Monday Morning, November 13, 2006

Applied Surface Science
Room 2005 - Session AS+BI+NS+NM-MoM

Organic Surface Modification and Nanoscale Chemical Patterning

Moderator: R. Haasch, University of Illinois, Urbana

8:00am **AS+BI+NS+NM-MoM1 Biomolecular Lithography on GaAs Surfaces*, A. Ivanisevic,*** Purdue University **INVITED**

Atomic force microscopy (AFM) was used to fabricate well-defined peptide templates onto GaAs surfaces via Dip-Pen Nanolithography (DPN). DPN is a powerful technique to write specific organic and/or inorganic molecules onto a surface with an AFM tip. In this work, DPN was used to construct arrays of peptides with nanometer features. TAT peptides (e.g. CGISYGRKKRRQRRR) which exhibit rapid uptake in cells, were patterned onto the surface in either contact or tapping mode. Several techniques were used for the characterization of the modified surfaces: X-ray photoelectron spectroscopy (XPS), Fourier Transforms Infrared (FT-IR) spectroscopy and contact angle. Transmission FT-IR provided structural information such as peptide conformation. The complementary analysis confirmed the binding of the peptide onto the substrates and allowed to quantify the density of immobilized peptides on a given surface. Furthermore, the nanoscopic features were successfully used in recognition experiments where an RNA sequence with a loop structure, known for its specific interaction with the peptide, was tested. The results in this report indicate that one can use nanolithographic strategies to pattern GaAs surfaces, and therefore provide a proof-of-concept experiment that can be transferred in complex microfabricated semiconductor architectures.

8:40am **AS+BI+NS+NM-MoM3 The Effect of Ring Substitution Position on the Structural Conformation of Mercaptobenzoic Acid Self-Assembled Monolayers on Au(111)*, J.R.I. Lee,*** Lawrence Livermore NAtional Laboratory*; T.M. Willey, J. Nilsson, L.J. Terminello, J.J. De Yoreo, T. van Buuren,* Lawrence Livermore National Laboratory

Mercaptobenzoic acid (MBA) is a viable alternative for preparing SAMs with carboxyl functionality. These molecules, as opposed to carboxyl-terminated alkylthiols, offer an extended pi-bonded system formed by the aryl and carboxyl groups facilitating charge transfer, and these extremely thin SAMs (< 8 Angstroms) have been shown via STM to contain a high degree of structural order. Furthermore, three different isomers of mercaptobenzoic acid may lead to differing surface properties. In this work, the orientation and bonding of self-assembled monolayers of the three positional isomers of mercaptobenzoic acid adsorbed on gold are investigated using near edge X-ray absorption fine structure (NEXAFS) spectroscopy and photoemission spectroscopy (PES). The isomer of MBA and solvent chosen in SAM preparation has considerable bearing upon film morphology. Monomers of 3- and 4-MBA assume an upright orientation on the Au substrates in monolayers prepared using an acetic acid in ethanol solvent. The aryl ring and carboxyl group of these molecules are tilted from the surface normal by a colatitudal angle of ~ 30 degrees. Preparation of 4-MBA SAMs using pure ethanol solvent, a more traditional means of synthesis, had no appreciable effect upon the monomer orientation, but S(2p) PES measurements illustrate that it results in extensive bilayer formation via carboxyl group hydrogen-bonding between 4-MBA monomers. In 2- MBA monolayers prepared using acetic acid/ethanol solvent, the monomers adopt a more prostrate orientation on the Au substrates, in which the aryl ring and carboxyl group of the molecules are tilted ~ 50 degrees from the surface normal. This configuration is consistent with an interaction between both the mercaptan sulfur and carboxyl group of 2-MBA with the underlying substrate. This work was supported by the Division of Chemical Sciences, Office of Basic Energy Science, and performed under the auspices of the U.S. DOE by LLNL under contract No. W-7405-ENG-48.

