

## Surface Science

### Room 327 - Session SS+OF-WeA

#### Growth and Characterization of Organic Films

**Moderator:** L.A. Baker, Naval Research Laboratory

**2:00pm SS+OF-WeA1 Electronic and Geometric Structures of Pentacene Molecules Grown on Au(100), Y.J. Song, K. Lee, J. Yu, Y. Kuk, Seoul National University, Korea**

A pentacene molecule has attracted much interest for its possible application to organic-based electronic devices with its interesting electronic properties. Despite reported semiconducting property of the bulk crystal, it is hard to grow the high-quality film. Here, we report our scanning tunneling microscopy studies on the geometric and electronic structures of pentacene molecular layers on a Au(100) surface. Because of the high diffusivity of the molecule at room temperature, the STM studies were done at low temperature. At submonolayer coverage, the molecules are confined to the troughs of the reconstructed Au(100)-(5x20), forming a chain structure perpendicular to the reconstructed ridges. We resolved the HOMO and LUMO states of pentacene molecules on a Au(100) surface with atomic resolution. The DFT (density functional theory) results of the molecular layer reveal good agreement with the observed geometric and electronic structures. The electronic levels of pentacene molecules are shifted in the presence of metallic substrate. This result can be valuable when one makes metal-pentacene junctions for device applications. The electronic levels are also shifted with pentacene-pentacene interactions. At the coverages higher than 2 monolayers, a single phase was observed. The pentacene-pentacene interaction plays an important role to the growth structures. The 5 pentacene molecules work as a base unit for the multilayer film. The correlation between the growth structure and the transport property will be discussed.

**2:20pm SS+OF-WeA2 Pentacene Thin Films on Clean and Chemically Modified Si(001) Surfaces, K.P. Weidkamp, L. Fang, R.J. Hamers, University of Wisconsin-Madison**

We have investigated the microstructural, chemical and electronic properties of pentacene thin films formed on Si(001) surfaces. Using FTIR and valence-band photoemission spectroscopy, we find that the initial pentacene molecules deposited onto the surface undergo a transition from sp<sup>2</sup> to sp<sup>3</sup> bonding and partial dissociation, all indicating the formation of covalent C-Si bonds that inhibit diffusion and thereby result in poor pentacene crystal formation. In contrast films prepared by deposition on to Si(001) surfaces that were initially modified with a monolayer of pentacene molecules show no evidence for dissociation and exhibit highly reversible adsorption and desorption, demonstrating that the pentacene molecules do not form covalent bonds with the underlying organic-modified surface. In order to understand how the molecular structure of the interfacial organic layer affects that structure and electronic properties of the pentacene thin films, we have investigated pentacene thin films deposited onto silicon surfaces that were modified with several different organic molecules including cyclopentene, dodecene, and phenanthrenequinone. These three molecules are expected to differ significantly in thickness, molecular rigidity, and effective molecular conductivity. AFM images show that each organic molecular layer induces specific changes in the microstructure of the pentacene films deposited on top. Measurements of the electrical properties through the films will also be presented.

**2:40pm SS+OF-WeA3 Spectroscopic Measurements on Ultra Thin Highly Ordered Films of Organic Semiconductors, T. Fritz, TU Dresden, Germany**  
**INVITED**

Research activity on molecular solids has gathered pace in recent years as these materials have a wide range of interesting properties, emerging industrial interest with real applications at the horizon, and possible future applications that will enable electronics to move into the nanoscale. High quality samples, precise structural data, and a detailed understanding of the physical properties are essential, with special emphasis on thin films and interfaces. In this respect, the use of highly controlled growth techniques like Organic Molecular Beam Epitaxy (OMBE) is becoming more and more important, aiming at high quality thin films with controlled crystal structure and morphology, and therefore displaying well defined physical properties. In order to investigate those physical properties deeply, spectroscopy methods are required which allow to characterize films with film thicknesses down to even submonolayers. In our

contribution two different spectroscopy methods will be discussed in detail. By the first one, called Scanning Tunneling Spectroscopy (STS), one can determine the energetic positions of both filled and empty states of a molecular layer on an inorganic substrate in a single measurement. Due to the high spatial resolution small domains with different ordering can be electronically distinguished. Despite electron spectroscopies, optical spectroscopy on organic materials is a very powerful tool and can even provide structural information. Given the fact that exciton confinement effects in quasi-one-dimensional organic crystals will become apparent only if the layer is sufficiently thin (usually less than 4 monolayers), a method is required which will allow to measure the optical absorption down to submonolayer coverage with a sufficient signal-to-noise ratio. The method of choice is the Differential Reflection Spectroscopy (DRS, a variant of reflection absorption spectroscopy), carried out in situ, i.e., during the actual film growth.

