

Surface Science Division

Room 606 - Session SS1+AS+BI-FrM

Organic Films/Self-Assembled Monolayers

Moderator: G.E. Poirier, National Institute of Standards and Technology

8:20am SS1+AS+BI-FrM1 Simple Viscosity Model Analysis of Hydronium Ion Motion in Nanometer Organic Films, K. Wu, M.J. Ledema, J.P. Cowin, Pacific Northwest National Laboratory

Nanometer organic films such as methylcyclohexane and 3-methylpentane were vapor-deposited at 30 K on Pt(111) with a molecular beam. Pure hydronium ions were soft-landed on top of the films at a kinetic energy less than 1.2 eV. The voltage change and desorption of the organic films were simultaneously monitored by a Kelvin probe and a mass spectrometer. Ion dosing on the organic films was a capacitive charging process, therefore the film voltage change actually reflected the ion motion in the organic films, assuming the dielectric constants of the organic films do not change much with temperature. When the films were warmed, ions gradually moved into the films. The experimental results were analyzed by a simple viscosity model. To a large extent, the temperature (or time) evolution of the film voltage could be well predicted by the model. The film voltage fall-off temperature width from the theory was, however, about half of that from the experiment. Further experimental evidence showed that the ion self-generated electric field strength had a strong effect on the ion motion. For example, when the electric field strength was higher than 0.05 V/Angstrom, the theoretical prediction seriously deviated from the experimental result, indicating that a high electric field might trigger non-linear ion motion and made the Stokes-Einstein equation not accurate. When films were prepared at higher temperatures, methylcyclohexane could crystallize on Pt(111), making ions more difficult to transport in the crystalline films. But, 3-methylpentane never crystallized before ion motion in it completed, indicating that it's a good glass material. With this general approach, we could attack many important issues such as ion motion across liquid-liquid interfaces, hydration of ions and so on.

8:40am SS1+AS+BI-FrM2 Direct Observation of Topological Defect Evolution and Domain Motion in Ultrathin Films of PS-b-PMMA Diblock Copolymers Using Atomic Force Microscopy, J. Hahn¹, W.A. Lopes, H.M. Jaeger, S.J. Sibener, The University of Chicago

We report the tracking of individual topological defects in the microdomain patterns of cylinder-forming polystyrene-block-polymethylmethacrylate (PS-b-PMMA) films. These films undergo vertical and lateral phase separation when they are thermally annealed. The vertical phase separation results in thickness quantization where each layer exhibits its own topology and dynamics. The lateral phase separation provides height contrast between the two components of the diblock in single-cylinder-layer thick films. In the atomic force microscopy (AFM) topographic images, the PMMA is higher by approximately 1nm as compared to the PS blocks. 50nm thick films, containing a single layer of cylinders aligned parallel to the film plane, were repeatedly and non-destructively probed with AFM in an attempt to elucidate the evolution of the diblock domain topology between annealing treatments. We show explicitly that the evolution of topological defects takes place through relinking, joining, clustering and annihilation of defects. Such processes form the basis for predicting structural changes in polymer thin films. We also have used time-lapse AFM imaging to observe directly the kinetics of domain mobility responsible for topological evolution. Domains of different thicknesses were monitored as a function of annealing temperature and time. The higher mobility and lower activation energy associated with thicker domain mobility are accounted for by the essentially negligible substrate interactions where polymer-polymer rather than polymer-substrate interactions govern the dynamics. Our hope is that the combined understanding of topological changes, such as those reported in this talk, when combined with mobility kinetics, will give us a predictive understanding of the thermally activated structural changes that occur within thin polymer films. @FootnoteText@ Supported by the NSF-MRSEC at the University of Chicago and AFOSR.

