

Nanometer-scale Science and Technology Room 2020 - Session NS2-TuM

Nanoscale Manipulation and Assembly

Moderator: J. Randall, Zyvex Corporation

8:00am **NS2-TuM1 Deterministic Growth of Individual Ge Nanowires within Lithographically Patterned Arrays, C.E.D. Chidsey**, Stanford University
INVITED

Germanium nanowires and microwires are grown epitaxially from lithographically defined regions on silicon substrates in preferred crystallographic directions from electrodeposited gold nanoparticles and gold alloy nanoparticles. Nucleation, growth, surface termination and gold removal are discussed.

8:40am **NS2-TuM3 Investigating the Motion of Molecular Machines on Surfaces: Driving Nanocars, K.F. Kelly, A.J. Osgood, J. Zhang, Y. Shirai, T. Sasaki, J.-F. Morin, J.M. Tour**, Rice University

We have investigated by STM the controlled molecular motion of individual molecules on surfaces through the rational design of fullerene- and carborane-based nanostructures. The NanoCar molecule (four fullerene wheels connected by rotating alkyne axles to a central chassis) and the related molecular structures are designed and fabricated specifically for nanoscale manipulation. Our work has consisted of characterizing by variable-temperature microscopy and manipulating these molecules using the STM tip to probe the effects of surface-molecule interactions on the direction and speed of motion. This family of molecules is all built from a similar set of "molecular tinker toys" that includes interchangeable components for "chassis," "axles," and "wheels." The results of these studies underscore the ability to control directional motion in molecular-sized nanostructures through precise molecular synthesis with possible applications to surface catalysis and nanoscale tribology.

9:00am **NS2-TuM4 Toward Stable Molecular Devices: Desorption of Cyclopentene from p-Si(100) with UHV-STM and Density Functional Theory, N.L. Yoder, N.P. Guisinger, M.C. Hersam**, Northwestern University

In recent years, substantial progress has been made in the emerging field of molecular electronics. Of particular interest is the integration of molecular electronic devices with conventional silicon microelectronic technology. The presence of the energy band gap in silicon allows for resonant tunneling through individual molecules, leading to interesting effects such as room temperature negative differential resistance. Additionally, studies of organic molecule-silicon junctions can yield important insights into the feasibility of future hybrid molecule-silicon devices. In particular, the reliability of these molecular junctions is of critical importance to potential devices, and consequently warrants further investigation. Single cyclopentene molecules on silicon provide a useful test case, since the binding geometry has been studied both experimentally and theoretically. In this study, a combination of experimental and theoretical tools were employed to investigate the stability of cyclopentene molecules on a degenerately doped p-type Si(100) surface. Experiments were performed using a cryogenic ultra-high vacuum scanning tunneling microscope. At 80 K, cyclopentene desorbs from the surface at both positive and negative sample bias polarities over a range of tunneling currents. The desorption rate is roughly linear with tunneling current, indicating a single-electron/hole process. The desorption yield is a strong function of bias, and has turn-on voltage of -2.5 V at negative bias and 3.5 V at positive bias. The magnitude of the yield ranges from 2×10^{-12} to 1×10^{-8} events/electron at both polarities, which is 500-1000x smaller than the reported yields of Benzene on Si(100) and Chlorobenzene on Si(111). Density functional theory and reaction path calculations were performed in order to determine the details of the desorption process. Nano Letters 4, 55 (2004) and Proc. Nat. Acad. Sci. 102, 8838 (2005).

9:20am **NS2-TuM5 Site-Specific Force spectroscopy and Following Artificial Nanostructuring, S. Morita, Y. Sugimoto, O. Custance, M. Abe**, Osaka University, Japan
INVITED

We are developing a novel versatile "Bottom Up Nanotechnology", which can construct artificial nanostructures consisted of many kinds of elements by using a high-resolution and high-performance AFM that can identify chemical species of individual atoms and can manipulate individual atoms even at room temperature (RT). Noncontact AFM image can give different contrast between intermixed two chemical species. However, we cannot

identify chemical species of intermixed atoms from atom selective imaging on only one sample without changing relative ratio of intermixed atom species. To achieve more straightforward chemical identification than atom selective imaging at RT, we developed precise atomic force measurement method of individual atoms as a function of tip-sample distance at RT by compensating thermal drift using an atom tracking method and then by averaging reproducibly obtained many site-specific frequency shift curves. Next we converted site-specific frequency shift curve to site-specific force curve. Then, by subtracting long-range force due to Van der Waals force, we obtained short-range atomic force curve of selected individual atoms at RT. Thus we achieved precise force spectroscopy of selected individual atoms at RT. In addition, AFMs under non- and near-contact modes operated at low-temperature (LT) and at room-temperature (RT) were used for investigations of vertical and also lateral atom manipulations of selected single atoms on semiconductor surfaces. Recently, using nearcontact AFM, we found a lateral atom-interchange phenomenon at RT and constructed "Atom Inlay", that is, atom letters "Sn" consisted of 19 Sn atoms embedded in Ge(111)-c(2x8) substrate. Furthermore, we observed atom interchange manipulation phenomena even in Sn/Si(111)-(@sr@3x@sr@3), In/Si(111)-(@sr@3x@sr@3) and Sb/Si(111)-(7x7) intermixed systems with not only Si but also In (acceptor element in crystal Si) or Sb (donor element in crystal Si) atoms.

