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.

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