

Surface Science

Room: 611 - Session SS2+EM+TF-FrM

Organic Films II: Semiconductors and C₆₀

Moderator: J.E. Reutt-Robey, University of Maryland

8:00am **SS2+EM+TF-FrM1 Unravelling Molecular Contrast Formation Obtained by NC-AFM on Titania**, R. Bechstein, J. Schütte, P. Rahe, A. Kühnle, University of Osnabrueck, Germany

The (110) surface of TiO₂ constitutes an interesting model substrate for molecular adsorption studies due to its importance in applications such as organic solar cells and light emitting diodes. Several experiments revealed that organic molecules can be anchored to the surface through carboxylic groups both under ultra-high vacuum conditions¹ as well as from solution.² We investigated a perylene-3,4,9,10-tetracarboxylic-3,4,9,10-diimide (PTCDI) derivative without carboxylic anchor groups by non-contact atomic force microscopy (NC-AFM) under ultra-high vacuum conditions. The molecules were deposited at room temperature onto TiO₂ (110) by evaporation from a Knudsen cell. We achieved true atomic resolution on the bare substrate as well as submolecular resolution on individual molecules. The molecules were observed to align along the [001] direction with the ability to move along this direction. They are found to be homogeneously distributed on the terraces without any tendency to cluster at step edges even at elevated temperature. Two molecular contrast modes are clearly distinguished. In one mode the molecules appear cloudy and are observed to be centred on top of bright rows. In the other mode the molecules are imaged with a dark bone-shaped centre and a bright rim, centred on top of dark rows. Scanning tunnelling microscopy measurements allow to conclude that the molecules are always centred on top of the bridging oxygen rows, demonstrating a contrast reversal between the two NC-AFM imaging modes. By comparing these results with previous NC-AFM studies,³ we can assign the two modes to positive and negative terminated tips showing that in NC-AFM imaging strongly depends on the tip termination.

¹ A. Sasahara, H. Uetsuka, and H. Onishi, J. Phys. Chem. B 105, 1 (2001)

² C. L. Pang, T.-a. Ishibashi, and H. Onishi, Jpn. J. Appl. Phys. 44, 5438 (2005)

³ J. V. Lauritsen, et al., Nanotechnology 17(14), 3436 (2006).

8:20am **SS2+EM+TF-FrM2 Characterization of Para-Sexiphenyl Thin Films Grown on KCl Substrates**, A. Andreev, Univ. of Leoben, Austria, A. Montaigne, Univ. Linz, Austria, T. Haber, Graz Univ. of Tech., Austria, A. Kadashchuk, National Academy of Sci. of Ukraine, G. Hlawacek, Univ. of Leoben, Austria, D.-M. Smilgies, Cornell Univ., R. Resel, A. Winkler, Graz Univ. of Tech., Austria, H. Sitter, N.S. Sariciftci, Univ. Linz, Austria, C. Teichert, Univ. of Leoben, Austria

Para-sexiphenyl (6P) films grown on mica(001) and KCl(001) substrates show large morphological and optical anisotropy, which makes them attractive for nano-scale photonic devices. In this work we use Atomic Force Microscopy (AFM), electron microscopy, x-Ray diffraction (XRD), and photoluminescence (PL) in order to find the parameters controlling film morphology, structure, and quality. It is shown that the initial growth stage of 6P on KCl(001) is characterized by the formation of μm -long needles, generating a rectangular network in accordance with the substrate surface symmetry. With increasing coverage, terraced mounds composed of upright standing molecules developing between the needles are observed and subsequent growth is characterized by a coexistence of both features. It is demonstrated that both features grow directly on the substrate surface, i.e., there is no wetting layer during the deposition of 6P on KCl(001). It is also found that both needles and terraced mounds grown on KCl(001) are single crystalline, in contrast to mica(001), where different oriented 6P domains are formed inside of the chains. PL studies have shown that, as in 6P films on mica, the emission spectra contain two different components - a conventional structured spectrum due to intrinsic excitons and a broad red-shifted band ascribed to some kind of defects. The latter band most clearly can be distinguished in delayed fluorescence spectra of the studied films. It is remarkable, however, that the relative intensity of the defect band was much weaker in the films grown on KCl substrates comparing to that on mica, which corresponds well with results of morphological and structural investigations. This finding confirms the high quality of the films and implies that the defect band is rather sensitive to the structure and morphology of the films. We also discuss a correlation between growth condition of 6P and a relative intensity of the defect PL band.

