Tuesday Afternoon, October 3, 2000

Processing at the Nanoscale/NANO 6
Room 302 - Session NS+NANO6+SS+MC-TuA

Self-assembly and Self-organization

Moderator: R. Wiesendanger, University of Hamburg, Germany

2:00pm **NS+NANO6+SS+MC-TuA1 Dip-Pen Nanolithography: A New Tool for Generating and Studying Soft Nanostructures***, **C.A. Mirkin**, S.A. Brennan, L.M. Demers, S. Hong, P.V. Schwartz, D.A. Weinberger,* Northwestern University **INVITED**

A new type of ultrahigh resolution soft-lithography, Dip-Pen Nanolithography (DPN) that is interfaceable with biomolecules and biofunctionalized building blocks will be presented. This soft lithography allows one to routinely pattern structures, in serial or parallel fashion, with sub 50 nm spatial and line-width resolution with near-perfect alignment. Implications in materials synthesis, electronics, and biodiagnostics will be discussed.

2:40pm **NS+NANO6+SS+MC-TuA3 A Step Toward Making and Wiring-up Molecular-Scale Devices with a Self-Directed Growth Process***, G.P. Lopinski, D.D.M. Wayner, D.J. Moffatt,* National Research Council of Canada*; **R.A. Wolkow**,* National Research Council of Canada, Canada

Our understanding of and control over molecular adsorption on silicon has advanced very significantly in the last several years. It is now possible to provide a microscopic picture of structure and bonding in covalently attached molecule-silicon surface systems. This detailed understanding of adsorbate-surface structures was entirely lacking when the first wave of enthusiasm for molecular devices crested roughly 20 years ago. While many ideas for molecule-scale devices have been put forward in the past, the tools - both synthetic and analytical - to pursue those ideas did not exist. Now, the control necessary to begin exploring ways to incorporate organic function into existing technologies or, eventually, to make new molecule-scale devices is within reach.@footnote 1@ Experimental and modeling methods have emerged that effectively extend the resolution of STM to see the details of adsorbed molecule structure and bonding. In the next several years it is now realistic to expect structures and concepts dreamed about for decades to begin to be realized. This talk will focus on a self-directed growth process for creating molecular nanostructures on silicon.@footnote 2@ @FootnoteText@ @footnote 1@ Controlled Molecular Adsorption on Si: Laying a Foundation for Molecular Devices, R.A. Wolkow, Annual Review of Physical Chemistry, volume 50, 413-41, 1999. @footnote 2@ Self-Directed Growth of Molecular Nano-Structures on Silicon, G.P Lopinski, D.D.M. Wayner and R.A. Wolkow, Nature in press.

3:00pm **NS+NANO6+SS+MC-TuA4 Control of Spatial Distribution of Self-Assembled Diacetylene Compounds by Co-deposition with Fatty Acid Molecules***, **Y. Kuwahara**, G.-M. Zhang, J.-W. Wu, M. Akai-Kasaya, A. Saito, M. Aono,* Osaka University, Japan

Control of self-assembled surface structure of functional organic molecules has been attracting intensive interest from a viewpoint of future applications such as novel material structures for nanometer-scale molecular devices. We have investigated self-assembled surface structures of two different chain organic molecules co-adsorbed on HOPG by use of scanning tunneling microscopy. The subject molecule was 10,12-tricosadiynoic acid, which is one of the diacetylene compounds possessing the possibility of being polymerized into macromolecular wire and/or sheet, and several kinds of fatty acids were used as buffer molecules. We used Langmuir Blodgett method for the fabrication of the molecular monolayers. In order to achieve the parallel molecular arrangement, the surface pressure for the deposition was deliberately controlled much lower than the saturate pressure and the substrate was horizontally oriented. A variety of molecular patterns inside the two-component monolayers were revealed, which could be briefly grouped into 'phase separation pattern', where microscopically pure 10,12-tricosadiynoic acid and fatty acid were observable respectively, and 'alternative pattern', in which the lamellae of the two sorts of molecules emerged alternatively. In order to evaluate the mechanism for the two dimensional surface ordering, we have also done the ab-initio molecular orbital calculation and the proposed structural model of the surface self-assembly is in good agreement with the theoretical simulations. Consequently, the possibility of controlling the spatial distribution of the diacetylene compounds on the solid surface has been demonstrated.

3:20pm **NS+NANO6+SS+MC-TuA5 The Interaction of Metal Atoms with Self-assembled Organic Monolayers***, **A.V. Walker**, B.C. Haynie, N. Winograd,* The Pennsylvania State University

Organic monolayers show great promise as materials for a wide range of technological applications. An understanding of the nature of the metal atom - organic monolayer interaction is vital in the development of molecular electronic devices. Recently it was demonstrated that deposited Al atoms can penetrate through an n-alkyl monolayer to the monolayer / Au (111) interface. This phenomenon is believed to occur via thermally activated transient defects in the monolayer. In this paper, we explore the thermodynamics of this system using time-of-flight secondary-ion-mass-spectrometry (TOF SIMS) and demonstrate that at low temperatures the rate Al atom penetration into the monolayer is reduced. We have also studied the interaction between other promising molecular wire candidates and metal atoms.