**3:20pm SS+OF-WeA5 Epitaxial Growth of Pentacene on Bi/Si(111) Films, G.E. Thayer, IBM T.J. Watson Research Center; J.T. Sadowski, Tohoku University, Japan; R.M. Tromp, IBM T.J. Watson Research Center**

Electrical contacts between organics and metals have been known to limit charge injection in organic electronic devices. Thus it is not surprising that there is a considerable amount of current work modifying metal surfaces and interfaces in an effort to align conduction with organic molecular levels. The solution to this problem begins with understanding the fundamental mechanisms that control both the morphology and electronic structure at the interface between metal and organic materials. Although the interfaces of organic films grown on many clean substrates (semiconductors, insulators, and metals) are found to be poorly ordered, our work has revealed that pentacene grows epitaxially on Bismuth (a semimetal). Using LEEM, PEEM, LEED, AFM, and STM our efforts have focused on understanding how pentacene molecules order in Pn/Bi/Si(111) thin films (1ML-10MLs). In contrast to the frequently used Pn/Au system, in the first ML of Pn/Bi the pentacene molecules stand up and are highly ordered as seen by the sharp LEED patterns that we observe. Our LEED analysis finds that the structure of Pn/Bi/Si(111) thin films is similar to the bulk structure of Pentacene with lateral 2D cell dimensions of a=7.8Å, b=6.2Å, and  $\gamma=84.9^\circ$ . In one dimension, this structure is 1:1 commensurate in the  $\sqrt{3}$  direction of the underlying hexagonal Bi surface structure. However, in the other direction it is rotated by a small angle and is incommensurate with the Bi lattice. Control of Pn crystal orientation on metal electrodes will enable the fabrication of organic FFT's whose electrical characteristics are not degraded by large angle grain boundaries at the source and drain junctions.

**3:40pm SS+OF-WeA6 AFM Study of Carboxylic-Acid Functionalized Pentathiophenes on Mica Surfaces, J. Chen, Lawrence Berkeley National Laboratory; A.R. Murphy, University of California; D.F. Ogletree, M. Salmeron, Lawrence Berkeley National Laboratory; J.M.J. Frechet, Lawrence Berkeley National Laboratory and University of California**

We studied SAM films of the oligothiophene derivative (D5TBA @footnote 1@) with AFM to determine its growth and structure and its response to mechanical excitations. We found that self-assembled films formed on mica substrates from hydrophilic (THF) and hydrophobic (chloroform) solutions were totally different in their structure and mechanical properties. In one case methyl groups were exposed while in the other carboxylic groups (COOH) were exposed, resulting in very different friction properties. Friction anisotropy was observed between domains of different orientations. Scanning polarization force microscopy (SPFM) was used to obtain contact potential maps (Kelvin Probe mode) to confirm film structures deduced from contact mode imaging. Generally, deposition from THF solutions produced stable monolayer aggregates with exposed methyl groups. Multilayer regions were sometimes observed, with alternate methyl and carbonyl group terminations. During contact AFM imaging the third and higher layers could be progressively peeled off by increasing the load applied to the tip, however the second layer was found to incorporate into the first layer in a densification process. Deposition from chloroform solutions usually produced unstable multilayer films with methyl groups contacting the mica surface. @FootnoteText@ @footnote 1@ D5TBA, or 4-(5'-Decyl-[2,2';5', 2"; 5", 2'''; 5''', 2'''''] pentathiophen-5-yl)-butyric acid, was prepared by Stille cross-coupling methods using functionalized thiophene monomers.

# Wednesday Afternoon, November 5, 2003

4:00pm **SS+OF-WeA7 Surface Polymerization by Ion Assisted Deposition for Polythiophene Film Growth**, *S. Tepavcevic, Y. Choi, L. Hanley*, University of Illinois at Chicago

