

Surface Science

Room 202 - Session SS+EM-WeA

Organic Film Growth and Characterization

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

2:00pm **SS+EM-WeA1 Comparison of the Electronic Structure of Ferroelectric Polymers**, *J. Xiao, L.G. Rosa, M. Poulsen, D.Q. Feng, S. Ducharme*, University of Nebraska-Lincoln; *P.A. Dowben*, University of Nebraska-Lincoln, US

We compare the electronic structure of copolymers of polyvinylidene fluoride with trifluoroethylene (P(VDF-TrFE, 70%:30%) with polymethylvinylidencyanide (PMVC). Crystalline thin films can be formed from both ferroelectric polymers and we find that in both cases the dipole is aligned along the surface normal. The P(VDF-TrFE) copolymer is generally observed to have the chemical potential close to the lowest unoccupied molecular orbital, with a band gap of about 6 eV. PMVC exhibits a much greater band gap, with the Fermi level placed roughly mid way within the highest occupied to lowest unoccupied molecular orbital (HOMO-LUMO) gap. The implications of these differences in electronic properties will be discussed, in particular with regard to electron-phonon coupling. @footnote 1@ @FootnoteText@ @footnote 2@ @footnote 3@ @FootnoteText@ @footnote 1@Jaewu Choi, P.A. Dowben, S. Pebley, A. Bune, S. Ducharme, V.M. Fridkin, S.P. Palto, N. Petukhova, Phys. Rev. Lett. 80 (1998) 1328-1331@footnote 2@Chun-gang Duan, W.N. Mei, J.R. Hardy, S. Ducharme, J. Choi, P.A. Dowben, Europhys. Lett. 61 (2003) 81-87@footnote 3@Luis G. Rosa, Ya.B. Losovij, J. Choi, and P.A. Dowben, J. Physical Chemistry B 109 (2005) 7817-7820.

2:20pm **SS+EM-WeA2 Energetics of Metals Adsorption on Polymers: Calorimetric Studies**, *J.F. Zhu, S.F. Diaz, P. Goetsch, J.J.W. Harris, C.T. Campbell*, University of Washington

We report here the first calorimetric measurement of any metal adsorption energy onto any polymer surfaces wherein the sticking probability of the metal also was measured. The heat of adsorption and sticking probability were measured for Pb and Ca gas atoms adsorbing onto clean poly(methyl methacrylate) (PMMA) and electron-irradiated PMMA. The PMMA film was spin coated directly onto the heat detector, a pyroelectric polymer foil (polyvinylidene fluoride - PVDF) precoated on both sides with metal thin films to serve as electrodes. This provides a detector sensitivity of ~450 V/Jabs with a pulse-to-pulse standard deviation of 1.2 kJ/mol and an absolute accuracy within 2%. The Pb atoms interact very weakly with the outgassed pristine PMMA surface, with a sticking probability of 0.02 ± 0.02 . They deposit a heat into the PMMA of 12.7 ± 0.7 kJ per mole of dosed Pb, independent of Pb exposure up to 10 ML. This is slightly less than would be expected even if no Pb atoms stuck to the PMMA, but if they completely thermally accommodated to the substrate temperature during their collisions with the surface. This proves that thermal accommodation is incomplete, highlighting the weakness of the Pb - PMMA interaction. Calcium interacts with pristine PMMA much more strongly, with an initial sticking probability of ~0.5 and an initial heat of adsorption above 240 kJ/mol. Damaging the PMMA surface with electrons causes an increase in reactivity with Pb, as evidenced by increases in the initial heat of adsorption up to 134.0 ± 0.7 kJ/mol and the initial sticking probability up to 0.51 ± 0.01 . Both increase with increasing coverage toward values expected for Pb adsorption onto bulk Pb.

3:00pm **SS+EM-WeA4 Contrasting the Assembly and Molecular Architecture of N-heteroaromatic Molecular Films on Ag(111): ACA vs. INA**, *H. Li, B. Xu, D. Evans, J. Reutt-Robey*, University of Maryland at College Park

Monolayer films of isonicotinic acid (INA) and 9-acridine carboxylic acid (ACA) were prepared by physical vapor deposition and investigated with complementary scanning tunneling microscopy (STM) and spectroscopy (XPS, RAIRS) under UHV conditions. These N-heteroaromatic acids offer the same H-bonding motifs, but varied sizes and electrostatic properties, which should impact film architecture. In the monolayer regime, STM images reveal that both molecules readily assemble at room temperature into ordered "2-D" structures with typical domain sizes exceeding 100 nm for INA and 1000 nm for ACA. Differences between the domain structures (INA domains being more anisotropic and with much sharper (molecularly smooth) boundaries) are related to differences in their intermolecular forces. We propose structural models consistent with high resolution STM images and test these structural models with detailed spectroscopic

measurements. XPS studies of N 1s and O 1s core level shifts identify a predominant H-bonding motif based upon N head-to- carboxyl tail interaction, in agreement with the proposed structural model. Surface infrared measurements of INA molecular films detect a pronounced out-of-plane aromatic H bending mode at 858 cm⁻¹, and an intensity analysis determines the aromatic plane to be tilted by ~20° from the substrate plane. The proposed structural model for ACA involves an arrangement of ACA molecules with greater and alternating tilt angles, which we are presently testing with infrared experiments. We will account for these distinct molecular film architectures with the differences in the intermolecular forces and discuss the generality of these effects.

