

Surface Science

Room: 201 A - Session SS1-ThA

Organic Layers on Surfaces

Moderator: A.J. Gellman, Carnegie Mellon University

2:00pm **SS1-ThA1 Stability Reversal and Superstructure Formation of Photochromic Diarylethene on Noble Metals**, T.K. Shimizu, J. Jung, H. Imada, Y. Kim, RIKEN, Japan

We have studied using scanning tunneling microscopy (STM) and density functional theory calculations one of the diarylethene molecules [1] adsorbed on Au(111) and Cu(111). Two isomers of this molecule, open-form and closed-form, are known to be thermally stable, and its isomerization reactions are induced by irradiation of UV and visible light for the cyclization and cycloreversion reaction, respectively, in solution and single crystalline. Based on STM measurements after deposition of either form of the isomer as well as with and without annealing process, we found that the closed-form was more stable than the open-form on both Au(111) and Cu(111), which is opposite to gas phase. We expect that the stability reversal upon adsorption could arise from the partial ionization of the molecule due to the charge transfer between the molecule and the substrate metal, which stabilizes the closed-form isomer more than the open-form. It is also revealed that while small clusters are formed on clean metallic surfaces, a largely extended 2D superstructure can be fabricated when NaCl is co-deposited on Cu(111). Similar to earlier studies of other organic molecules [2,3], x-ray photoelectron spectroscopy data can be reasonably explained by assuming Na ion incorporation into the superstructure and Cl diffusion into the bulk. We propose a superstructure model where a Na ion binds fluorine and sulfur atoms of the adjacent molecules.

[1] M. Irie, S. Kobatake and M. Horichi, *Science* 291, 1769 (2001).

[2] Ch. Wackerlin et al., *Chem. Commun.* 47, 9146 (2011).

[3] D. Skomski et al., *J. Am. Chem. Soc.* 134, 14165 (2012).

2:20pm **SS1-ThA2 Transient Effects in Optical Properties of Organic Semiconductor Blends Observed in Real Time during Growth and Their Connection to Film Structure**, K. Broch, A. Gerlach, C. Lorch, J. Dieterle, J. Novak, A. Hinderhofer, F. Schreiber, University of Tuebingen, Germany

As possible active layers in optoelectronic devices, binary blends of organic semiconductors are of high relevance for applications. A detailed understanding of the structure-property relation in these complex systems is crucial for device optimization, but due to the variety of film structures and associated optical properties also a challenge for fundamental research [1,2]. In particular for vacuum deposited thin films, post growth studies are often not sufficient for a detailed characterization due to possible pronounced transient effects observable during film growth [3]. These effects can include film thickness dependent changes in the average molecular tilt angle or intermolecular spacing, which may result in significant variations in the relative intensities or energy position of specific peaks in the absorption spectra [3].

Using organic molecular beam deposition we prepare thin mixed films of the prototypical organic semiconductors perfluoropentacene (PFP, C₂₂F₁₄) and diindenoperylene (DIP, C₃₂H₁₆) and follow the film growth in situ in real-time simultaneously using grazing incidence X-ray diffraction and optical spectroscopy. We discuss the result of the competing effects of strong and favourable donor-acceptor interaction and steric incompatibilities due to the size mismatch of PFP and DIP on the structure formation in mixed films, concentrating on the size of coherently scattering islands, which is related to the structural order within the films. By exploiting the advantages of a simultaneous measurement of structural and optical properties of the samples we are able to relate pronounced changes in the relative intensities of specific peaks in the optical absorption spectra to the observed changes in the structural order. The results of these experiments give insight in the complex mechanisms of structure formation and structure-property relations in mixed systems and point towards the possibility to tune the structural and optical properties for the optimization of opto-electronic devices.

[1] A. Hinderhofer and F. Schreiber, *ChemPhysChem*, **13**, 628 (2012),

[2] A. Aufderheide et al., *Phys. Rev. Lett.*, **109**, 156102 (2012),

[3] U. Heinemeyer et al., *Phys. Rev. Lett.*, **104**, 257401 (2010),

2:40pm **SS1-ThA3 Charge Transfer between Donor-Acceptor Molecular Networks and Metal Surfaces**, K. Lauwaet, IMDEA-Nanociencia, Spain, J. Rodríguez Fernández, M.R. Relano, S. Díaz-Tendero, M. Alcamí, Universidad Autónoma de Madrid, Spain, N. Martín, Universidad Complutense de Madrid, Spain, F. Martín, Universidad Autónoma de Madrid, Spain, J.M. Gallego, R. Otero, R. Mirando, IMDEA-Nanociencia, Spain

Organic charge-transfer (CT) complexes are molecular compounds mixing two species with different electron affinities: an electron donor (D) and an electron acceptor (A). Charge transfer processes between D-A complexes and metallic electrodes are at the heart of novel organic optoelectronic devices such as solar cells [1]. In contrast with the existing exhaustive study of the bulk properties of CT solids, very little is known about the thin-film behaviour. The transition from bulk D-A complexes to ultra-thin films of monolayer thickness deposited on metals introduces a new phenomenology related to the organic-inorganic interface [2]. Effects like hybridization, CT with the surface and molecular level alignment become factors that may govern the electronic transport. Hence, the adsorption of an ultra-thin D-A layer on a metal opens a new field of research for the potential application of CT complexes as devices in the nanoscale.

