

## Processing at the Nanoscale Room 317 - Session PN-ThA

### Molecular Monolayers

Moderator: P.S. Weiss, The Pennsylvania State University

2:00pm **PN-ThA1 AFM-Based Lithography and Conductive Probe Measurements with Substituted Oligo(phenylene ethynylene) Molecular Wires on Au(111)**, *J.C. Garno, J.D. Batteas*, National Institute of Standards and Technology

AFM-based lithography is combined with conductive probe AFM (CP-AFM) measurements to characterize the surface structure and conductive properties of designed test platforms comprised of substituted oligo(phenylene ethynylene) molecules within a matrix of alkanethiol self-assembled monolayers (SAMs). Oligo(phenylene ethynylene)s on Au(111) are excellent candidates for molecular electronics, due to their rigid, planar structure and pi-conjugated backbone. When substituents are attached to oligo(phenylene ethynylene)s, electronic properties such as negative differential resistance and molecular scale switching behavior have been reported. Nanopatterned test platforms may provide a means to obtain a highly reproducible contact area in which the alkanethiol matrix of the test platforms serves as a boundary and provides an insulating frame of reference in the areas surrounding test elements. In CP-AFM, the probe is placed directly on the surface of the fabricated nanostructure, at a certain applied force. The alkanethiol matrix may be used as an internal calibration for CP-AFM measurements, with direct side-by-side comparisons of the alkanethiol matrix versus test molecule. Nanopatterns generated using AFM-based nanofabrication furnish local measurements of the thickness of molecular wire SAMs, using matrix alkanethiols as a height reference. By systematically varying certain parameters, such as the size, composition, geometry, and arrangement of test elements, we anticipate that changes can be correlated with measured conductivity, to shed light on predicting how electrical properties vary with molecular structure. Useful design parameters for molecular electronics which could be gained from this approach include the critical geometry and size thresholds for functional device elements, differences in electrical conductivity of materials, and the structural motifs best suited for devices.

2:20pm **PN-ThA2 Chemical Nanostructures as Templates for the Fabrication of Laterally Patterned Polymer Brushes**, *A. Paul, A. Küller*, Universität Heidelberg, Germany; *U. Schmelmer, R. Jordan*, TU München, Germany; *A. Ulman*, Polytechnic University; *M. Grunze, W. Eck*, Universität Heidelberg, Germany; *A. Götzhäuser*, Universität Marburg, Germany  
Chemical Nanolithography@footnote 1@ utilizes electron beams for the controlled modification of self-assembled monolayers (SAMs). E-beam irradiation of SAMs of nitrophenylthiol causes a lateral cross-linking reaction of the biphenyl mesogen along with a simultaneous conversion of the terminal nitro groups to the amine.@footnote 2@ Consecutive reactions such as chemical coupling of chromophores or surface-initiated polymerization can be performed in predefined (irradiated) areas.@footnote 3@ We show the fabrication of polymer brushes with lateral dimensions down to 50 nm by utilizing chemical nanolithography templates for surface-initiated polymerization. Limits of resolution and potential applications will be discussed. @FootnoteText@ @footnote 1@ A. Götzhäuser et al., Adv. Mater. 13, 806, (2001)@footnote 2@ W. Eck et al., Adv. Mater. 12, 805, (2000)@footnote 3@ U. Schmelmer et al., Angew. Chem. Int. Ed. 42, 559 (2003)

2:40pm **PN-ThA3 Reactions of Silicon and Gold Nanostructures on Surface-Templated Molecule Corrals**, *Y. Liu, Z Zhang, M. Wells, A.V. Teplyakov, T.P. Beebe, Jr.*, University of Delaware  
Semiconductor and metal nanostructures display novel size-dependent properties as a result of quantum confinement. New concepts and new challenges evolve with regard to the potential applications of these nanostructures in molecular electronics, sensors, biological interfaces and biomedical applications, advanced material design, charge storage, light-emitting diodes, energetic materials, and other applications that remain unknown at present. Semiconductor and metal nanostructures on surface-templated molecule corrals are unique because large numbers of these nanostructures with controlled size, height, shape, surface density, and position or pattern can be produced quickly and efficiently with a narrow size dispersion in a parallel process that takes only minutes. In this work, the formation and modification of silicon and gold nanostructures templated on the highly oriented pyrolytic graphite (HOPG) basal plane will

be discussed. Molecule corrals are typically formed with a high degree of control by a simple bench-top process in an oven operating at approximately 650 Å°C in the ambient air from the preexisting natural defects or manmade (ion-beam bombardment) defects on the surface. Silicon and gold nanostructures are vacuum evaporated onto these size- and shape-controlled molecule corrals. These nanostructures are then functionalized with a number of reagents, including organosilanes and organothiols. Scanning tunneling microscopy, atomic force microscopy, time-of-flight secondary ion mass spectrometry, Fourier-transform infrared spectroscopy and X-ray photoelectron spectroscopy are used to characterize the degree of chemical modification of surface-templated nanostructures before and after modification.