3:20pm **SS+EM-WeA5 Intermolecular Interactions in Ultrathin Organic Films**, *N.V. Richardson*, University of St Andrews, UK **INVITED**

Across the complexity of molecular systems, which have now been studied in great detail at well-defined, single crystal surfaces, particularly metal surfaces, there is a great variety in the strength, nature and significance of the intermolecular interactions which are possible. It is the balance of these interactions with the adsorbate/substrate interaction that is a key determinant of the two dimensional order, which can be achieved in the system. In the simplest cases, the interaction may be limited to Van der Waals' attractions balanced by local steric repulsion, while in more complex cases, highly directional H-bonding interactions can dominate the interadsorbate interaction. In the case of adsorption on relatively soft metals such as copper, silver and gold the strength of the interaction of the molecule with the surface atoms can be comparable with or even greater than that between the surface metal atoms, this can lead to the formation of highly ordered 2D adsorbate structures involving significant translocation of metal atoms, most likely in the form of metal adsorbate complexes, and consequential large scale restructuring of the surface. In this presentation, some examples of the relevance of intermolecular interactions in determining adsorbate structures in the sub-monolayer to monolayer regime will be given based on our studies of molecules ranging from aromatic hydrocarbons, through alkane and fluoroalkane thiols to simple biomolecules, such as amino acids and nucleic acid bases. In a somewhat more detailed description of two adsorbate-substrate systems, the role of a two dimensional monolayer in templating a novel three dimensional bulk structure will be described and, in the other example, the ability of a racemic mixture of adsorbing molecules to exploit intermolecular interactions leading to chiral phase segregation will be demonstrated.

4:00pm **SS+EM-WeA7 Conformational Changes and Chiral Ordering in Adsorbed Molecular Layers Investigated by Time-resolved STM**, *S. Weigelt¹, C. Busse, L. Petersen, T.R. Linderoth, E. Rauls, B. Hammer, K.V. Gothelf, F. Besenbacher*, University of Aarhus, Denmark

Detailed understanding of intermolecular interactions and molecular dynamical processes is required to control, and ultimately exploit, molecular self-assembly on surfaces. Recently, self-assembled structures formed from molecules that become chiral once confined to the surface plane have received particular attention. In this contribution we investigate a family of organic molecules that surprisingly can switch chirality as well as switch between chiral and non-chiral forms after adsorption by undergoing spontaneous conformational changes. The molecules (oligo-(phenylene-ethynylene)'s) consist of a central benzene ring with two or three ethynylene spokes each terminating in a tert-butyl substituted salicylaldehyde moiety. Upon vapour deposition onto the Au(111) surface under UHV conditions, the molecules assume different surface conformers, distinguishable in STM images by the positions of the tert-butyl groups relative to the molecular backbone. Some of these surface conformers are chiral and the chirality of the conformers and the chirality of the assumed molecular tiling patterns are highly correlated. The correlation is enabled by an intra-molecular switching mechanism, allowing the adsorbed molecules to flip between different surface conformers (and hence between different chiral forms) by rotating their end groups around the axis of the ethynylene spoke. This chiral switching enable the molecules to form extended homo-chiral domains by dynamically accommodating to the chiral template found at domain perimeters. We have performed a detailed investigation of this intra-molecular dynamic process by monitoring the surface with time-resolved STM at substrate temperatures in the interval 150-220K. The rate for the conformational change follows an Arrhenius dependence on temperature with activation energy ~0.3 eV. Theoretical modeling is currently being performed to illuminate this novel intra-molecular dynamical process.

¹ Morton S. Traum Award Finalist

Wednesday Afternoon, November 2, 2005

4:20pm **SS+EM-WeA8 Resonant Soft X-Ray Emission and Inelastic X-Ray Scattering Studies of Electronic Structure in Metal Phthalocyanines**, Y. Zhang, S. Wang, L. Plucinski, Boston University; J.E. Downes, Victoria University of Wellington, New Zealand; C. McGuinness, Trinity College Dublin, Ireland; P.A. Glans, T. Learmonth, K.E. Smith, Boston University