10:40am **NS2-TuM9 Tuning the Self-Assembly of Metal Nanoclusters on Diblock Copolymer Templates, S.B. Darling, A. Hoffmann**, Argonne National Laboratory

Polymers and metals are increasingly becoming intertwined in technological systems. In particular, hybrid materials that take advantage of the ability of soft matter to self-assemble and the ability of hard matter to incorporate magnetic, electronic, catalytic, or photonic functionality are of great interest. In this study, we have investigated how spatially selective electron irradiation modifies the diffusion behavior of silver evaporated onto poly(styrene-block-methylmethacrylate) (PS-b-PMMA) films. This diblock copolymer self-assembles into cylinders of PMMA in a PS matrix, where the film thickness has been chosen such that both materials are present at the free interface in an alternating stripe structure. On unexposed films, the Ag selectively adsorbs to the PS domains due to different diffusion mobilities on the two polymeric materials. Exposure to an electron beam affects the polymer blocks in different ways and thereby provides a means to manipulate this motion. Furthermore, this methodology enables a connection between the nanoscopic length scale of diblock copolymer self-assembly with conventional top-down mesoscopic length scales. We performed Kinetic Monte Carlo simulations in order to provide some insight into the diffusion behavior and, hence, the relative significance of polymer-metal and metal-metal interactions.

11:00am **NS2-TuM10 Selecting and Driving Nanoscale Assembly in Monolayer Films through Tailored Intermolecular Interactions, T.J. Mullen, P.S. Weiss**, The Pennsylvania State University

We have developed, applied, and characterized molecules with varied intermolecular interaction strengths that control stability and impart directionality into patterned monolayers. In addition to employing molecules with tailored interactions, we have exploited self- and directed assembly techniques to fabricate, to register, and to functionalize chemical surface structures at the supramolecular 1-100 nm scale. We will highlight specific examples, including applications in molecular electronics and chemical patterning, where specifically tuned molecules were designed, custom self-assembly processing techniques were utilized, and the resulting chemical surface structures were characterized on both the ensemble and the molecular scales.

11:20am **NS2-TuM11 Exploring and Manipulating Fullerenes at the Single Molecule Level, M.F. Crommie**, University of California, Berkeley, U.S.
INVITED

Fullerene molecules provide powerful building blocks for creating nanostructures with unique electronic properties. The flexible nature of these molecules arises from a combination of molecular orbital geometry, Coulomb interactions, and electron-phonon coupling. We have used scanning tunneling microscopy to examine and manipulate these factors in order to explore fullerene molecules in different physical regimes. We find that it is possible to reversibly change the charge and magnetic state of individual C60 molecules through single-atom doping, and we have spatially mapped electron-phonon interaction strengths over the surface of single fullerene molecules. When fullerenes are packed into 2-dimensional surface assemblies we find that molecular electron-electron and electron-phonon interactions combine to create novel long-range order.

Tuesday Morning, November 14, 2006

12:00pm NS2-TuM13 Electrochemical STM Investigations of Redox-Active Tetrathiafulvalene Islands Embedded in Alkanethiol SAMs, Y. Yokota, A. Miyazaki, K. Fukui, T. Enoki, M. Hara, Tokyo Institute of Technology, Japan

Stochastic apparent height changes in scanning tunneling microscopy (STM) images of self-assembled monolayers (SAMs) have been reported by some groups.^{1,2,3} From the viewpoint of molecular electronics, one of the goals of our studies is to control the structure and electronic properties of molecular assemblies by using electric charging effects. We report the electrochemical STM (EC-STM) studies of redox-active tetrathiafulvalene (TTF) islands embedded in n-decanethiol (C10SH) SAMs on Au(111).⁴ We performed EC-STM measurements of TTF islands of varied sizes at various potentials in 0.05 M HClO₄ solution. While the larger island always protruded from the C10SH matrix independent of potential, the smaller island (less than ten molecules) changed their apparent height from flat surface to clear protrusion. This change was reversible against potential change. From the cyclic voltammetry of TTF SAMs, the electronic states of TTF moieties in each STM images were characterized. The behavior of the apparent height change of the smaller island can be explained by the orientational change induced by charging of TTF moieties. Meanwhile, the behavior of the potential-inactive one is associated with a stacking effect of TTF moieties in the large island. These results indicate that not only the oxidation state but also the orientation of the electroactive moiety responds to electrochemical potential and that orientational change is also a key factor in designing molecular devices under potential control. Furthermore, we report that the larger the size of the large islands, the higher the apparent height in the STM images, although the physical height of the islands can be assumed to be same. We think that the effective electron transfer between TTF moieties leads to increase of electron-transfer passes, and to the higher apparent height. ¹ Z. J. Donhauser et al., Science 292, 2303 (2001). ² G. K. Ramachandran et al., Science 300, 1413 (2003). ³ R. A. Wassel et al., Nano Lett. 3, 1617 (2003). ⁴ Y. Yokota et al., J. Phys. Chem. B 109, 23779 (2005).

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