8:40am **SS2+EM+TF-FrM3 A Nanoengineering Approach to Regulate The Lateral Heterogeneity of Self-Assembled Monolayers**, J.-J. Yu, Y.H. Tan, X. Li, University of California, Davis, P.K. Kuo, Wayne State University, G.-Y. Liu, University of California, Davis **INVITED**

Using a scanning probe lithography method known as nanografting in conjunction with knowledge of self-assembly chemistry, regulation of the heterogeneity of self-assembled monolayers (SAMs) is demonstrated. It is known that phase segregated domains would form if SAMs are grown from thiol solutions of mixed compositions. The size and distribution of these domains depend on the interplay between reaction kinetics and dynamics, which can be regulated by varying the reaction conditions including concentration, temperature and reaction time. The reaction mechanism in nanografting, however, differs significantly from self-assembly in the conventional mix-and-grow methods. The spatial confinement in nanografting bypasses the lying-down to standing up transition process, and thus leads to a much fast kinetics. Knowledge of the reaction pathways enables development of methods for shifting the interplay between the kinetics and thermodynamics in SAM formation, and thus the heterogeneity of mixed SAMs. By varying fabrication parameters such as shaving speed, and reaction conditions such as concentration and ratio of the components, the lateral heterogeneity can be adjusted ranging from near molecular mixing to segregated domains of several to tens of nanometers.

9:20am **SS2+EM+TF-FrM5 Mechanistic Aspects of Organic Thin Film Growth from Energetic Sources: Insights from Experiment and Molecular Dynamics Simulations**, J.E. Goose, A.S. Killampalli, P. Clancy, J.R. Engstrom, Cornell University

We have used a combination of experiments and molecular dynamics simulations to investigate the fundamental molecular mechanisms contributing to the evolution and final morphology of thin films of pentacene deposited at hyperthermal incident kinetic energies ($E_i = 1-10$ eV). Experimentally, using supersonic molecular beam scattering techniques and atomic force microscopy we have characterized the adsorption probability as a function of both E_i and the angle of incidence (θ_i). Interestingly, we observe differences in the dynamics of adsorption for pentacene interacting with a clean SiO₂ substrate (submonolayer growth) vs. a SiO₂ substrate covered by a pentacene thin film (multilayer growth). Specifically, for E_i greater than $\sim 1-2$ eV, contribution of a new mechanism for pentacene adsorbing on pentacene is implicated. To determine the nature of this mechanism, we have used the non-reactive empirical MM3 potential to model the collision of pentacene molecules with a pentacene thin film using molecular dynamics. Our simulation cell consists of ca. 100 molecules, and includes an upper terrace of $4 \times n$ unit cells, bounded by (010) step edges. Accounting for impacts both near the middle of the terrace and near the step edge, our results from simulation for the probability of adsorption compare very well with those measured experimentally. In particular, adsorption is found to decrease with increasing E_i , and, in general, with increasing θ_i . More importantly, the simulations give us insight into nature of the events that occur at high incident kinetic energies. For thermal incident kinetic energies we observe mostly simple trapping (molecular adsorption), with near unit probability. At higher E_i of 1-5 eV, a significant fraction of molecules ($\sim 30\%$) are found to directly insert into the upper terrace, whereas a higher fraction ($\sim 90\%$) of molecules impacting near the step edge in this same energy regime also end up incorporating into the upper terrace. Indeed, direct molecular insertion into the pentacene crystal structure is the dominant interlayer process when both the molecule's orientation and incident angle are aligned normal to the surface, which leads to the formation of interstitials for the time scale of these simulations.

9:40am **SS2+EM+TF-FrM6 Growth of Pentacene Thin Films from a Supersonic Source: Unexpected Behavior in the Presence of Molecular Cluster Formation**, A. Amassian, S. Hong, S. Bhargava, A.R. Woll, T.W. Schroeder, A.S. Killampalli, J.D. Ferguson, J.D. Brock, G.G. Malliaras, J.R. Engstrom, Cornell University

We have examined the growth of pentacene thin films on SiO₂ using supersonic molecular beam techniques and in situ real-time synchrotron x-ray scattering. At low-to-moderate rates of deposition [ca. 0.001 to 0.1 monolayer(ML)/s] we observe an abrupt transition from 2D, layer-by-layer growth to 3D, islanded growth after deposition of the first few monolayers of pentacene on SiO₂. At high rates of deposition (ca. 1 ML/s), however, we find persistent 2D crystal growth, and the development of a highly textured film possessing significantly flatter and smoother surface morphology than at low rates of deposition. Concomitantly, in this regime we also observe new polymorphs of pentacene, as significant changes occur in the crystalline structure of the thin films. The transition to this anomalous, yet

promising growth behavior corresponds very strongly with the onset of the formation of van der Waals clusters of pentacene within the supersonic expansion. We suggest that the presence of clusters in the incident flux acts to change the dynamics of growth due to a variety of reasons which we discuss. These findings raise the distinct possibility that organic crystals may be synthesized with ultra-flat surface morphology, making them suitable for use in a number of electronics applications where the requirement for abrupt and smooth interfaces has traditionally defaulted to the use of amorphous organic thin films.

