Surface Science
Room 210C - Session SS2-MoA

Assembled Monolayers
Moderator: M.R. Linford, Brigham Young University

2:00pm **SS2-MoA1 Surface Liquid Behavior of Organic Molecules in Nanoscale Direct Deposition Processes**, ***N. Cho***, *S. Hong,* Seoul National University, South Korea

Nanoscale direct deposition processes such as dip-pen lithography (DPN) have been extensively utilized to pattern organic molecules on solid surfaces. However, complicated 2-dimensional nanoscale diffusion phenomenon in the DPN process has not been clearly understood yet. We propose the surface liquid-based diffusion model that can fully explain complex humidity and temperature dependence of dip-pen lithography. In addition, the study of the long term dependence of DPN deposition rate and phase-separation in the mixed molecular system revealed strong intermolecular interactions during the DPN diffusion process, which also confirms our surface liquid model.

2:20pm **SS2-MoA2 The First Demonstration of the Gas Phase Modification of Scribed Silicon**, ***M.V. Lee***, Brigham Young University; *S.M. Casey,* University of Nevada, Reno; *M.R. Linford,* Brigham Young University

Chemomechanical Surface Functionalization (CMSF) is a simple and versatile method for patterning and functionalizing silicon surfaces. Using this method very small (ca. 30 nm) features have been scribed on silicon using an AFM, as well as much larger features (many microns) using a diamond tip. To date, CMSF has been demonstrated with a variety of neat liquids, including different alkenes, alkynes, alkyl halides, alcohols, aldehydes, and epoxides. However, in spite of the power of this approach for the direct modification of silicon at any desired point on its surface, a drawback of this method is that the unreacted liquid must be removed from the surface by washing following CMSF. Washing creates an opportunity for unwanted surface reactions and/or surface contamination. A CMSF method that would eliminate the surface cleaning step would be an important advance for this technique. Here we show that that two gas phase reagents (ethylene and acetylene) react with scribed silicon. It is noteworthy that this process takes place in an open laboratory using a simple laboratory apparatus that directs a jet of these reactive gases onto the silicon surface during scribing. The resulting surfaces were characterized by X-ray photoelectron spectroscopy, wetting, time-of-flight secondary ion mass spectrometry, Auger electron spectroscopy, and temperature programmed desorption. @FootnoteText@ Niederhauser, T.L.; Lua, Y.-Y.; Jiang, G.; Davis, S.D.; Matheson, R.; Hess, D.A.; Mowat, I.A.; Linford, M.R. Arrays of Chemomechanically Patterned Patches of Homogeneous and Mixed Monolayers of 1-Alkenes and Alcohols on Single Silicon Surfaces. Angew. Chem. Int. Ed. 2002, 41(13), 2353-2356.

2:40pm **SS2-MoA3 Displacement Printing of Adamantanethiolate Self-Assembled Monolayers**, ***A.A. Dameron***, *R.K. Smith, J.R. Hampton, P.S. Weiss,* The Pennsylvania State University

We have fabricated 1-adamantanethiolate self assembled monolayers (SAMs) on Au{111} and characterized them with scanning tunneling microscopy (STM). The adamantanethiolate SAMs are highly ordered and have less prominent domain boundaries than alkanethiolate SAMs, but the adamantanethiolate molecules are easily displaced by other molecules both during and after SAM formation. Taking advantage of this displacement, we have used adamantanthiolate SAMs in conjunction with microcontact printing to pattern molecules that are difficult to microcontact print by normal methods. Using STM and lateral force microscopy (LFM) we have studied the molecular order of the printed features.

3:20pm **SS2-MoA5 Controlling Surface Architecture on the sub-100 nm Length Scale with Dip-Pen Nanolithography**, *C.A. Mirkin,* ***K. Salaita***, Northwestern University **INVITED**

Dip-Pen Nanolithography (DPN) is a scanning-probe technique that permits the chemical functionalization of surfaces with nanoscale precision. Based upon a conventional Atomic Force Microscope, DPN combines ambient operation and resolutions superior to those of e-beam lithography, and allows one to create combinatorial libraries of soft matter nanostructures that can be used in fundamental surface science studies, biological diagnostics, and organic nanoelectronics. This talk will describe the fundamental capabilities of DPN and its use to generate and study a wide variety of nanostructures using materials ranging from oligonucleotides to proteins to conjugated polymers. Moreover, recent efforts to transform DPN into a high throughput tool through the use of 1 million pen cantilever arrays will be presented.