9:00am **AS+BI+NS+NM-MoM4 XPS Analysis of Arenes and Proteins on Gold Substrates Attached by Electrochemical Reduction of Aryldiazonium Salts*, J.L. Fenton,*** University of New Mexico*; S.M. Dirk, D. Wheeler,* Sandia National Labs*; J.E. Fulghum,* University of New Mexico

The properties of most materials can be altered by the attachment of molecules to their surface. Recent work has shown that diazonium salts can be used to attach aryl compounds to metal and semiconductor surfaces including silver, iron, platinum, silicon, and glassy carbon. Diazonium salts can be electrochemically reduced in acetonitrile leading to the attachment of aryl groups to the surface of a substrate. The attachment of aryl compounds using diazonium salts developed in our work, allows one to attach aryl compounds with different organic moieties onto metal substrates including gold. Aryl organic layers can be made of different thicknesses, and stacked structures can be created by alternating layers of molecules. This work is then expanded upon to attach proteins to metal surfaces. This approach provides a methodology to generate arrayed proteins on electrode arrays without the use of microfluidic methods such as ink jetting etc. The development of protein arrays can often provide high-throughput, quantitative measurement of receptor-ligand complexation giving an understanding of protein function, modification, and regulation. X-ray photoelectron spectroscopy (XPS) is used to deduce the different types of chemistries in single molecule samples, stacked structures, and surface tethered proteins. Angle resolved XPS is used to determine the relative location of each molecule in the stacked structures and possible orientation of proteins as well as to deduce the existence of azo linkages.

9:20am **AS+BI+NS+NM-MoM5 Challenges in the Modification and Characterization of Two- and Three-Dimensional Biointerfaces*, M. Textor*,** ETH Zurich, Switzerland **INVITED**

Surface modifications based on biochemical or biological principles are important tools for the fabrication of biosensor chips, biomedical devices such as implants, and of drug delivery carriers. Moreover, well-designed model biointerfaces have substantially contributed in the last decade to a better insight into fundamental aspects of cell-surface interaction. An overview will be given on tools enabling the surface engineer to tailor the interface of biomaterials, with special emphasis on the approach of eliminating non-specific adsorption and adding to such a silent surface biological functionalities. Preservation of active conformation and optimum presentation (orientation, density) of surface-immobilized moieties are particular challenges in this field. Different approaches to micro- and nanopatterning of surfaces, their specific advantages/disadvantages and applications in biorelated fields are discussed. Special emphasis is placed on methods that combine top-down (e.g., lithography) and bottom-up (self-assembly) approaches. Substantial new insight into the factors that govern cell-surface interactions and cell differentiation has recently be gained by using two-dimensional (2D) patterns. There is, however, an increasing interest to explore (stem) cell development in 3D microwells with well-controlled geometry (shape/size), surface chemistry and mechanical properties (substrate stiffness). The challenges of independently tailoring chemistry and structure/topography are addressed; self-assembly techniques are in this respect particularly useful. Finally, characterization/imaging techniques that allow the monitoring of biointerface reactions in situ, in real time and quantitatively are important tools; selected methods will be presented based on highly surface- and detection-sensitive evanescent-field-based sensing.

10:20am **AS+BI+NS+NM-MoM8 Nanoscale Chemical Patterning and Architectures*, P.F. Nealey*,** University of Wisconsin **INVITED**

Diblock copolymers are self-assembling materials consisting of two polymer chains connected at one end that tend to form ordered nanostructures, including spheres, cylinders, and lamellae, whose shape and dimensions depend on the molecular weight and composition of the polymer. Block copolymer lithography refers to the use of these ordered structures in the form of thin films as templates for patterning through selective etching or deposition. Already block copolymer lithography has been used to pattern dense periodic arrays for the applications such as quantum dots, nanowires, magnetic storage media, increased capacitance gate devices and FLASH memory. One of the current goals in block copolymer nanolithography is to reproduce many of the characteristics of the lithographic process used ubiquitously in nanomanufacturing, including pattern perfection over macroscopic areas, the ability to pattern arbitrary and non-regular geometries, dimensional control of features within exacting tolerances and margins, and registration and overlay. Two strategies will be discussed to integrate self-assembling materials into existing manufacturing practices so as to achieve molecular-level process control and the ability to produce useful architectures: directed assembly of block copolymers on topographically patterned substrates, and directed assembly of block copolymers on chemically nanopatterned substrates.