3:40pm **NS+NANO6+SS+MC-TuA6 Chiral Surface Reconstruction by Largish Molecules***, **M. Schunack**, L. Petersen, A. Kühnle, E. Laegsgaard, I. Steensgard, F. Besenbacher,* University of Aarhus, Denmark

Temperature-controlled scanning tunneling microscopy studies provide insight into the bonding, ordering and mobility of large organic molecules at metal surfaces. This is illustrated by investigations of disc-like molecules on a Cu(110) surface with a variable temperature STM, which can be operated down to 25 K.@footnote 1@ Hexa-tert-butyl decacyclene (HtBDC) self-assembles upon deposition onto Cu(110) above 250 K and forms a double-row structure in two directions surrounded by fast-diffusing single molecules. Nano-manipulation experiments with the STM at low temperatures revealed an underlying chiral reconstruction of the Cu surface. This consists of holes of approximately 14 Cu atoms pulled out of the surface. Surprisingly, the observed reconstruction is chiral. By gently annealing of the molecule structure at higher coverages, large enantiomerical pure domains with two different orientations build up. By means of simple effective medium theory calculations, we estimate the lower bound of the adsorption energy to be E@sub ad@ = 0.45 eV, and can give a plausible explanation for the observed structure. @FootnoteText@ @footnote 1@ L. Petersen, M. Schunack et al., submitted to Review of Scientific Instruments.

4:00pm **NS+NANO6+SS+MC-TuA7 From Functionalisation of Single Molecules to Self-organisation of Nano-structured Thin Films***, **Q. Guo**,* University of Birmingham, U.K. **INVITED**

The combination of functionalisation of individual molecules with self-organisation of the molecules into functional structures is a promising route for the fabrication of nanoscale electronic and optoelectronic devices. In this talk I will present experimental findings of nanostructured thin films prepared using this method. The dependence of the structure of molecular monolayers on the functionality of individual molecules will be demonstrated using chemisorbed acetate and benzoate species on TiO@sub 2@ surfaces as an example. Both acetate and benzoate attach to the substrate through strong bonding between the carboxyl end of the molecules and the metal cations at the surface of TiO@sub 2@. In the case of benzoate, the phenyl ring offers an extra functionality for intermolecular linkage, leading to the formation of dimerised rows of benzoate. Self assembled monolayers (SAMs) of functionalised alkanethiols adsorbed on Au(111) surfaces will also be discussed. Functionalisation of the tail group of thiol molecules gives rise to SAMs with different surface energies, allowing the fine tuning of the reactivity of the surfaces towards binding of deposited atoms and molecules. The formation of nano-particles of gold on carboxyl terminated SAMs has been investigated using scanning tunnelling microscopy (STM) and electron energy loss spectroscopy(EELS) and results will be presented to demonstrate the important role of functionality of individual molecules on nano-structure formation.

4:40pm **NS+NANO6+SS+MC-TuA9 Ion Beam Assisted Self-Organization of Periodic Nanowire-Arrays on CaF2 Substrates***, **M. Batzill**[1], F. Bardou, K.J. Snowdon,* University of Newcastle, UK

The fabrication of well ordered nanowire arrays over large areas is a challenge with many potential applications. Here we report a novel glancing incidence ion beam assisted self-organisation approach to form periodic wire-arrays over large areas on a CaF2(111) substrate. Preferential erosion of fluorine by the ion beam creates a surface enriched in calcium. The calcium self-organises in elongated island structures of preferential width and separation. If the sample is irradiated along a fixed azimuth we observe formation of nanowires with ~10 nm periodicity and wire lengths

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[1] **NSTD Student Award Finalist**

of at least several micrometers oriented along the azimuthal direction of ion beam incidence. Electrical conductivity measurements reveal a three order of magnitude lower conductivity normal to the wires than along the wires.

5:00pm **NS+NANO6+SS+MC-TuA10 Quantum Engineering of a Pb Nanostructure: Controlling the Thickness with Monolayer Precision***, **C.-S. Jiang**, H.-B. Yu, X.-D. Wang, C.-K. Shih,* University of Texas at Austin

We report a novel quantum engineering of Pb mesas on Si(111), designing the quantum number (N) of the electron resonator of Pb by modifying its thickness with monolayer precision. Pb deposition on Si(111) forms mesas on the surface, and the mesas serve as electron resonators because of the strong quantization along the surface normal direction. To modify the mesas into desired thickness, mass-transfer was first triggered by an STM-tip under controlled conditions. The triggering lead to the formation of single layer with annular shape at the edge of the mesa by transferring the Pb mass from the wetting layer. Once triggered, the mass transfer from the wetting layer to the top of the mesa continue until the new layer involving millions of atoms is completed. Once this layer is completed, no more mass transfer is observed unless a new triggering is performed. Each triggering leads to addition of one complete monolayer on top of the plateau. Using this process, the Pb mesa thickness can be engineered in a quantized fashion. Detailed mechanisms involved in the engineering will be discussed.

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