Wednesday Afternoon, October 4, 2000

Organic Films and Devices Room 313 - Session OF-WeA

Self-Assembled Monolayers: Electron Transfer and Film Properties

Moderator: J.N. Russell, Jr., Naval Research Laboratory

2:00pm **OF-WeA1 Rates of Interfacial Electron Transfer Across Well-Defined Model Interfaces,** *C.E.D. Chidsey***, Stanford University INVITED** The injection of electrons and holes into molecular or polymeric organic materials is a key process in many organic devices such as light-emitting diodes, transistors and sensors. Injection is normally accomplished by the thermal transfer of electrons across interfaces between metallic or semiconducting electrodes and the organic material. I will discuss methods to measure the rate of this process across well-defined model interfaces and our developing understanding of the role of molecular structure in determining these rates.

2:40pm OF-WeA3 Charge Transfer in Alkanethiol Self-Assembled Monolayers on Au Surfaces, K. Son, H.I. Kim, J.E. Houston, Sandia National Laboratories

Charge transfer in self-assembled monolayers (SAM) has been studied extensively for molecular electronics applications, and Scanning Probe Microscopy studies have led to a general agreement on the role of force induced structural deformation on the conductivity of alkyl based SAMs. However, controversies about the level of tip/sample contact remain unresolved, and the evidence for structural deformation is vague. Here we investigate charge transfer in alkanethiol SAMs on Au(111) using Interfacial Force Microscopy (IFM). This technique enables the first simultaneous measurements of conductivity, normal-force, and friction over the entire range of tip/sample interaction. For alkanethiols (C@sub n@H@sub 2n+1@SH, n>10), we observe no current until the IFM tip makes physical contact with the SAM surface (down to the fA level). The current then increases exponentially with applied stress. Current and force profiles track each other from the initial conduction point, and both show a strong correlation with the rise in friction. I-V data taken at various force levels show both linear and resonance regions while the slope and the transition point are strongly dependent on the force level as well as molecular chain length. Based on these results, we conclude that the current flow through SAM films occurs by a tunneling process with necessary tip/film contact. We attribute the conductivity increase to the force-induced changes in film structure resulting in a redistribution of the film's electronic states, as evidenced by both the friction and the I-V characteristics. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the U.S. Dept. of Energy under Contract DE-AC04-94AI 85000

3:00pm OF-WeA4 Low Energy Electron Microscopy Studies of the Growth of Thin Pentacene Films, *R.M. Tromp*, *F. Meyer zu Heringdorf, C. Dimitrakopoulos, J. Shaw*, IBM T.J. Watson Research Center

We have used Low Energy Electron Microscopy (LEEM) to study the growth and structural evolution of thin pentacene films on a variety of surfaces and substrates. LEEM allows the growth process to be followed in real time with high spatial resolution (5 nm), and at videorate. Thin film nucleation and subsequent growth can be studied in much detail. For instance, diffusion of pentacene on the starting substrate (for instance clean Si, or SiO2) is isotropic, giving rise to fractal two-dimensional islands. These islands are nonetheless crystalline. The second layer grows on this crystalline template, with highly anisotropic diffusion. Substrate and substrate preparation give a certain degree of control over the polycrystalline grain size. In addition to the growth morphology, LEEM allows the observation of what appear to be molecular size defects in the film, giving rise to charge trapping. Such traps charge and discharge on timescales of 0.1 to several seconds. The density of such traps depends critically on the growth conditions. It appears that traps can be eliminated by careful control of the evaporation parameters. These studies, the first to observe the growth of organic semiconductors in real space, and in real time, enable a detailed understanding of the basic processes underlying the growth process. Direct parallels can be drawn between organic thin film growth, and the epitaxial growth of very different materials such as Si and Pt. These basic insight allow a careful optimization of the growth conditions, optimizing defect densities, grain size, and growth morphology.

3:20pm OF-WeA5 Self-assembled Monolayers on Silicon Surfaces via Si-O Linkages, V. Boiadjiev, R.C. Major, X.-Y. Zhu, University of Minnesota

Monolayer assemblies on silicon surfaces are of interest for a number of technological reasons. Here, we present a novel, two-step strategy for assembly formation directly on silicon surfaces. In the first step, a Hterminated Si(100) or Si(111) surface reacts with Cl2 to give a Cl-capped surface. In the second step, the CI-Si surface is immersed in an alcohol/isooctane solution for monolayer formation via Si-O linkages, with the removal of surface CI likely in the form of HCI. This reaction mechanism is confirmed by X-ray photoelectron spectroscopy. X-ray reflectivity measurement shows that the thickness of the monolayer film is close to molecular dimension and the density is about 85% of that in crystalline paraffine. Fourier transform infrared spectroscopy and water contact angle measurements suggest that the alkyl chains within the monolayer possess, to a limited degree, conformational order. Atomic force microscopy image with molecular lattice resolution shows intermolecular distance corresponding to close packing of alkyl chains. The monolayer coatings show both chemical and mechanical stability. The possible mechanism for monolayer assembly formation on covalent Si surfaces is discussed.