11:00am **AS+BI+NS+NM-MoM10 Tailoring of Functional Nano-Patterned Surfaces for Biosensing Applications by Combination of Plasma Processes and Electron-Beam Lithography**, *F. Brétagnol, L. Ceriotti, A. Valsesia, T. Sasaki, D. Gilliland, G. Ceccone, P. Colpo,* ***F. Rossi,*** JRC-IHCP-BMS, Italy

Fabrication of micro and nano-patterned surfaces with a well defined geometry and a controlled chemistry is a fundamental step for the development of bioengineered materials Micro-arranged surfaces containing functionalities such as cell or protein adhesive in a non non-adhesive matrix provide a very useful tool in a large field of applications (tissue engineering, cell behavior investigations , artificial growth of neurons networksâ?¦) . Numerous methods have been successfully developed for the production of such surfaces including conventional photolithography, photochemistry , micro-contact printing , micro fluidic patterning . Nevertheless, the development of surfaces chemically patterned at nano scale is still a challenging issue for the implementation of new generation of miniaturized biochips and for the study of cell surface interactions. In this study, we present an innovative method for the fabrication of chemically nano-patterned surfaces. Maskless lithography based on electron-beam technique was successfully combined with plasma-based processes to create COOH terminated spots over a PEO-like matrix. Spots from micron to submicron size have been created. Quality control of the patterned surface was studied by Atomic Force Microscopy, XPS and ToF-SIMS analysis. Experiments with fluorescent proteins on the patterned surfaces exhibit a preferential adhesion on the active region showing the ability of this technique for the design of biosensing platforms.

11:20am **AS+BI+NS+NM-MoM11 Optically-Stimulated Surface Diffusion Exploited for Directed Self-Assembly on Amorphous Semiconductors***, E.G. Seebauer,* ***Y. Kondratenko****,* University of Illinois at Urbana-Champaign

Nanoscale device fabrication technologies require toolsets for miniaturization and organization of materials at nanometer dimensions. Current toolsets have developed from two diametrically opposite strategies: top-down and bottom-up. This laboratory is taking a different approach based on a new physical mechanism for photostimulated diffusion discovered here. This new strategy combines attractive features of top-down and bottom-up approaches by exploiting the self-organization capabilities latent in amorphous materials, but in a way that can be controlled by optical or electron beam exposure tools. We have developed a new surface self-assembly method at the 10-200 nm length scale using amorphous semiconducting materials. Patterned optical or electron beam exposure yields a spatially varying surface mass flux that, when performed at an annealing temperature just at the cusp of crystallization, provides the extra nudge to crystallize subcritical nuclei in regions dictated by the light flux. The full-fledged crystallites then grow by surface diffusion and Ostwald ripening until the desired fraction of the film has accreted onto the original nuclei. We have demonstrated this technique with titanium dioxide as the substrate material. This scheme should apply to a wide variety of semiconducting materials on nearly arbitrary substrates to form nanoarrays, nanowalls, and possibly three-dimensional structures. Possible applications include chalcogenide semiconductors for data storage media; nanoparticles arrays for direct use in sensors and solar cells; and semiconductor arrays for indirect use as seed layers for the subsequent deposition of sintered particle films in fabricating advanced ceramics and devices such as rechargeable batteries, solar cells, gas sensors, and photonic band gap materials in solar windowpanes.

11:40am **AS+BI+NS+NM-MoM12 Nanowires and Nanodevices via Assembly of Clusters***,* ***S.A. Brown****,* Nano Cluster Devices Ltd, New Zealand

We report the achievement of contacted electronic devices, self-assembled from atomic nanoclusters. Features of this technology, which overcomes the difficulties in the assembly of building blocks inherent to many bottom-up approaches to nanotechnology, include: Interchangeable cluster sources so as to have available a wide variety of cluster materials in a useful size range, allowing exploitation of novel structures and properties. Self-assembly methods which avoid time consuming positioning of building blocks. Use of lithographic processes which are compatible with both cluster deposition technology and standard microelectronics fabrication protocols. Understanding of basic physical assembly processes in order to predict and control device formation, including availability of suitable computer simulations. In this paper we will review the assembly methods developed, which include directed assembly in silicon V-grooves and on polymer-patterned surfaces, as well as stencilling techniques. We will then focus on the application of these techniques to one class of devices which have been realised i.e. cluster-assembled hydrogen sensors. These sensors are realised by the deposition of Pd clusters on a substrate such that one or several conduction paths are formed between a pair of contacts. The sensing principle relies on the expansion of Pd clusters and the resulting change of conductance as a result of their absorption of hydrogen and we have demonstrated very high sensitivities.

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