with Carboneous Contamination Rezists below 10 nm Linewidth**, ***M. Malac***, University of Alberta, Canada, *J. Lau,* Brookhaven National Laboratory, *R. Egerton, M. Freeman,* University of Alberta, Canada, *Y. Zhu*, Brookhaven National Laboratory

We have studied the processes determining the resolution limits of contamination patterning in a transmission electron microscope (TEM) as a means to produce magnetic nanostructures. By optimizing the exposure parameters we achieved linewidth of 7 nm. Sputter etch was used to transfer the pattern to cobalt, permalloy and bismuth films on silicon nitride membranes. Previously the resolution of the technique was determined by the crystallite size of the patterned film.[1] We have investigated patterning of our structures within one large crystallite and we have studied the limitations dictated by the kinetics of the surface diffusion processes. A comparison of pattern writing at conditions when importance of surface diffusion is suppressed (high dose rate and high writing speed) with diffusion controlled writing (slow writing at low dose rate) was made. We have explored the reproducibility and suitability of different types of materials for precontaminating the samples. Transmission electron microscopy, electron holography, electron energy loss spectroscopy and high resolution TEM was used to characterize structure and to study properties of such structures.

[1]Broers et al, Appl. Phys. Letters 29 (9), 1976 page 596.

2:40pm **PN-ThA3 A Study of PMMA EBL Cross-sections Prepared by a Novel Process**, ***W. Hu***, *T. Orlova, G.H. Bernstein*, University of Notre Dame

We have developed a novel technique of silicon cross-section preparation with high breaking precision with which we have studied cross-section profiles of sub-50 nm electron beam lithography (EBL) patterns in PMMA resist, including post-exposure aging effects. This technique enables us to break our samples along a desired axis with about 1 µm precision, and gives cross-sections allowing imaging with scanning electron microscope (SEM) at any angle. This is a complementary method to cleaving, wedge-polishing and focused ion beam, the last two of which create damage to the surface of the exposed edges. The precise breaking of the wafer or small sample was accomplished by high-aspect-ratio plasma etching of a 2~10 µm wide line in an inductively coupled plasma etcher using the Bosch process (Alcatel 601E) with small sample areas in the line unetched for EBL. After EBL, wafers were broken along the etched line using a simple mechanical. Cross-section studies can provide improved information on the nanometer scale about PMMA EBL profiles, development contrast, and the metal or molecule liftoff process. However, damage to PMMA by the SEM imaging, cross-section preparation and sample metal coating interfere with data analysis. We have developed an optimized process which enables us to obtain nearly original PMMA EBL profiles by coating samples with AuPd alloy using thermal evaporation first and followed by a plasma sputter coating. The fully-covered PMMA trenches are broken along the desired axis and imaged with our Hitachi S-4500 cold cathode field emission SEM. Using these techniques, we studied the aging effect of PMMA resist before development of EBL, which is seldom taken into consideration in fabrication processes. Our cross-section results of PMMA EBL trenches indicate a loss of contrast due to one week aging prior to development, and will result in unsuccessful liftoff. Other cross-sectional views of EBL in a variety of resists will be discussed.

3:00pm **PN-ThA4 Nanometer Scale Patterning of Dielectric Surfaces with Combined Electron/laser Beams and Chemical Exposure**, ***K.H. Nwe***, *J.T. Dickinson*, Washington State University

We examine the nanometer scale patterning of insulating surfaces exposed to simultaneous beams of radiation and reactive chemicals. Specifically, we show that ionic crystals in the presence of low pressure water exposure leads to rapid material etching in self-organized patterns under UV laser or keV electron irradation. Radiation effects on reactive layers on single crystal inorganics are poorly understood. We find that dense ordered arrays of highly oriented nanoscale conical structures, with aspect ratios greater than 200, are produced under such exposure. We show that the nanostructure formation mechanism involves photo/electron stimulated decomposition of the matrix via defect mediated interactions. Using time resolved mass spectroscopy we are able to provide detailed kinetics for these electronic etching processes.

3:20pm **PN-ThA5 Field Emitter Arrays with Sharp Tips for THz Microwave Source**, ***C. Peng***, *S.W. Pang*, The University of Michigan

Ballistic tunneling transit time device consists of a field emitter cathode, a drift region, and a collecting anode. These new transit time devices can produce mW level power in THz range with optimized operating voltage and anode to cathode separation. The field emission devices also need to have sharp tips, high emission current, low threshold voltage, and small dimensions for high packing density. In this work, nanofabrication technology to generate large arrays of sharp Si field emitters is developed. Sharp Si tips with tip radius of 20 nm are fabricated by dry etching with Cl_2 in an inductively coupled plasma system. The tip sharpness, height, and profile are controlled by balancing the lateral etch rate of the SiO_2 mask and the vertical etch rate of the Si substrate. It is found that tip height and tip radius vary with rf power applied to the plasma source and the etch time. Tip height decreases with rf power and increases with etch time, while tip radius increases with source power and decreases with etch time. Uniform, large arrays of Si field emitters are formed with tip density of $1.1x10^7$ tips/cm^2 and tip height varying from 2 to 4 µm. For these field emitters to function as THz microwave source, close tip to anode spacing in the range of 0.5 to 2 µm is needed. Etch time, spacer, and bonding technology are used to provide flexible and precise control of the tip to anode distance. In addition, emitter tip sharpening by oxidation and coating the tips with low work function materials will be studied to improve the emission current characteristics.