3:40pm OF-WeA6 Friction Force Microscopy Study on Photodegradation of Organosilane Self-assembled Monolayers Irradiated with a Vacuum Ultraviolet Light at 172 nm, *H. Sugimura*, *K. Hayashi*, *O. Takai*, Nagoya University, Japan

Photodegradation of organosilane self-assembled monolayers (SAMs), under the presence of atmospheric oxygen molecules, has been studied using an excimer lamp radiating vacuum ultra-violet (VUV) light of 172 nm in wavelength. A SAM was prepared on each of Si substrates covered with native oxide from a precursor of octadecyltrimethoxysilane by a chemical vapor deposition method.@footnote 1@ The SAM-covered samples were photoirradiated under a controlled pressure from 10 to 10@super 5@ Pa. As confirmed by water contact angle measurements, infrared reflectionabsorption spectroscopy and X-ray photoelectron spectroscopy, the SAM was decomposed and removed due to the VUV-irradiation. This photodegradation mechanism is ascribed to dissociative excitation of C-C and C-H bondings in the organosilane molecules and to subsequently proceeded oxidation with atomic oxygen radicals generated simultaneously by the VUV-irradiation of O@sub 2@ molecules. Furthermore, micropatterning of the SAM was demonstrated by a simple photomaskcontacting method.@footnote 2@ Due to a distinct difference in frictional force in contact-mode atomic force microscopy between the VUVirradiated and unirradiated regions, the photoprinted pattern was clearly imaged. The VUV-irradiated region showed stronger frictional force than the unirradiated SAM surface. Patterning conditions were optimized based on these results obtained by frictional force microscopy. A micropattern of 2 µm in width was successfully photoprinted on the SAM. @FootnoteText@ @footnote 1@A. Hozumi et al. Langmuir,15 (1999) 7600. @footnote 2@H. Sugimura et al. Langmuir,16 (2000) 885.

4:00pm OF-WeA7 Generation of Reactive Intermediates on Platinum by Photolysis of Pyridyl-@alpha@-Diazocarbonyl Self Assembled Monolayers, J.L. Pitters, D.K. Adkinson, P.R. Norton, M.S. Workentin, University of Western Ontario, Canada

There is considerable current interest in understanding the chemistry of organic molecules as Self Assembled Monolayers (SAMs) on metal surfaces. Much of the effort in this regard has focused on long chain alkyl thiols on gold with the ultimate goal of being able to control the interfacial properties for use in wide ranging material and device applications. However, there has been a growing interest in small molecule SAMs and their relevance to surface modification. We have prepared a series of photoreactive pyridine based molecules for study as SAMs on single crystal Pt. Monolayers (saturated layers) of pyridyl-diazoketones, pyridyldiazoesters and pyridyl-diazoaldehydes have been characterized using Ultra High Vacuum (UHV) Reflection Absorption Infrared Spectroscopy (RAIRS) and other surface sensitive techniques. Diagnostic out-of-phase C=N=N and C=O absorptions indicate that the diazo and carbonyl groups are stable on the Pt surface and that binding most likely takes place through the pyridyl nitrogen as is the case in most substituted pyridines. Upon exposure to 300-400 nm light, the diazo group releases nitrogen quantitatively to yield either carbene or ketene intermediates depending on the original substrate. Most notably is the formation of a ketene functionality (C=C=O) at the interface through the Photo-Wolff rearrangement. The ketene is identified by the diagnostic out-of-phase infrared absorption at approximately 2110 wavenumbers. This study represents the first direct spectroscopic evidence of a photoreactive diazo-

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carbonyl monolayer and the subsequent photochemical formation of a stable ketene monolayer on a metal surface. Ketene and carbene reactivity is versatile and we believe that knowledge of the interfacial reactivity in the present systems can be extended to provide a novel surface for template synthesis and surface modification.