10:00am **SS2+EM+TF-FrM7 Vibrational and Structural Investigation of Ferrocene Adsorption on Au(111) Surfaces**, *G. Pirug, M. Kazemipoor*, Forschungszentrum Jülich, Germany, *J. Myslivecek*, Charles University in Prague, Czech Republic, *B. Voigtländer*, Forschungszentrum Jülich, Germany

The adsorption of ferrocene ($\text{Fe}(\text{C}_5\text{H}_5)_2$) on Au(111) surfaces has been studied spectroscopically applying HREELS and XPS as well as structurally by means of LEED and STM under UHV conditions. The vibrational modes observed by HREELS indicate reversible molecular adsorption of ferrocene at temperatures of about 110 K. The corresponding frequencies are not significantly shifted with respect to IR or Raman data from solution, indicating a weak adsorbate - substrate interaction. Multilayer adsorption can be distinguished from the physisorbed first layer based on the sequential appearance and relative intensity changes of vibrational modes. In the monolayer regime vibrational modes with a perpendicular dipole moment from ferrocene molecules with an upright standing molecular axis dominate, as concluded from on- and off-specular HREEL spectra applying the surface dipole selection rules. Dissociation into cyclopentadienyl ring radicals (C_5H_5) can be excluded due to the missing related vibrational losses, such as the wagging mode expected at about 760 cm^{-1} . For multilayer coverages the orientation of the condensed ferrocene molecules is no longer exclusively perpendicular to the surface which results in the appearance of additional vibrational losses. Molecular self assembly yields a well ordered surface structure as shown by topographical STM pictures and LEED pattern.

10:20am **SS2+EM+TF-FrM8 Uncovering Molecular Dewetting: Growth and Morphology of C_{60} and PTCDA on Insulators**, *S.A. Burke, J.M. Mativetsky, S. Foster, P. Grutter*, McGill University, Canada

Despite considerable interest in recent years in the properties and structural characteristics of molecular deposits for organic based devices, there has been only limited study of growth and morphology of molecular materials on insulating substrates. The majority of traditional surface science tools are significantly hindered by the use of an insulating substrate due to complications with charging and surface damage. Over the past decade, non-contact atomic force microscopy (nc-AFM) has proven a powerful surface science tool, and is increasingly being applied to molecular studies on insulators. The power of the technique lies in its ability to image in real-space with sub-angstrom resolution as well as measure structure up to the micron scale allowing for a connection between molecular scale structures and the overall growth morphologies. The nc-AFM technique, operated in UHV, has been applied to two prototypical organic semiconductors: C_{60} and PTCDA, on two well-known insulating surfaces: KBr (001) and NaCl(001). Both systems showed island growth modes with evidence for dewetting, though the resulting morphologies differ considerably. C_{60} on both of these alkali halides forms distinctive branched island shapes. A quantitative analysis of the morphology and its connection to the underlying epitaxy will be discussed. The formation of this branched morphology appears to be a dewetting process which was observed directly in a series of nc-AFM images. The energetics of this system will also be discussed in terms of annealing and deposition onto a heated substrate. PTCDA on NaCl also undergoes a dewetting process, though in a rather different manner. At low coverages, monolayer islands are observed in a highly strained $c3 \times 3$ epitaxy. However, at larger coverages these single layer islands are seen to coexist with tall crystallites exhibiting the same morphology and herringbone structure as observed for PTCDA on KBr, indicating a coverage induced dewetting transition between 0.7 and 0.8 ML. The dewetting was also induced by annealing of the single layer islands yielding molecular crystals up to several microns long with the familiar herringbone structure of the PTCDA (102) plane. Dewetting has recently been recognized in several other organic systems as a significant factor in the growth and morphology of thin films. The examples presented here may indicate that dewetting is also an important consideration in molecule-on-insulators systems as well.

10:40am **SS2+EM+TF-FrM9 STM/STS Studies of C_{60} :Pentacene Interface Formation**, *D.B. Dougherty*, National Institute of Standards and Technology, *W. Jin, W.G. Cullen, G. Dutton, J.E. Reutt-Robey*, University of Maryland at College Park, *S.W. Robey*, National Institute of Standards and Technology