4:00pm **SS2-MoA7 Competition as Design Concept in Self-Assembled Monolayers**, ***P. Cyganik***, *M. Buck,* St Andrews University, UK

Self-assembled monolayers (SAMs) of aromatic thiols adsorbed on Au(111) substrates were studied using scanning tunneling microscopy (STM). Our experiments show that a molecular design, which is not based on the usual concept of energy minimization but employs competing forces, opens an unexpected additional dimension in the control of structure and properties of thiol SAMs. Based on thiols which are characterized by a combination of a biphenyl unit and an alkane spacer (CH@sub 3@(C@sub 6@H@sub 4@)@sub 2@(CH@sub 2@)@sub n@SH, BPn, n = 2, 3, 4, 5, 6), the length of the spacer is chosen such that different factors which determine the energetics of a SAM structure (e.g. sulfur bonding geometry vs. intermolecular interactions) enter in a competing rather than a cooperative way. The SAMs prepared according to this concept show thermally induced irreversible transitions into new structures. This transition is paralleled by striking improvement in the structural perfection of the SAM and changes in the stability against exchange by other thiols.

4:20pm **SS2-MoA8 Tuning of Orientation and Chiral Recognition of a Single Chiral Molecule in Self-Assembly through Modulation of Anchoring Sites**, ***B.I. Kim***, Boise State University; *C.Z. Cai, S.S. Perry,* University of Houston

Rod-like aromatic systems with conducting @pi@-backbones are of interest as potential building blocks for electronic devices. Hydrogen bonding could be used as a conductive linkage of molecular wire on a surface. When we build up a self-assembly with rod-like molecules on a surface through hydrogen bonding, we can use chirality to control the configuration of the nanostructure. Recent studies show that chirality plays an important role in site-specific adsorption of molecules, formation of extended chiral domains, and enhancement of stability of clusters and chains. However, those observations have been limited to specific chiral adsorption configurations without addressing more tunable modification of them for a novel nano-engineering. Here we present scanning tunneling microscopy studies of a chiral molecule with two functionalized benzene rings, 4-trans-2-(pyrid-4-yl-vynyl) benzoic acid(PVBA), on surfaces. PVBA shows chiral separation on Ag(111) but not on Pd(111) while it shows orientational separation on Pd(111) but not on Ag(111). An angle dependent model calculation indicates that the orientation and chiral recognition could be tuned through modulation of double anchoring sites, applicable for flexible nano-wire and chiral separation on the surface.

4:40pm **SS2-MoA9 Resonance-Assisted Hydrogen Bonds Stabilize Guanine Quartet Networks on Solid Surfaces**, ***R. Otero***, *M. Schöck, L.M. Molina, E. Laegsgaard, I. Stensgaard, B. Hammer, F. Besenbacher,* University of Aarhus, Denmark

Hydrogen bonding between DNA bases is one of the main interactions that control the conformation and hence the biochemical function of nucleic acid molecules@footnote 1,2@. Apart from the Watson-Crick model for base pairing@footnote 1@, DNA bases can form other hydrogen-bonded complexes that lead to different DNA structures, like G-quadruplexes@footnote 3@ or i-motifs@footnote 4@. In spite of the increasing evidence for the existence and in vivo function of these DNA structures@footnote 5@, a convincing biophysical model for their stability is still missing. By combining high-resolution, variable-temperature Scanning Tunneling Microscopy (STM) and state-of-the-art Density Functional Theory (DFT), here we show that the DNA base guanine (G) deposited under ultra-clean conditions onto a suitably inert substrate such as Au(111) self-assembles into a hydrogen-bonded network of G-quartets, whose structure corresponds perfectly with the quartet structure of telomeric DNA@footnote 3@ determined by X-ray crystallography. The strong preference of G molecules to form quartets can be explained by a cooperative effect that strengthens the hydrogen bonds within the G-quartet network over the hydrogen bonds in isolated dimers. This result underlines the necessity of going beyond the picture of isolated hydrogen bonds in order to properly describe the interactions between biomolecules. @FootnoteText@ @footnote 1@ Watson, J. D. & Crick, F. H. C. A structure for deoxyribose nucleic acid. Nature 171, 737-738 (1953).@footnote 2@ Sinden, R. R. DNA Structure and Function (Academic Press, San Diego, 1994).@footnote 3@ Sundquist, W. I. & Klug, A. Telomeric DNA dimerizes by formation of guanine tetrads between hairpin loops. Nature 342, 825-829 (1989).@footnote 4@ Gehring, K., Leroy, J.-L. & Guéron, M. A

tetrameric DNA structure with protonated cytosine-cytosine base pairs. Nature 363, 561-565 (1993).@footnote 5@ Kipling, D. The telomere (Oxford University Press, Oxford, 2002).

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