3:00pm **PN-ThA4 Molecular Monolayers for Interfacing Organic and Biological Molecules to Group IV Semiconductors**, *R.J. Hamers*, University of Wisconsin-Madison  
**INVITED**

The burgeoning fields of organic electronics, molecular electronics, and bio-electronics are all placing increased emphasis on electrically interfacing inorganic materials such as silicon and diamond with organic and biological materials. Over the last several years we have been exploring new methods for fabricating and patterning hybrid interfaces on silicon and diamond surfaces, and understanding how the specific chemical chemical bonds and nanometer-scale structures control the resulting electrical properties of the interfaces. In ultrahigh vacuum the reactions of C=C bonds, S-H bonds, and O-H bonds can be used as the basis for preparing covalently-bonded layers that exhibit specific reactive and/or non-reactive functional groups, which can in turn be used for linking more complex films (pentacene) and structures (DNA) to the surfaces. Essentially identical reactions are used to link organic molecules with H-terminated silicon and diamond under ambient (atmospheric pressure) conditions, using ultraviolet light to initiate the reactions. We have been assessing the molecular conductivity on an atomic level via STM measurements of the apparent height, and on more macroscopic scales by measuring interfacial impedance after the molecular monolayers are covered with conductive materials such as the pentacene or after they are linked to biological molecules such as DNA. In this talk I will summarize what we have learned about how to use organic monolayers as electrical interfaces to pentacene films, DNA molecules, and other nanometer-scale structures of interest.

3:40pm **PN-ThA6 Covalent Linkage of Hydrocarbon Moieties and Addition of Organic Functional Groups on Si(111)**, *T. Yamada, H.S. Kato, K. Shirasaka, M. Noto, M. Kawai*, RIKEN, Japan

Deposition of unsaturated hydrocarbon moieties (CH@sub 2@=CH- etc.) on H-terminated H:Si(111)(1x1) surface was performed by Grignard reaction, and addition of boranes and halogens to the C=C double bond was attempted by the methods of wet chemical organic synthesis. The adsorbates formed on Si(111) were investigated by HREELS, AES, etc. in ultrahigh vacuum. Treating H:Si(111) in a tetrahydrofuran (THF) solution of CH@sub 2@=CHMgCl resulted formation of adsorbates with a major amount of -CH@sub 2@- and a minor amount of CH@sub 2@=, detected by HREELS. The formation of saturated -CH@sub 2@- seems to be due to inter-adsorbate bonding of vicinal CH@sub 2@=CH-groups right after deposition. This parasitic reaction was avoided by using a 1:3 - 5 mixture of CH@sub 2@=CHMgCl and CH@sub 3@MgBr in THF to insert inactive CH@sub 3@- groups among CH@sub 2@=CH- adsorbates. HREELS revealed the ratio of CH@sub 3@:CH@sub 2@=CH in the adlayer was approximately equal to that in the Grignard solution. This sort of CH@sub 2@=CH- moieties diluted in CH@sub 3@- can be useful in reactions with bulky reagents. To realize the terminal hydration of CH@sub 2@=CH:Si(111) into OH-CH@sub 2@-CH@sub 2@:Si(111), hydroboration reaction with a borane reagent 9-BBN was attempted in THF. Deposition of boron was detected by AES, indicating that 9-BBN was bonded by breaking CH@sub 2@=CH bonds. Further attempt to complete the hydration by H@sub 2@O@sub 2@ solution was made, and we are trying to distinguish the OH group on the -CH@sub 2@-CH@sub 2@- moiety from OH attached on surface SiO@sub 2@ impurities by HREELS. Addition of HBr on CH@sub 2@=CH:Si(111) was performed by a moderate reaction with HBr in organic solvents. Our goal is to gain a freedom of terminating Si surface with desired functional groups. This is a key technology in grafting polymers and biomolecules such as DNA and peptides to construct intelligent chemically functional system on silicon.

# Thursday Afternoon, November 6, 2003

4:00pm **PN-ThA7 Templated Growth of One-dimensional Molecular Wires on Si(100) Using Multi-step Feedback Controlled Lithography**, *R. Basu, N.P. Gusinger, M.C. Hersam*, Northwestern University

This study demonstrates the fabrication of one-dimensional molecular wires on the Si(100) surface with atomically precise control over the position and length of each wire. Specifically, styrene molecules, which are known to experience self-directed growth on Si(100) surface along dimer rows, have been induced to grow from individual dangling bonds that have been created on the hydrogen-passivated Si(100)-2x1 surface through feedback controlled lithography (FCL) using a room temperature ultra-high vacuum (UHV) scanning tunneling microscope (STM). The site-specific creation of individual dangling bonds allows control over the position of the styrene wires whose growth is confined along a dimer row. FCL has also been used to create an additional pair of dangling bonds at two different positions within the same dimer row to allow for controlled chemisorption of the organic free radical, 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO). The presence of the bounded TEMPO molecules physically restricts the growth of the styrene chain beyond the specified length along the dimer row and thus allows unprecedented control over the length of the molecular wires. Current-voltage spectroscopy has been performed on the styrene and TEMPO molecules. Based on the spectroscopic data, bias dependent STM conductance images of the molecular wires have been obtained.

