

## Surface Science

### Room 2004 - Session SS2+EM-WeA

#### Organic Film Growth and Characterization

Moderator: J.N. Russell, Naval Research Laboratory

#### 2:00pm SS2+EM-WeA1 Organic-on-Inorganic Thin Film Deposition and Vice Versa, *J.R. Engstrom*, Cornell University **INVITED**

Thin films of organic materials differ fundamentally in many respects when compared to inorganic materials (metals, semiconductors and oxides). A key difference involves the presence of strong covalent/ionic bonding in the latter, whereas organic materials are often bound by rather weak dispersion forces. Another important difference involves the methods and conditions used to assemble, fabricate and/or pattern these materials. For example, inorganic materials are often deposited at high temperatures, and patterned using aggressive subtractive techniques. Organics, on the other hand, can be deposited at very mild conditions, and can be patterned using additive techniques such as self assembly. Interestingly, in many emerging technologies, fabricating robust interfaces between these two diverse classes of materials is absolutely essential, yet extremely challenging. In this talk we will present a summary of recent findings concerning the formation of two important interfaces: organic-on-inorganic and inorganic-on-organic. Concerning the former, we are currently conducting studies of the deposition of pentacene on clean and modified SiO<sub>2</sub> surfaces using supersonic molecular beam techniques. In this work we have focused initially on the effects of incident kinetic energy, angle of incidence and substrate temperature on both submonolayer and multilayer growth. Some of our more interesting observations include an effect of incident kinetic energy on the ratio of deposition rates observed for submonolayer vs. multilayer growth, and the presence of so-called rapid roughening for multilayer thin films. Concerning the latter type of interface, we are currently investigating the use of self-assembled monolayers (SAMs) to promote nucleation and growth of ultrathin inorganic films (TiN) via atomic layer deposition. In this work we have focused particularly on the initial nucleation regime, where we find that the SAMs affect nucleation significantly and in unexpected ways.

#### 2:40pm SS2+EM-WeA3 Organic Semiconductor Growth: Real-Time Observation of Growth Dynamics and Structural Evolution, *S.M. Kowarik*, University of Oxford, UK, Germany; *A. Gerlach*, *S. Sellner*, *F. Schreiber*, Universitaet Tuebingen, Germany; *L. Cavalcanti*, *O. Kononov*, ESRF, France

We use in-situ and real-time X-ray scattering during growth of the organic semiconductor diindenoperylene (DIP) to study the evolution of the film structure and morphology with time. Time resolved measurements in a broad  $q$  range, i.e. sampling a large number of Fourier components simultaneously, allow to directly measure (kinetically limited) growth dynamics and reveal transient structures which would be missed in post growth experiments. We identify structural and orientational transitions for the few-monolayer (ML) regime, as well as for thick (several 10's of ML) films. We show that the differences in the interaction of DIP with the substrate change the thickness as well as temperature range of the transitions, which include (transient) strain, subtle changes of the orientation, as well as complete reorientation. These effects should be considered rather general features of the growth of organics, which, with its orientational degrees of freedom, is qualitatively different from growth of inorganics. @FootnoteText@ S. Kowarik et al., Physical Review Letters, 96, 125504 (2006).

#### 3:00pm SS2+EM-WeA4 Resonant Soft X-Ray Emission and Resonant Inelastic X-Ray Scattering: New Probes of Electronic Structure in Organic Semiconductors, *Y. Zhang*, Boston University; *J.E. Downes*, Macquarie University, Australia; *A. DeMasi*, Boston University; *A. Matsuura*, AFOSR; *C. McGuinness*, Trinity College Dublin, Ireland; *P.A. Glans*, *T. Learmonth*, *S. Wang*, *L. Plucinski*, *K.E. Smith*, Boston University

We report the use of synchrotron radiation-excited resonant soft x-ray emission spectroscopy (XES) and resonant inelastic x-ray scattering (RIXS) to study the electronic structure of thin film organic semiconductors. @Footnote 1@ XES directly measures the element-specific partial density of states (PDOS) in materials. When excited at a core level absorption threshold, RIXS features can be observed in the spectra, which are related to low energy excitations. The materials studied to date include a selection of metal phthalocyanines (Cu-Pc, FCuPc, VO-PC, TiO-PC, Ni-Pc), as well as other organic semiconductor materials such as Alq<sub>3</sub> and QAD.