The most efficient small-molecule organic solar cells employ heterojunctions between donor and acceptor materials.¹ In order to push the performance of such devices into a regime of cost-effective power generation, it is necessary to develop a detailed understanding of organic-organic interface morphology and its relationship to electronic band alignment. We have approached this question by studying the technologically relevant² system of C_{60} deposited onto pentacene, using STM/STS to provide clues to the relative importance of competing intermolecular interactions. When C_{60} is deposited onto a pentacene bilayer on a Ag(111) surface,³ STM measurements show two unique structures in the first layer. The pentacene bilayer forms a well-ordered structure on Ag(111) with the long molecular axis nearly parallel to the surface. At the lowest coverages, C_{60} forms linear chains whose direction is templated by the underlying pentacene rows, with C_{60} molecules located between rows of pentacene molecules. The details of the observed structural arrangement are related to electrostatic interactions between C_{60} and the pentacene bilayer structure. Information on local relative band alignment for these structures is measured using constant-current distance-voltage spectroscopy.⁴ The local transport gap for C_{60} linear chains is $4.4 \pm 0.2\text{ eV}$ compared with a gap of $3.7 \pm 0.2\text{ eV}$ for the surrounding pentacene bilayer. The magnitudes of the gaps are influenced by local polarization energies in each structure. At higher coverage, domains of C_{60} with no discernable long range order dominate the first layer. This disorder probably arises from frustrated intermolecular interactions between the two different chemical species. The lateral interactions between C_{60} molecules (favoring hexagonal ordering) cannot be optimized simultaneously with the comparable strength interactions between C_{60} and the underlying pentacene film (favoring an oblique unit cell). *This work has been partially supported by the Dept. of Commerce through the NIST Center of Nanomanufacturing and Metrology and the NSF-funded MRSEC via DMR-05-20471.

¹P. Peumans, J. Appl. Phys. 93, 3693 (2003).

²S. Yoo et al., Appl. Phys. Lett. 85, 5427 (2004).

³Eremtchenko et al., Phys. Rev. B 72, 115430 (2005).

⁴S.F. Alvarado, et al., Phys. Rev. Lett. 81, 1082 (1998).

11:00am **SS2+EM+TF-FrM10 Potassium Induced Long Range Superstructure on C_{60} /Ag (111) Surface**, *C.-C. Kuo, W.W. Pai*, National Taiwan University

Various long range superstructures were observed for potassium (K) doped C_{60} monolayer on Ag (111) by scanning tunnelling microscopy (STM). Pristine C_{60} monolayer exhibits a bright-dim contrast in the most stable $(2\sqrt{3} \times 2\sqrt{3})\text{-R}30$ phase, whereas the molecular contrast is uniform in other metastable phases (denoted as R12 or R48 phases). Upon K doping, K segregate into compact islands at room temperature and the bright-dim contrast in the R30 phase is eliminated. Furthermore, ordered quasi-hexagonal patterns with periodicities of $\sim 7\text{ nm}$ to $\sim 40\text{ nm}$ appear. The ordered superstructures show distinct characteristics in each C_{60} phase. Close inspection reveals that the super lattices are not exactly hexagonal but exhibit uni-directional distortion. Therefore, the finding is perplexing as it cannot be explained by, e.g., Morie patterns. We propose that the superstructures are due to overlaying an orthorhombic one-dimensional polymerized KC_{60} phase over the hexagonal silver lattice. This is supported by high-resolution STM images showing the signature of $[2+2]$ covalent bond formation.

11:20am **SS2+EM+TF-FrM11 Thiol-Modified Diamondoid Monolayers on Silver and Gold Studied with Near-Edge X-ray Absorption Fine Structure Spectroscopy**, *T.M. Willey*, Lawrence Livermore National Lab., *J.D. Fabbri*, Stanford Univ., *J.R.I. Lee*, Lawrence Livermore National Lab., *P.R. Schreiner, A.A. Fokin, B.A. Tkachenko, N.A. Fokina*, Justus-Liebig Univ. Giessen, Germany, *J.E. Dahl, R.M.K. Carlson, S.G. Liu*, MolecularDiamond Tech., *T. van Buuren*, Lawrence Livermore National Lab., *N.A. Melosh*, Stanford Univ.

Higher diamondoids, hydrocarbon cages with a diamond-like structure, have evaded laboratory synthesis and have only recently been purified from petroleum sources. Initial calculations on these unique diamond-like molecules show they may have negative electron affinity, a desirable property for electron emission. Readily available adamantane, the smallest diamondoid, can be thiolated and has shown to absorb on gold with high coverage. The availability of diamantane, triamantane, and tetramantanes opens new possibilities for surface-modification as multiple sites are available for thiol or other chemical functionalization. Surface-attached diamondoids have technological possibilities as high-efficiency electron emitters, as well as crystals for diamond growth or other nanotechnological applications, and fundamental studies of the electronic and structural

properties of these molecular monolayers are a necessary precursor. We have investigated the effects of thiol substitution position, polymantane order, and metal substrate on diamondoid film morphology. Using Near-Edge X-ray Absorption Fine Structure Spectroscopy (NEXAFS) we show that the orientation of the diamondoids within each type of monolayer depends highly upon these parameters. We thus demonstrate control over the assembly, and hence the surface properties, of this exciting new class of diamond-like carbon molecules.

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