9:00am SS1+AS+BI-FrM3 Properties of Self-Assembled Monolayers of Biphenyl-Based Thiols, T. Felgenhauer, H.-T. Rong, M. Buck, M. Grunze, University of Heidelberg, Germany

Despite their versatility to modify surface properties, self-assembled monolayers (SAM) based on alkane thiols have limitations concerning conformational stability or structural perfection. In search for more rigid molecules, thiols based on aromatic moieties offer an alternative. However, in contrast to SAMs consisting of alkane thiols experiments on aromatic thiols are relatively scarce. Our experiments focus on thiol SAMs consisting of 4,4'-substituted biphenyls (BP). To allow systematic investigations the number of methylene units between the biphenyl moiety and the thiol group was varied between zero and six. The electrochemical behavior of BP-SAMs turns out to be very different from alkane thiols. In general, the charge permeability of BP-SAMs is higher by orders of magnitude even though the electrochemical stability of BP-SAMs is dependent on the methylene spacer. Exposure to an etching solution reveals a stability significantly higher compared to alkane thiols and suggests an improved structural perfection of BP-SAMs. Spectroscopic characterization of the BP-SAMs yields an orientation of the biphenyl units alternating with the methylene chain length. Comparison of BP-SAMs on Au with those on Ag shows a reversal of the odd-even effect and demonstrates that the sulphur-substrate bond is crucial for the molecular orientation of the biphenyl-SAMs.

9:20am SS1+AS+BI-FrM4 Structure of Self-assembled Monolayers of Alkanethiols and Disulfides on Au(111), H. Nozoye, National Institute of Materials and Chemical Research, Japan; C. Kodama, T. Hayashi, University of Tsukuba, Japan

Self-assembled monolayer (SAM) films of alkanethiols and alkyldisulfides have been attracting an increasing interest. However, we do not have a concrete picture of SAM, e.g. is the SH bond broken on the surface?, is the SS bond formed on the surface?, or where is the adsorption site of S?. We studied these problems by means of STM, HREELS, high-sensitivity LEED, and TPD. Alkanethiols (C1-C10) and alkyldisulfides (C2-C12) were adsorbed on a Au(111) single crystal surface at room temperature or at around 120 K. Desorption of H₂, parent alkanethiol, alkylthiolate radical, and alkyldisulfide were observed in TPD and a vibration peak assigned to a SS bond was missing in HREEL spectra. We clearly concluded that the SH bond of alkylthiols breaks at low temperature forming alkylthiolates on the surface. Furthermore, the SS bond of alkyldisulfides was shown to be broken on the surface, forming alkylthiolate. The Au-S bond of alkylthiolates on the surface gave a relatively strong peak in HREEL spectra. We will discuss the formation process and the relation between the local structure and the long-range order of SAM.

9:40am SS1+AS+BI-FrM5 Toward Vapor Deposition of Polycyanurates: The Surface Chemistry of Phenyl Cyanate and Phenol on Al(111), B. Bartlett, J.M. Valdisera, J.N. Russell, Jr., Naval Research Laboratory

Polycyanurates, formed by polymerization of monomers containing two cyanate groups, show promise as vapor depositable, low dielectric parameter materials for microelectronics applications. Consequently, we are examining the chemistry of a model system, phenyl cyanate on Al(111) surface, with temperature programmed desorption (TPD), Auger electron spectroscopy (AES), and X-ray photoelectron spectroscopy (XPS). (Aluminum was chosen as a substrate because it is used for interconnects in microelectronics.) For submonolayer coverages, XPS shows that the phenyl cyanate undergoes O-CN bond cleavage between 150 and 200 K, leaving phenoxide and cyanide groups on the surface. Benzene and hydrogen decomposition desorption products were observed at 620 K, and between 500 and 800 K, respectively. This is analogous to the reaction of phenol on Al(111). Deuterium labeling was used to determine the sequence of C-H bond scission on the phenoxy species. XPS and AES reveal the formation of aluminum oxide, nitride and carbide on the surface above ~ 400 K. After multilayer exposures, the formation of the phenyl cyanate trimer, triphenoxotriazine, was observed with XPS between 160 and 200 K. The trimerized multilayer was stable up to ~ 500 K before it decomposed. This data suggests that at high coverages, a dicyanate functionalized molecule may chemically attach to aluminum by cleavage of an O-CN bond, while the other cyanate group is available for trimerization, thus anchoring a polycyanurate film to the surface. The surface chemistry of a dicyanate functionalized molecule, 1,1-bis(diphenylcyanato)ethane, is currently under investigation to confirm this hypothesis.