3:40pm **PN-ThA6 Structure and Field Emission Properties of SiC Nanotip Arrays Fabricated by Electron-cyclotron-resonance Plasma Process of Monolithic Si Wafer**, ***L.C. Chen***, National Taiwan University, *H.C. Lo, J.S. Hwang, J.S. Hsu,* Institute of Atomic and Molecular Sciences, *C.F. Chen,* National Chiao-Tung University, Taiwan, *D. Das, K.H. Chen*, Institute of Atomic and Molecular Sciences

Fabrication of SiC nanotip arrays of a few microns in height and around 1 nm in diameter at the tip and of density as high as 10^{12}cm^{-2} is reported. The mechanism of the nanotip formation by electron cyclotron resonance (ECR) plasma process and detailed structure analyses using high resolution TEM will be presented. It is concluded that the tips are primarily composed of SiC. The nanotip arrays showed magnificent field emission property with typical field emission current of 0.5 mAcm^{-2} at an applied field as low as 0.8 V/µm. Furthermore, the nanotip arrays also exhibited excellent stability, as evident by temporal evolution of the emission current at a constant applied voltage measurement which showed less than 3% fluctuation in one hour. The SiC nanotip array produced by ECR-plasma process of monolithic Si wafer offers a reliable, economic field emission electron source alternative to carbon nanotubes. Formation of the SiC nanotip on top of a Si cantilever has also been demonstrated. Such geometry provides potential applications in ultrahigh resolution SPM and field emission microscopy.

4:00pm **PN-ThA7 Field Emission from Well-Aligned Heterojunctions of Carbon Nanotubes and Silicon Nanowires**, ***M. Lu***, *M.-K. Li, H.-L. Li*, Lanzhou University, P.R. China

Silicon nanowires (SiNWs) has recently attracted much attention due to its unusual properties. However, it is easily oxidized in air, which can hurt the uniformity and the efficiency of electron emission. It is our motivation to design nanowire/tube growth process and fabricate well-aligned

CNTs/SiNWs heterojunctions by chemical vapor deposition (CVD) based on AAO template-synthesis method.[1] It is clearly observed from SEM and TEM images the junctions consist of a core-sheath structure and have a highly-orientation. The filling material is proved to be a polycrystalline Si from SAED pattern. Field emission measurements show the turn-on field of the junctions decreases to ~7 V/μm from ~14 V/μm (pure SiNWs) and the maximum emission current density increases to ~35 mA/cm^2 from ~3 mA/cm^2 (pure SiNWs). A significant improvement in the turn-on field, the total emission current and the emission stability is apparent from the junctions compared with pure SiNWs. We also notice that the threshold field is in the range of 22-25V/μm for the junctions. The Fowler-Nordheim plot almost follows a linear relationship that indicates the field emission from the junctions is a barrier tunneling, quantum mechanical process. Moreover, the field emission increased with decreasing diameter of the junctions. During 24 h of continuous operation at 5 mA/cm^2, the current fluctuation was as low as ±4% and the average current did not decrease over this period. When a sample was found to air for weeks after it was grown, it exhibited essentially the same emission behavior as the freshly grown surface. This suggests that the sheath of CNTs is indeed stable and chemically inert.

[1], C.W. Wang, M.K. Li, and H.L. Li, Science in China 44(2), 234 (2001)

4:20pm **PN-ThA8 Evolution of Surface Morphology and Microstructure during Ion Sputtering of Diamond**, ***D.P. Adams***, *T.M. Mayer, M.J. Vasile*, Sandia National Laboratories

This work investigates the morphology and structure of diamond surfaces that evolve during focused ion beam (FIB) sputtering and chemically amplified processes. We include a detailed study of morphology for a broad range of ion incidence angles (0-88 deg) and dose. A single ion (Ga) and incident energy (20keV) are used. For incidence angles between 30-75 degrees referenced from substrate normal, we observe the formation of ripple patterns. Ripples form with a wavevector aligned to the incident beam direction over this range of angles, similar to that predicted by Bradley-Harper for small theta. In order to develop an understanding of the mechanisms underlying a rippled topography, we analyze the evolution of morphology for increasing dose. AFM is used to quantify changes in ripple wavelength and amplitude, while TEM and Raman spectroscopy probe the structure in the near surface region. Beginning at 75 and continuing to 87 degrees, a step/terrace morphology forms during sputtering. Microfacets develop at the earliest stages (lowest dose) indicating a role of initial surface topography. Obvious changes in terrace length over this range of angles suggest that morphology is affected by shadowing between neighboring features. In general, a decrease in yield is discovered with increasing dose over this entire range of angles (30-87 deg). The presence of ripples/microfacets and, more specifically, their evolving shape influence the number of sputtered atoms per ion. Dramatic effects on yield (200% decrease) with increasing dose are observed at angles >80 degrees. Additional research investigates the effects of chemical environment on morphology. Experiments involve ion bombardment in the presence of H2O, methanol and H2O2. When sputtering in the presence of these gases, dramatic changes in morphology result as a function of dose and incidence angle. Changes in sputter yield due to the presence of a gas are also quantified as a function of incidence angle from 0-88 degrees.

4:40pm **PN-ThA9 Nanoscale Morphology Control Using Ion Beams**, ***M.J. Aziz***, Harvard University **INVITED**

Low energy ion irradiation of a solid surface can be used to control surface morphology on length scales from 1 micron to 1 nanometer. Focused or unfocused ion irradiation induces a spontaneous self-organization of the surface into nanometer-sized ripples, dots, or holes; it also induces diameter increases and decreases in a pre-existing nanopore by a tradeoff between sputter removal of material and stimulated surface mass transport. Here we report experiments that illuminate the kinetics of evolution of the surface morphological instability; the influence of initial and boundary conditions on guiding the self-organization; and the kinetics governing the fabrication of nanopores for single-molecule detectors.

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