Organic Films and Devices
Room: C-102 - Session OF+SS+EL+SC-TuA

Organic Molecular Films
Moderator: H. Fairbrother, Johns Hopkins University

2:00pm **OF+SS+EL+SC-TuA1 Reactivity of Polymers Containing Nitrogen and Oxygen Functional Groups with Vapor Phase Metal Atoms**, ***A.J. Wagner***, *G. Wolfe, D.H. Fairbrother*, The Johns Hopkins University

The surface reactions during the initial stages of polymer metallization are crucial in determining bonding and adhesive characteristics with native and plasma treated polymers. In this study, we have compared the reactivity of different nitrogen and oxygen containing functional groups with a variety of vapor phase metal atoms during the initial stages of metallization. The reactivity of different nitrogen containing functional groups during the vapor deposition of Ti, Fe, Ni, Cu and Au on Nylon 6, containing an amide group (-NH-(C=O)-and nitrogen implanted Poly(ethylene) (N-PE) containing a mixture of C-N, C=N and CN groups was studied. In addition, the reactivity of vapor phase metal atoms with specific functional groups was also investigated using a nitrile (CN) terminated self-assembled monolayer (CN-SAM). For each of the metals studied except Au reaction with Nylon 6 and N-PE resulted in the formation of the metal-nitride (MN), although the extent of reaction increased in the order Ti > Fe > Ni ~ Cu, scaling with the M-N bond strength. Experimental evidence, however, indicated that the different nitrogen containing functional groups present in the nitrogen-modified PE were not equally reactive. Ti and Fe also reacted with the C=O functional group in Nylon 6 to form their respective oxides while Cu, Ni and Au were unreactive with the C=O functional group. Metal nitride formation was also observed during evaporation of Ti and Fe on the CN-SAM although Cu and Au were unreactive towards the CN functional group. In contrast, metal carbide production was only evidenced during reactions with Ti. Results from this investigation will be interpreted in terms of the relative bond strengths associated with specific functional groups within the polymer and potential product species (e.g. metal oxide, nitrides).

2:20pm **OF+SS+EL+SC-TuA2 A New Crystalline Form of Pentacene: pi-stacked Thin Films Grown on Au(111)**, ***J. Kang***, *X.-Y. Zhu*, University of Minnesota

The recent demonstration of pentacene and related molecules in high-mobility field effect transistors (FETs), including superconducting FETs, has attracted great interest in this class of organic semiconductors. Carrier mobility is known to depend intimately on crystalline quality. In order to establish a molecular level understanding of structure-property relationship, we have carried out a scanning tunneling microscopy (STM) and spectroscopy (STS) study of the growth of crystalline pentacene thin films on Au (111). The use of high bias voltage (~ 5 V) and low tunneling current (~ 1pA) has enabled us to image, with molecular resolution, the growth of a new crystalline phase of pentacene well beyond the first a few layers. High resolution imaging shows that pentacene molecules form a pi-stacked crystalline phase with their long-axis parallel to the surface. This is attributed to the strong molecule-surface interaction, which seeds the growth of this new crystalline phase.

2:40pm **OF+SS+EL+SC-TuA3 Vapor Deposition and Polymerization of Low-k Polycyanurate Films**, ***J.N. Russell, Jr.***, *V.J. Bellitto, B. Bartlett, MJ Brooks, P.G. Santangelo, A.W. Snow*, Naval Research Laboratory **INVITED**

Future microelectronics will require advanced materials and processes for smaller, faster and more robust devices. Polymers address these needs and range from ultra-low permittivity materials to molecular semiconductors. Developing and understanding solventless deposition processes such as vapor deposition polymerization is important for producing conformal, voidless polymer films. One class of low-k polymers, polycyanurates, shows promise as a vapor depositable material. Yet little is known about the surface chemistry of the cyanate functionality and the conditions required for surface polymerization. Initially the surface chemistry of key functionalities in the monomer and polymer are examined using model compounds such as phenyl cyanate and triazine on Al(111). Aluminum was chosen because it is used for interconnects in microelectronics. Then, the in situ vacuum deposition and polymerization chemistry of NCO-CH2(CF2)6 CH2-OCN (F6Cy) is studied on Al, Cu, and Si surfaces. The vapor deposited F6Cy monomer film undergoes a photo-induced cyclotrimerization process to form cross-linked cyanurate networks with a permittivity of 2.1 at 1 GHz.