Cationic polymerization is induced at the gas-solid interface by hyperthermal organic cations coincident on a surface with a thermal beam of organic monomers. This process, termed surface polymerization by ion assisted deposition (SPIAD), produces films that maintain the chemical structure of the monomer. A polythiophene film is produced here by SPIAD with 100 eV thiophene ions and terthiophene monomers coincident on Si and indium tin oxide (ITO) substrates held under vacuum. X-ray photoelectron spectroscopy observes enhancement in film growth for SPIAD compared with either thiophene ion or terthiophene exposure alone. Polythiophene films grown by both mass-selected and non-mass-selected ions with coincident terthiophene dosing both display similar fluorescence intensity at two wavelengths characteristic of emission from films of the terthiophene monomer. Raman spectra of films from non-mass-selected ions display several vibrations also observed in terthiophene films. Ions therefore play a critical role in film growth from non-mass-selected ions, in addition to any radical or photochemically driven processes that may also occur. L. Hanley and S.B. Sinnott, *Surf. Sci.* 500 (2002) 500. S. Tepavcevic, Y. Choi, and L. Hanley, *J. Amer. Chem. Soc.* 125 (2003) 2396. L. Hanley, Y. Choi, E.R. Fuoco, F.A. Akin, M.B.J. Wijesundara, M. Li, A. Tikhonov, and M. Schlossman, *Nucl. Instr. Meth. Phys. Res. B* 203C (2003) 116.

4:40pm **SS+OF-WeA9 Molecular Dynamics Simulation Study of Continuous C<sub>3</sub>F<sub>5</sub><sup>+</sup> and CF<sub>3</sub><sup>+</sup> Ion Depositions on Polystyrene Surfaces**, *I. Jang, S.B. Sinnott*, University of Florida

Fluorocarbon plasma treatment is widely studied and used to change surface properties and to grow thin polymer films. However, it is difficult to determine the detailed mechanisms responsible for the surface reactions that lead to thin film growth due to the complexity of plasma systems. Computer simulations of the deposition of mass selected fluorocarbon ions have been used to isolate the effects of polyatomic ions in low energy plasma deposition of thin films. In this study, the continuous deposition of a beam of polyatomic fluorocarbon ions (C<sub>3</sub>F<sub>5</sub><sup>+</sup> and CF<sub>3</sub><sup>+</sup>) on polystyrene surfaces is performed using classical molecular dynamics simulations. The forces are determined using the reactive empirical bond order method for short-range interaction and Lennard-Jones potential for long-range van der Waals interaction. The incident energy of the ions is 50 eV/ion and they are deposited normal to polystyrene surface. The simulations allow us to determine the mechanisms responsible for thin-film growth and surface modification by the ion beam deposition. Specifically, they show how fluorocarbon polymer precursors are formed and react with one another. Overall, the simulations predict that CF<sub>3</sub><sup>+</sup> depositions are more effective in fluorination of polystyrene surface than C<sub>3</sub>F<sub>5</sub><sup>+</sup> depositions. This work is supported by the NSF under grant CHE-0200838.

5:00pm **SS+OF-WeA10 Exploring the Reactivity of Atomic Oxygen with Organic Surfaces**, *G.M. Wolfe, A.J. Wagner, J. Torres, C.C. Perry, D.H. Fairbrother*, Johns Hopkins University

Atomic oxygen is a major component in oxygen and air-based plasmas and also plays a major role in the erosion and degradation of polymeric coatings in spacecrafts as they pass through Low Earth Orbit (LEO). Through the use of self-assembled monolayers and well-defined polymeric substrates an understanding of the fundamental molecular level surface reactions of atomic oxygen with organic surfaces can be determined. Our work explores the interactions of O radicals, with a series of self-assembled monolayers (SAMs), employed as models for polymer surfaces. In situ X-ray photoelectron spectroscopy (XPS) is used to elucidate the mechanism of radical reactions occurring with dodecane, hexadecane, and X-ray modified hexadecane SAMs, as well as a semi-fluorinated SAM (CF-SAM). In the hydrocarbon SAMs, the reaction with atomic O progresses through three stages. Initially, reactions at the vacuum/film interface generate a steady state concentration of C-O, C=O and O-C=O groups. Sustained atomic oxygen exposure on hydrocarbon-based SAMs promotes the formation of volatile oxygen-containing carbon species, e.g. CO<sub>2</sub>, leading to the development of a steady state etch front. Ultimately, oxygen penetrates to the film/substrate interface to form sulfonate and Au<sub>2</sub>O<sub>3</sub> species. Experiments on the CF-SAM reveal an induction period of ~90 minutes prior to oxygen incorporation, an effect ascribed to the inertness of C-F and C-C bonds towards atomic oxygen and the well-ordered structure of the CF-SAM. In contrast to the hydrocarbon SAMs, reactivity

within the CF-SAMs are initiated by O atom reactions at the film/substrate interface leading to desorption of intact adsorbate chains. Results on the interaction of atomic O with phosphorous ion-implanted poly(ethylene) will also be presented.

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