Friday Morning, October 29, 1999

10:00am **SS1+AS+BI-FrM6 Formation of Organic Layers by Cycloaddition Reactions at Germanium Surfaces**, *S.W. Lee*, University of Missouri, Columbia; *J.S. Hovis*, *R.J. Hamers*, University of Wisconsin, Madison; *C.M. Greenlief*, University of Missouri, Columbia

The formation of ordered organic layers on Ge(001) substrates is explored. Ge substrates are prepared by a novel method and exposed to a variety of cyclic hydrocarbons, including cyclopentene and cyclohexene. The subsequent surface interactions are followed by a variety of surface sensitive techniques. Bonding configurations are determined by photoelectron spectroscopy and scanning tunneling microscopy. The strength of surface interactions are also monitored by temperature programmed desorption. Cyclopentene and cyclohexene react with Ge dimer bonds via a [2+2] cycloaddition reaction. This reaction generates rows of the surface complex oriented along the dimer bond direction of the Ge(001) surface, which is easily observed by scanning tunneling microscopy. Experiments using other cyclic hydrocarbons and attempts at further surface modification will be discussed.

10:20am **SS1+AS+BI-FrM7 Multilayer Phases in Self-Assembled Monolayers Based on Silane Coupling Agents**, *B.C. Bunker*, *R.W. Carpick*, *M. Hanks*, *M.L. Thomas*, *R. Assink*, *M. DeBoer*, Sandia National Laboratories

Thin films prepared using silane coupling agents are used extensively to chemically modify surfaces. In micromachines, such films are used to control stiction, friction, and adhesion of moving parts. The films are commonly depicted as self-assembled monolayers, in which each silane molecule forms extensive Si-O-Si linkages to the surface and to other molecules. However, many workers report that it is difficult to produce self-assembled monolayers on a reproducible basis, especially for films having fluorinated hydrocarbon chains. In this paper, atomic force microscopy studies are used to show that irreproducible film formation is associated with the fact that silane coupling agents can self-assemble into a range of structures described in common surfactant phase diagrams. Evidence is presented suggesting that hydrocarbon and fluorocarbon silanes form lamellar and inverse micelle structures on silica and silicon nitride surfaces. In some instances, multilayer structures are produced during fabrication. Films which start out as monolayers can also reorganize into multilayer phases after deposition. Factors influencing the phases observed include surface pretreatment, the solvent, silane and water concentrations in the deposition solution, and environmental parameters such as temperature and relative humidity. Mechanisms for the evolution of the observed range of self-assembled structures vs. reaction conditions are described.

10:40am **SS1+AS+BI-FrM8 Self-assembled Monolayers on Silicon Surfaces: The Opposite to Siloxane Chemistry**, *J.A. Mulder*, *R.P. Hsung*, *X.-Y. Zhu*, University of Minnesota

Self-assembled monolayers (SAMs) on silicon surfaces are of interest for a number of reasons: they may be used as monolayer resists in high resolution lithography, as dielectric layers, as active components in hybrid sensor devices, as passivation and lubrication layers in MEMS, and as a new platform for biochips. SAMs on silicon are traditionally formed via siloxane chemistry on oxidized surfaces from organosilicon derivatives, such as alkyltrichlorosilane. The problems with siloxane SAMs are well known: they are difficult to prepare and suffer from poor reproducibility; the contradiction between cross-linking and close-packing is inherent; the presence of the amorphous and insulating oxide layer is not desirable in some applications. There is much incentive to develop simple processes for the formation of stable molecular layers directly on the silicon surface. We present a novel approach which, in essence, is the opposite to the siloxane SAM process. The assembly processes are based on the reaction between R-OH or R-NH₂ with chlorinated silicon surfaces, leading to molecular assembly via Si-O or Si-N linkages. These reactions are not only efficient but also sufficiently versatile for the assembly of a wide variety of functional organic molecules. A particular advantage of this new assembly chemistry is that it is compatible with both vacuum and solution phases and can be carried out under very benign experimental conditions. We characterize these SAMs using a variety of techniques, such as multiple internal reflection FTIR, X-ray photoelectron spectroscopy, contact angle measurements, and scanning probe microscopy. We address structural and stability of these SAMs and their dependence on molecular structure, such as alkyls and aromatics. We also discuss immediate and future applications.