We report synchrotron radiation-excited resonant soft x-ray emission (SXE) spectroscopy and resonant inelastic x-ray scattering (RIXS) studies of the electronic structure of thin films of metal phthalocyanines (M-Pc). SXE measures the element-resolved partial density of states (PDOS) in materials. At a core level resonance, SXE measures the non-ionized PDOS associated with specific chemical sites. Furthermore, RIXS features can be observed which are related to low energy excitations in the system. We discuss the application of SXE and RIXS in the study of M-Pc. Our results are in excellent agreement with theory, but differ significantly from previously published experiments. The films were found to be highly susceptible to beam damage. We successfully circumvented this effect by continuous film translation during measurement. Resonant SXE spectra from undamaged Cu-Pc samples show spectral features near the Fermi level (E_F) that, although predicted, have not previously been observed. We have also studied vanadium oxide phthalocyanine (VO-Pc), and in addition to measuring the element resolved PDOS, have observed dipole forbidden $V\ 3d - V\ 3d^*$ and $O\ 2p - V\ 3d^*$ charge transfer transitions across the band gap. The ability to accurately measure states near E_F is significant, as is the discovery that many SXE studies of organic semiconductors are dominated by beam damage effects. Supported in part by the ACS PRF, by NSF DMR-0304960, and by DOE DE-FG02-98ER45680. The spectrometer system is funded by U.S. ARO DAAD19-01-1-0364 and DAAH04-95-0014. Experiments performed at the NSLS which is supported by the U.S. DOE, Divisions of Materials and Chemical Sciences. J.E. Downes, C. McGuinness, P.-A. Glans, T. Learmonth, D. Fu, P. Sheridan, and K.E. Smith, Chem. Phys. Lett. 390, 203 (2004).

4:40pm **SS+EM-WeA9 Effects of Incident Kinetic Energy on the Nucleation and Morphological Evolution of Organic Thin Films**, A.S. Killampalli, T.W. Schroeder, J.R. Engstrom, Cornell University

The deposition and growth of thin films of organic materials differs fundamentally from that of the more conventional inorganic materials. A key difference involves the presence of strong covalent and ionic bonding in the latter class of materials, whereas organic materials are often bound by rather weak dispersion forces. As a consequence, considerable promise exists in the use of energy tunable molecular beams for the deposition of organic thin films, as incident species with energies on the order of a few eV may produce substantial changes in the growth habit. We have been examining the deposition of pentacene thin films using a supersonic molecular beam source producing hyperthermal ($E_{\text{subi}} = 1.4 - 10.6\ \text{eV}$) kinetic energies. In both the monolayer and multilayer regimes of growth of pentacene on SiO_2 we find that as E_{subi} is increased from 1.5 to 6.7 eV, the growth rate at a fixed incident flux decreases, consistent with trapping-mediated adsorption. In the monolayer regime the data is well explained by nucleation theory, where the critical island size is 4.5 ± 1.3 . The situation is more complex in the multilayer regime - here the decrease in the rate is less than that observed in the monolayer regime, and at sufficiently large $E_{\text{subi}} (> 4\ \text{eV})$, the rate of deposition in the multilayer regime exceeds that in the monolayer regime by about a factor of 3. The evolution of surface roughness provides additional clues as to the dynamics of growth in the multilayer regime. For all incident kinetic energies, the growth exponent, β , is greater than 0.5, indicative of rapid roughening. Our results demonstrate clearly that the morphological evolution of organic thin films can be modified substantially at high incident kinetic energies.

5:00pm **SS+EM-WeA10 Para-Sexiphenyl Thin Films Grown by Hot Wall Epitaxy on KCl(001) Substrates**, A.Yu. Andreev, A. Montaigne, University Linz, Austria; G. Hlawacek, University of Leoben, Austria; T. Haber, R. Resel, Graz University of Technology, Austria; H. Sitter, University Linz, Austria; C. Teichert, University of Leoben, Austria

Para-sexiphenyl (p-6P) is a blue emitting organic semiconductor widely investigated for optoelectronic applications. Especially, p-6P thin films grown on mica(001) and KCl(001) substrates show large morphological, electrical and optical anisotropy, which makes them attractive for nanoscale optoelectronic and photonic devices. In this work, we use Atomic Force Microscopy (AFM) and X-Ray diffraction (XRD) to study the growth of p-6P on crystalline KCl substrates, in order to find the process controlling parameters. It is shown that the growth process of p-6P on KCl(001) is quite complex and can be divided preliminary in two steps. The initial growth

stage is characterized by the formation of the long needle-like crystallites build of "laying" molecules (as shown by XRD), generating a rectangular network in accordance with substrate surface symmetry. If the surface coverage increases, terraced crystalline mounds composed of upright standing molecules start to develop between the needles. These mounds are clearly formed due to repeated 2D nucleation of p-6P molecules. Consequently, all terraces found are in average about 2.6 nm high, which corresponds to one monolayer of standing p-6P molecules. Further, growth is characterized by a coexistence of the constantly growing needles and mounds, whereby the last ones cover finally almost the whole surface between the needles. By means of phase imaging in AFM tapping mode, it could be clearly demonstrated that both needle-like crystallites and flat terraced mounds grow directly on the substrate surface, i.e., there is no wetting layer formed during the deposition of p-6P on KCl(001).

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