4:20pm **PN-ThA8 UHV Characterization of Adsorbates Deposited in Ambient from Solution onto Si(001):H-(2x1)**, *L.A. Baker, A. Laracuente, L.J. Whitman*, Naval Research Laboratory

The marriage of nanoscale organic components with semiconductor devices for molecular electronics and sensing applications requires new approaches to fabrication. For example, whereas most device fabrication occurs in an ultra-high vacuum (UHV) system, organic materials chemistry often begins in a solution-filled beaker. We are using H-terminated Si(001) prepared in UHV as a robust substrate for ambient surface chemistry that can subsequently be characterized in UHV by STM. As demonstrated by Hersam, et al.,@footnote 1@ Si(001) terminated with H in UHV can be removed to an ambient environment for hours and still appear as a relatively clean, well-ordered Si(001):H-(2x1) surface upon return to UHV. We now find that this surface can be exposed in ambient to chlorinated solvents (e.g., CHCl@sub 3@) with minimal surface modification observed following reintroduction to UHV. In addition, we will present results showing that organic molecules, such as porphyrins, can be deposited in this way and subsequently characterized in UHV with STM. @FootnoteText@@@footnote 1@M. C. Hersam, et al., Appl. Phys. Lett. 78, 7 (2001).

4:40pm **PN-ThA9 Nanoscale Fabrication and Characterization of Chemically Modified Silicon Surfaces Using Conductive Atomic Force Microscopy in Liquids**, *C.R. Kinser, D.E. Kramer, M.W. Such, P. Bertin, H. Jin, S.T. Nguyen, M.J. Bedyzk, M.C. Hersam*, Northwestern University

Self-assembled monolayers of terminal alkenes on hydrogen passivated silicon provide an attractive route for covalent organic functionalization of silicon surfaces. This talk addresses two important experimental issues that improve the applicability of these surfaces for potential device applications: (1) Means of verifying the conformation of terminal reactive groups; (2) Strategies for patterning these monolayers down to the nanometer length scale. The first issue is addressed using X-ray reflectivity and X-ray standing wave techniques at the monolayer level. X-ray characterization of a bromine tagged analog of ethyl-undecylenate on Si(111) show that the monolayer coverage is 0.59 and the bromine lies 14.6 Å above the silicon surface. This data illustrates that the molecule is reacted to the surface via the terminal alkene, thus presenting the bromine functionality for post-chemistry. In this manner, the effectiveness of subsequent chemical reactions on functionalized silicon surfaces can be efficiently forecasted. The remainder of the talk describes a novel strategy for nanopatterning monolayers on hydrogen passivated silicon directly from the liquid phase. In Liquid Phase Nanolithography, hydrogen desorption is induced by applying a bias across a conductive atomic force microscope tip-sample junction submerged in an organic solvent. Appropriately chosen molecules suspended in the solvent directly chemisorb on the depassivated lines. We will present results for patterning neat undecylenic acid methyl ester on H:Si(111) with 50 nm spatial resolution using this technique and suggest approaches for utilizing this scheme to fabricate biomedical nanosensors.

5:00pm **PN-ThA10 Imaging of Monomolecular Lithographic Patterns by X-ray Photoelectron Spectromicroscopy and X-ray Absorption Spectromicroscopy**, *M. Zharnikov*, Universität Heidelberg, Germany; *R. Klauser*, National Synchrotron Radiation Research Center, Taiwan; *A. Paul, A. Götzhäuser*, Universität Heidelberg, Germany; *A. Scholl*, Lawrence Berkeley National Laboratory

The development of novel approaches for the fabrication of nanostructures and, in particular, chemical and biological patterns is an important technological and scientific issue. One of perspective methods applies electron-beam patterning of chemisorbed monomolecular films (so-called self-assembled monolayers - SAMs), with the major advantage to tailor the resist properties through the exact architecture and packing of the molecular constituents. We have utilized scanning soft X-ray photoelectron and X-ray absorption spectromicroscopy to image and characterize different electron-beam patterned SAMs on gold substrates. Both techniques rely on characteristic spectroscopic features, which makes them chemically sensitive. The XPM measurements have been performed with a scanned zone-plate-focused X-ray beam and a 16 channels photoelectron spectrometer while the XAM images were collected with a X-ray PEEM working in a total electron yield (TEY) acquisition mode. The lateral structures in all SAM-based patterns could be clearly distinguished by both XPM and XAM. Chemical and physical changes in some of the resists could be directly monitored. The strength and limits of XPM and XAM to image monomolecular lithographic patterns are discussed. The major constrains of XPM are a strong inelastic background at the position of characteristic emissions and a rather limited (at present) lateral resolution. The major constrain of XAM is a rather poor surface sensitivity due to a large probing depth in the TEY acquisition mode. Ways to overcome the experimental constrains are considered, along with the issue of X-ray damage, which might be relevant at an X-ray exposure required for the acquisition of high-quality XPM and XAM images.

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