3:20pm **OF+SS+EL+SC-TuA5 Formation of Chemically Patterned Surfaces using Gas-Phase Oxalyl Chloride**, ***M.C. Asplund***, *G. Husseini, M.R. Linford, E.T. Sevy*, Brigham Young University

Optical lithography is a common technique for the formation of electronic devices on semiconductor substrates. Here we show an analogous technique that allows the introduction of a reactive functional group (-COCl) onto an alkylated Si substrate, or onto any substrate that contains C-H groups. The importance of the -COCl group stems from its high reactivity with amino and hydroxyl groups. Our new method consists of exposing a C-H containing surface to a gaseous mixture of N2 and oxalyl chloride ($(COCl)_2$) and then illuminating with 355 nm light. The UV photons form free radicals from the oxalyl chloride that then react with the C-H containing surface. We have shown using wetting, XPS, elipsometry and FT-IR spectroscopies that we have been able to form acid chloride functional groups on surfaces. By using simple optical masks we have shown that this functionalization occurs only where the sample is exposed to light. The key step to understanding the reaction mechanism for the surface reaction is understanding the formation and subsequent reaction of the radicals formed from the oxalyl chloride. Previous liquid phase reaction studies of oxalyl chloride with adamantane led to the suggestion that at 266 Cl is the primary radical formed, while at 355 nm the primary radical is the COCl radical. We have looked at the formation of radicals as a function of wavelength to analyze dissociation mechanism, and product energy distributions as well as the effect of pressure on radical formation. The minimum feature size which can be made using this method is given by the diffusion length of the radical. Thus the quenching must be understood and optimized to have controlled patterning of surfaces.

3:40pm **OF+SS+EL+SC-TuA6 Characterization of Ultrathin Organic Films via Near-edge X-ray Absorption Fine Structure Spectroscopy**, ***T.M. Willey***, University of California Davis and Lawrence Livermore National Laboratory, *A.L. Vance, T. van Buuren, C. Bostedt, A.J. Nelson, L.J. Terminello,* Lawrence Livermore National Laboratory, *C.S. Fadley*, University of California Davis and Lawrence Berkeley National Laboratory

Self-assembled monolayers (SAMs) and other thiol compounds adsorbed on Au(111) surfaces have become increasingly important for achieving surface attachment and orientation of complex molecules. Surface-attached molecular species containing catenanes and rotaxanes promise to play a vital role in achieving molecular-scale electronics and other devices.[1] Only through a rigorous understanding of the structure and properties of such molecular monolayer species can a rational synthesis of these hybrid materials be realized. Orientation of chemical bonds and thus the orientation of molecules can be precisely determined with near-edge x-ray absorption fine structure (NEXAFS) spectroscopy. Here, we present NEXAFS results on the configuration of surface-attached fundamental building-blocks of such systems, including a simple surface-attached rotaxane and its constituents. This rotaxane consists of a crown ether ring, threaded by a molecule bound to the gold at one end and providing an athracene stopper at the other.[2] Investigating films of the stopper molecule only vs. the complete rotaxane we confirm the presence of the crown ether in the complete molecule. We present the orientation of the anthracene stopper and crown ether ring with respect to the surface by deconvoluting their respective features in the NEXAFS.

Acknowledgements: This work is supported by the U.S. Department of Energy, BES Materials Sciences under contract W-7405-ENG-48, LLNL; at the ALS under contract number DE-AC03-76SF00098 at LBNL; and at the SSRL under contract number DE-AC03-76SF00515 at SLAC.

[1] Collier et al., Science 289, 1172-5

[2] Kolchinski et al., Chem. Commun., 1998, 1437-8

4:00pm **OF+SS+EL+SC-TuA7 Interfaces with Evaporated Short Chain Polyaniline**, ***B. Xu****, *A.N. Caruso, M. Bai, Y. Ovchenkov, S. Ducharme, B. Doudin, P.A. Dowben*, University of Nebraska-Lincoln

The interface properties of evaporated short chain polyaniline (PANI) were investigated by X-ray photoemission spectroscopy (XPS), inverse photoemission spectroscopy (IPES), as well as angle integrated photoemission spectroscopy (UPS). With sodium doping, the valence bands, conduction bands as well as the characteristic core levels show consistent shifts to the higher binding energy. Sodium, as an electron donor, when added to the polyaniline system, results in increased electron populations in the polyaniline bands --- effectively filling the almost completely filled band. In the case of iodine doping, all the states shifted to

---

***** Morton S. Traum Award Finalist

lower binding energy. Iodine, as an electron acceptor, effectively depletes the electron population in the occupied bands polyaniline. There is no abrupt interface formed between sodium or iodine and polyaniline, as demonstrated by the angle-resolved XPS. By comparison, the interface between polyaniline and another polymer poly(vinylidene fluoride with trifluoroethylene) copolymer (PVDF-TrFE) is quite abrupt. A P-N diode was made by evaporating PANI (p type) on the top of PVDF-TrFE (n type). The results presented here should apply to the problems associated with improving heterojunction polymer devices.