4:20pm **OF-WeA8 X-Ray Induced Changes in Thiol-SAMs on Gold**, *B. Zeysing*, *T. Eickhoff*, University of Hamburg, Germany; *W. Drube*, Hamburger Synchrotronstrahlungslabor HASYLAB at Deutsches Elektronensynchrotron DESY, Germany; *A. Terfort*, University of Hamburg, Germany

Self-assembled monolayers (SAMs), in particular SAMs of alkanethiols on coinage metals, such as gold, receive a growing interest as convenient possibility to modify surfaces in an experimentally simple but very well adjustable manner. Since these layers are very thin (about 0.5 to 10 nm), they are typically characterized by surface sensitive techniques, often involving x-rays. On the other hand, it is known for some time that these monolayers are subject to massive changes upon irradiation, mainly caused by primary or secondary electrons generated in the supporting high-z material, which penetrate the monolayer.@footnote 1-4@ These electrons remove binding electrons from the molecules by impact ionization, leaving positive charges (holes) within the surface molecules. In alkane chains these holes remain localized and trigger chemical reactions. This results in altered monolayers with different properties and mixed' results which are usually difficult to interpret. In our talk, we present results obtained by using synchrotron radiation based methods to demonstrate how fast monolayers transform under illumination with x-rays, and what the detailed mechanism of this transformation is. Using total external reflection x-ray photoelectron spectroscopy (TER-XPS),@footnote 5@ we could determine the fate of the sulfur atoms. By understanding the mechanisms of destruction, we were able to design SAMs with significantly increased stability towards x-rays. @FootnoteText@ @footnote 1@Wirde, M.; Gelius, U.; Dunbar, T.; Allara, D. L. Nuclear Instr. Methods Phys. Res. B 1997, 131, 245. @footnote 2@Zubragel, Ch.; Deuper, C.; Schneider, F.; M. Neumann, N.; Grunze, M.; Schertel, A.; W@um o@ll, Ch. Chem. Phys. Lett. 1995, 238, 308. @footnote 3@Olsen, C.; Rowntree, P. A. J. Chem. Phys. 1998, 108, 3750. @footnote 4@Zerulla, D.; Chass@aa e@, T. Langmuir 1999, 15, 5285. @footnote 5@M.J. Bedzyk, G.M. Bommarito, J.S. Schildkraut, Phys. Rev. Lett. 1989, 62, 1376.

4:40pm OF-WeA9 Surface Stress of Self-Assembled Alkanethiols on Gold-Coated Cantilevers, *M. Godin*, McGill University, Canada; *P.J. Williams*, Acadia University, Canada; *V. Tabard-Cossa*, *P. Grütter*, McGill University, Canada

The commercial availability of atomic force microscope (AFM) microcantilevers has made possible the development of new ultrasensitive techniques aimed at measuring nanoscale quantities such as mass, heat and surface stress. We have adapted standard gold-coated silicon nitride AFM cantilevers as a chemical sensor. During chemical sensing, the cantilever bends due to the surface stress associated with the adsorption of specific target molecules onto a single side of the cantilever, which has been coated with a receptive layer. We have used our cantilever sensor to measure the surface stress associated with the self-assembly of alkanethiols on gold-coated cantilevers. This surface stress is strongly associated with the structural organization of the self-assembled thiol monolayer, as well as molecular chain-length. We will discuss the importance of the quality of the gold receptive surface with respect to thiol monolayer formation, as well as the kinetics of vapor-phase self-assembly of alkanethiols onto gold.

5:00pm OF-WeA10 Self-assembled Monolayers of 6-Phenyl-n-Hexanethiol and 6-(p-Vinylphenyl)-n-Hexanethiol on Au: An Investigation of Structure, Stability and Reactivity, *L. Duan, S. Garrett,* Michigan State University

The structure, stability and reactivity of 6-Phenyl-n-Hexanethiol (PHT) and 6-(p-Vinylphenyl)-n-Hexanethiol (VHT) monolayers on Au (111) is presented. RAIR spectroscopy, ellipsometry and STM have been used to characterize the self-assembled monolayers (SAMs). The RAIR spectral data indicated that both molecules chemisorbed on gold as thiolates, however, the alkyl chains were disordered for both SAMs. We investigated the structural changes of PHT monolayers with decreasing molecular surface density by annealing in ultrahigh vacuum. Three different "stripe" phases have been observed by STM. All three condensed phases are characterized by alignment of the molecular axes with the surface plane, but with decreasing degrees of out-of-plane interdigitation. On the contrary, VHT molecules are oriented almost parallel to the surface normal at room temperature. Polymerization of VHT SAMs can be achieved by either UV-

light irradiation or annealing. The polymerization process was followed by RAIR spectroscopy by observing the decrease in peak intensities associated with vinyl functionalities. UV-light irradiation produced long chain polymers with ~70% conversion rate after 25 min, while annealing produced short-chain polymers with CH@sub 3@ as the end group. The UV-light polymerized film is more robust to heating than thermally polymerized film.

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