Our results are in excellent agreement with theory, but differ significantly from previously published results. The films were found to be highly susceptible to radiation damage. We demonstrate the ability to accurately measure states near E<sub>F</sub>, and show that previously published XES studies of organic semiconductors are dominated by beam damage effects. This application of resonant XES has important consequences for the determination of band gap energies in organic molecular systems, since it allows determination of the non-ionized electronic structure. Supported in part by the U.S. AFOSR under FA9550-06-1-0157, by the Petroleum Research Fund, and by NSF under DMR-0304960. The spectrometer system is funded by the U.S. ARO under DAAD19-01-1-0364 and DAAH04-95-0014. Experiments were performed at the NSLS which is supported by the U.S. DOE, Divisions of Materials and Chemical Sciences. @FootnoteText@ @Footnote 1@ Y. Zhang, S. Wang, T. Learmonth, L. Plucinski, A.Y. Matsuura, S. Bernardis, C. O'Donnell, J.E. Downes, and K.E. Smith, Chem. Phys. Lett. 413, 95 (2005); J.E. Downes, C. McGuinness, P.A. Glans, T. Learmonth, D. Fu, P. Sheridan, and K.E. Smith, Chem. Phys. Lett. 390, 203 (2004).

#### 3:20pm SS2+EM-WeA5 Structure in Self-Assembled Organic Thin Films, *S.L. Bernasek*, *F. Tao*, Princeton University; *Y. Cai*, Brookhaven National Laboratory **INVITED**

In the self-assembly of long chain hydrocarbons and substituted hydrocarbons on solid substrates, three classes of interaction energies govern the self-assembly process. They are chain-chain interactions within a lamella on the surface, interactions between ordered lamellae, and interactions between the adsorbate molecules and the underlying substrate. These interactions may be dispersive, or more directed interactions such as hydrogen bonding or acid-base interactions. We examine the interaction energies in these self-assembled organic monolayers based on structural studies using molecular resolution scanning tunneling microscopy for a variety of functionalized hydrocarbon molecules. Competitive coadsorption studies, and the effects of solvent on the stability of the structures formed are examined. Long chain carboxylic acids, di-acids, esters, anhydrides, alcohols, and di-alcohols adsorbed on highly oriented pyrolytic graphite have been examined.

#### 4:00pm SS2+EM-WeA7 Epitaxial Nanolayers of Organic Small Band Gap Semiconductors: Growth and Electronic Properties of Quaterrylenes on Au, *R. Franke*, *C. Wagner*, *S. Franke*, TU Dresden, Germany; *S.C.B. Mannsfeld*, Stanford University; *F. Fritz*, TU Dresden, Germany

The understanding of the physical properties of organic thin films is of importance for their application in novel devices. Thin films grown by the Organic Molecular Beam Epitaxy technique often exhibit highly ordered layer structures. Their physical structure is usually governed by a fine balance between weak molecule-molecule interactions and a small lateral variation of the molecule-substrate interaction potential. In order to investigate the energetics of such a heteroepitaxial layer system, one has to consider large molecular domains. @Footnote 1,2@ Here we report on films of large molecules, namely quaterrylene (QT) and quaterrylenetetracarboxylic-dianhydride-diimide (QTCDI), on Au(111) in UHV. These materials are especially interesting due to their long-wavelength absorption in the NIR. In our combined LEED and STM study we found a point-on-line coincident growth with flat lying molecules for the first monolayer (ML) of QT, while we observe alternating upstanding and flat lying molecules in the second ML. @Footnote 3@ In contrast, the arrangement of the QTCDI molecules in the first ML differs strongly, due to the presence of the substituents. We will also show that our experimental results correspond nicely to potential energy calculations on large ordered QT and QTCDI domains. The electronic properties of these ultrathin films were investigated by Scanning Tunneling Spectroscopy. In case of QTCDI we found a HOMO-LUMO gap of 2.1 eV, while we obtained 2.5 eV for the smaller QT. The comparison to absorbance measurements on mica allows us to estimate the exciton binding energies. @FootnoteText@ @Footnote 1@ S.C.B. Mannsfeld and T. Fritz, PRB 93 (2004) 075416. @Footnote 2@ S.C.B. Mannsfeld, K. Leo, and T. Fritz, PRL 94 (2005) 056104. @Footnote 3@ R. Franke, S. Franke, S.C.B. Mannsfeld, C. Wagner, T. Diemel, and T. Fritz, APL 88, (2006) 161907.