4:20pm **OF+SS+EL+SC-TuA8 Controlled p-Doping of Organic Molecular Films**, ***W. Gao***, *A. Kahn*, Princeton University

We investigate the controlled electrical p-doping of the hole-transport organic molecular material α-NPD with the strong electron acceptor tetrafluoro-tetracyano-quinodimethane (F_4-TCNQ) using ultraviolet and inverse photoelectron spectroscopies (UPS/IPES), and in-situ I-V measurements. We previously examined p-doping of ZnPc co-evaporated with F_4-TCNQ,[1] and found an excellent energy match between the ionization energy (IE) of ZnPc (5.28eV) and the electron affinity (EA) of F_4-TCNQ (5.24eV), demonstrating host HOMO-to-guest LUMO charge transfer. The ZnPc thickness dependence of I-V data further demonstrated a 7 orders of magnitude increase in hole current injected from Au due to tunneling through the doping-induced narrow depletion region at the metal/organic interface.[2] In the present study, we show that α-NPD (IE=5.52eV) is also efficiently doped with F_4-TCNQ. The hole injection current increases by almost 5 orders of magnitude when only the first 80Å of α-NPD away from the metal/organic interface is doped, and increases by another factor of 10 when the entire organic film is uniformly doped. However, the doping-induced movement of E_F toward the HOMO appears to be more restricted than in ZnPc. Having excluded extrinsic effects like surface photovoltage, we propose that the substantial (~0.2 eV) ionization-induced relaxation of molecular energy levels moves the "doped" α-NPD HOMO upwards, and thus pins E_F deeper into the gap than for ZnPc, which is a planar molecule with a negligible relaxation energy (< 0.05eV). This interpretation is further confirmed with UPS study of the host material growth on a film of the dopant molecules. We also show that molecular level alignment at organic/organic interfaces is controllable by doping-induced dipole. Work supported by the NSF (DMR-0097133).

[1] W. Gao and A. Kahn, Appl. Phys. Lett., 79, 4040 (2001)

[2] W. Gao and A. Kahn, Organic Electronics (in press).

4:40pm **OF+SS+EL+SC-TuA9 Processable Optically Transparent Thin Films of Conducting Polymers**, ***B.D. Martin***, *N. Nikolov*, *R. Shashidhar*, Naval Research Laboratory

A major problem in the area of electronically conducting polymers is that attempts to enhance their electrical conductivity by adding ionic dopants are always accompanied by a decrease of optical transparency. In this study we show how molecular self-assembly of small carbohydrate molecules can decouple the optical transparency and electrical conductance of conducting polymer films. When a carbohydrate such as glycerol, which is essentially a non-ionic hydrogen bonding dopant, is added to a commercially available conducting polymer suspension (Baytron P), the carbohydrate forms an intercalated, hydrogen bonded sandwich between the ionic pairs of the conducting oligomer unit and its supporting polymer suprastructure. This results in a pronounced increase of the distance between the ion pairs, and hence, to decreased electrostatic interaction. As a consequence there is an enhanced mobility of the ions and hence an increased conductivity without an accompanying increase in optical absorption. This behavior, which is in striking contrast to the normally observed trends in conducting polymers doped with traditional ionic dopants, is very important to the development of plastic liquid crystal displays (LCDs) and organic light emitting diode (OLED) displays.

5:00pm **OF+SS+EL+SC-TuA10 Optical Properties of Ordered Ultrathin Films of PTCDA**, ***R. Nitsche***, *H. Proehl*, *S. Mannsfeld*, *T. Dienel*, *T. Fritz*, TU Dresden, Germany

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 is 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, therefore displaying well defined physical properties. In our contribution we will discuss the special optical properties of ultrathin films of an archetypal organic material, namely PTCDA (perylene-3,4,9,10-tetracarboxylic-3,4,9,10-dianhydride). Highly ordered organic thin films on a gold single crystal have been prepared by means of OMBE with submonolayer to multilayer coverage. All films were structurally characterized by combining Scanning Tunneling Microscopy (STM) with Low Energy Electron Diffraction (LEED), clearly indicating epitaxial growth in the point-on-line mode. Differential Reflection Spectroscopy (DRS, a variant of reflection absorption spectroscopy) both ex situ and in situ has been applied to measure the optical characteristics of those films. The results clearly show that ultrathin layers have different optical properties as compared to thicker films, which in turn match the results known for long from polycrystalline samples. The results are further compared to thin films grown on mica to discuss the influence of different substrates.

Authors Index

Bold page numbers indicate the presenter