11:00am **SS1+AS+BI-FrM9 The Photochemistry of Model Organosulfur Compounds Adsorbed on GaAs (110): Energy-Resolved Photofragment Angular Distributions**, *N. Camillone III*, *K. Adib*, *R.M. Osgood, Jr.*, Columbia University

Self-assembled monolayers of organothiols and related compounds hold promise for use in the semiconductor industry as ultrathin electron beam resists and precursors for the growth of II-VI materials, as well as for the growth of passivating gallium sulfide films on GaAs. An understanding of the structure and photon and electron chemistry of organothiols and related compounds is relevant to the development of these technologies. We report on our studies of the photoinduced chemistry of three model organosulfur compounds, CH₃SH, (CH₃)₂S, and CH₃SCH₃, on the (110) surface of GaAs. We find that the cross sections for the photoinduced reactions of these molecules in the adsorbed monolayers follows the trend CH₃SH > CH₃SCH₃ > (CH₃)₂S. Comparison of these measurements to photoinduced chemistry in the multilayer regime gives insight into the degree to which close proximity to the semiconductor surface perturbs the photochemistry. In addition, the structure and molecular orientation of these molecules is discussed in light of the results of energy-resolved photofragment angular distributions and low energy electron diffraction measurements. The post-irradiation chemistry of the trapped photofragments will also be discussed.

Author Index

Bold page numbers indicate presenter

— A —

Adib, K.: SS1+AS+BI-FrM9, **2**
Assink, R.: SS1+AS+BI-FrM7, **2**

— B —

Bartlett, B.: SS1+AS+BI-FrM5, **1**
Buck, M.: SS1+AS+BI-FrM3, **1**
Bunker, B.C.: SS1+AS+BI-FrM7, **2**

— C —

Camillone III, N.: SS1+AS+BI-FrM9, **2**
Carpick, R.W.: SS1+AS+BI-FrM7, **2**
Cowin, J.P.: SS1+AS+BI-FrM1, **1**

— D —

DeBoer, M.: SS1+AS+BI-FrM7, **2**

— F —

Felgenhauer, T.: SS1+AS+BI-FrM3, **1**

— G —

Greenlief, C.M.: SS1+AS+BI-FrM6, **2**
Grunze, M.: SS1+AS+BI-FrM3, **1**

— H —

Hahm, J.: SS1+AS+BI-FrM2, **1**
Hamers, R.J.: SS1+AS+BI-FrM6, **2**
Hankins, M.: SS1+AS+BI-FrM7, **2**
Hayashi, T.: SS1+AS+BI-FrM4, **1**
Hovis, J.S.: SS1+AS+BI-FrM6, **2**
Hsung, R.P.: SS1+AS+BI-FrM8, **2**

— I —

Iedema, M.J.: SS1+AS+BI-FrM1, **1**

— J —

Jaeger, H.M.: SS1+AS+BI-FrM2, **1**

— K —

Kodama, C.: SS1+AS+BI-FrM4, **1**

— L —

Lee, S.W.: SS1+AS+BI-FrM6, **2**
Lopes, W.A.: SS1+AS+BI-FrM2, **1**

— M —

Mulder, J.A.: SS1+AS+BI-FrM8, **2**

— N —

Nozoye, H.: SS1+AS+BI-FrM4, **1**

— O —

Osgood, Jr., R.M.: SS1+AS+BI-FrM9, **2**

— R —

Rong, H.-T.: SS1+AS+BI-FrM3, **1**
Russell, Jr., J.N.: SS1+AS+BI-FrM5, **1**

— S —

Sibener, S.J.: SS1+AS+BI-FrM2, **1**

— T —

Thomas, M.L.: SS1+AS+BI-FrM7, **2**

— V —

Valdisera, J.M.: SS1+AS+BI-FrM5, **1**

— W —

Wu, K.: SS1+AS+BI-FrM1, **1**

— Z —

Zhu, X.-Y.: SS1+AS+BI-FrM8, **2**