#### 4:20pm SS2+EM-WeA8 One-Dimensional Supramolecular Assemblies on Stepped Surfaces: What Makes Them Extend into the Mesoscale Length Regime?, *J. Schnadt*, University of Aarhus, Denmark, Sweden; *E. Rauls*, *Wei Xu*, *J. Knudsen*, *R.T. Vang*, *B. Hammer*, *F. Besenbacher*, University of Aarhus, Denmark

On perfect single crystal surfaces small organic molecules can self-assemble to form ordered one- and two-dimensional networks based on hydrogen

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bonding and other non-covalent interactions (see, e.g., Ref. 1). Such networks can grow very large and extend into the meso- and macroscale length regimes. Most real surfaces of interest, however, are afflicted with defects such as monatomic steps. These defects typically hinder the formation of large-scale networks. We show here for a particular example that it is possible to overcome this obstacle by choosing the right combination of surface and organic molecule. In the present case we investigated the self-assembly of 2,6-naphthalene-dicarboxylic acid (NDCA) on a stepped Ag(110) surface and compared it to the self-assembly of the same molecule on the Ag(111) and Cu(110) surfaces. The STM and XPS results show that NDCA on Ag(110) forms macroscopic-scale one-dimensional and directional structures across the step edges with maximum lengths in the micrometer range, notwithstanding the stepped character of the surface. This stands in contrast to the other surfaces, where the step-crossing behaviour is not observed. The experimental results together with density functional theory calculations show that the primary driving force for the formation of these long one-dimensional assemblies is hydrogen bonding, and that these bonds form also at the Ag(110) step edges. The bond formation across the step edges is driven by a combination of different factors, including the strength and bond directionality of the hydrogen bonds, the assembly directionality mediated by the substrate, and a sufficient flexibility of the adsorbate molecular backbone. A subtle balance of these factors, which depends on the particular adsorbate and the particular substrate, is required to achieve the observed step-edge tolerance of the assembly. @FootnoteText@ @footnote 1@ J. V. Barth, G. Costantini, and K. Kern, Nature 437, 671 (2005).

4:40pm **SS2+EM-WeA9 Controlled Self-Organization of Nanodots at Organic p-n Heterojunctions**, *E. Barrena, D.G. de Oteyza*, Max-Planck-Institut fuer Metallforschung, Germany; *J.O. Osso*, Institut de Ciencia de Materials de Barcelona, Spain; *S. Sellner, H. Dosch*, Max-Planck-Institut fuer Metallforschung, Germany

\*Many organic devices like Light-Emitting Diodes (OLEDs), solar cells or ambipolar transistors rely on p-n junctions of organic semiconductors. Although numerous studies have been devoted to the characterization and optimization of the performance of p-n organic-based devices, the present-day knowledge on the physical principles of the growth of organic heterostructures is still poor. By combining atomic force microscopy with surface-sensitive X-ray diffraction, we have been able to get a detailed in-situ insight into the microscopic processes which take place during the growth of p-conducting di-indenoperylene (DIP) molecules onto n-conducting copper-hexadecafluorophthalocyanine (F16CuPc) thin films. We demonstrate the self-organization of well-ordered DIP nanodots with high crystallinity and show that their growth is intimately related to a novel type of interface reconstruction of the underlying F16CuPc film which affects three monolayers adjacent to the organic p-n interface. This self-organized nanopatterning of an organic p-n-junction opens new possibilities for organic electronic functions.

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