Simultaneous characterization of the interdependent structural and electronic properties is required for a thorough understanding of the D-A complexes under study [3]. Here, by combining both Scanning Tunnelling Microscopy (STM) and X-ray Photoelectron Spectroscopy (XPS) *in situ*, we can study the delicate balance that exists between intermolecular and molecule-substrate interactions, as well as the hybridization, and the charge transfer taking place in model donor-acceptor assemblies at metal-organic interfaces.

We will show that the metal surface allows us to expand the variety of such D-A networks, permitting the design of D-A metal-organic frameworks with the formulation of D_mA_n (m,n ≥ 1). By controlling the stoichiometry between tetrathiafulvalene (TTF, electron-donor) and tetracyanoethylene (TCNE, electron-acceptor), we can tune the both the structural and the electronic properties of a donor-acceptor system on Ag(111). We show that this system exhibits various structural phases, depending on the stoichiometry, each leading to different levels of charge transfer. These results demonstrate that atomistic studies on the growth of organic thin films under ultrahigh vacuum (UHV) conditions can lead to the kind of accurate control needed in order to optimize device characteristics.

[1] L. Bartels, *Nat. Chem.*, **2**, 87 (2010).

[2] N. Gonzalez-Lakunza, I. Fernández-Torrente, K. J. Franke, N. Lorente, A. Arnau, and J. I. Pascual, *Phys. Rev. Lett.*, **100**, 156805 (2008)

[3] D. G. de Oteyza, J. M. García-Lastra, M. Corso, B. P. Doyle, L. Floreano, A. Morgante, Y. Wakayama, A. Rubio, and J. Enrique Ortega, *Adv. Funct. Mater.*, **19**, 3567 (2009)

3:00pm **SS1-ThA4 Extending Crystalline Organic Nanostructures at Surfaces into Multilayer Films**, S.L. Tait, D. Skomski, C. Tempas, Indiana University

Application of self-assembly strategies to complex, organic-based devices requires fabrication of many-layered architectures from multiple organic species. Recent advances in studies of organic adsorbates and supramolecular self-organization have provided examples of two-dimensional crystalline organic assemblies in the first molecular layer. Here, we demonstrate the extension of highly ordered organic layers into multiple layers away from a metal surface. High-resolution scanning tunneling microscopy and X-ray photoelectron spectroscopy are used to study structure and chemistry in these layers. Interfacial organic layers (IOLs) at the metal interface hold promise for the extension of supramolecular self-organization towards the multilayer regime, an area of surface assembly that had been insufficiently explored up to now. IOLs may enable the propagation of highly-ordered 2D supramolecular structure at the surface into the third dimension, thus enabling programmable, crystalline organic films. We illustrate that complex carboxyl and thiophene species can be self-assembled with atomic precision on top of a metal-templated IOL, even though the species are chemically unstable or do not form periodic structures when deposited directly onto the metal. In addition to yielding more complex architectures, the IOL decouples the organics from direct interactions with the metal surface, thereby protecting the species from metal-catalyzed degradation. We have also observed examples of crystalline film growth of up to 10 layers in thickness using STM and atomic force microscopy. These results provide new strategies to achieve long-range self-assembly of well-ordered complex molecular species incorporating technologically-relevant functional groups, which will be of interest in organic electronics and catalysis.

3:40pm **SS1-ThA6 Interface Formation and Nanocrystallization in Molecular Semiconductor Films.** *J. Reutt-Robey*, University of Maryland
INVITED

Molecular materials have a natural tendency toward polymorphism due to the highly anisotropic nature of intermolecular interactions. Because crystal structure dictates key material properties, such as solubility and charge transport, crystallographic phase control is of intense interest to applications ranging from pharmaceuticals to organic electronics. In this talk we describe the kinetic assembly of molecular semiconductors into controlled arrangements. We show how crystalline monolayer films of pentacene (P) and titanyl phthalocyanine (TiOPc) can be produced with varied packings and orientations through controlled deposition. We subject metastable film structures to chemical (fullerene adsorption) tests to create charge-separating interfaces expected in OPV devices. Low-density molecular films rearrange spontaneously under C_{60} (and C_{70}) deposition, yielding new co-crystalline phases with distinctive electronic features; whereas dense films generally yield abrupt semiconductor interfaces. We further show how highly polarizable fullerenes respond to the electrostatic contours of oriented molecular semiconductor films to form unexpected fullerene arrangements. Structure evolution in functionalized fullerenes further demonstrate how electrostatics impact phase selection. C_{60} - and C_{70} -PCBM molecular ordering is monitored from a glassy monolayer phase, produced by pulsed delivery of solute PCBM from a liquid microaerosol, to neat hcp crystalline arrangements inaccessible through homogeneous PCBM crystallization. We relate kinetic barriers for molecular ordering to solvent expulsion and PCBM reorientation, determining the critical PCBM surface density needed to induce nanocrystallization.

Acknowledgement: Portions of this work have been supported by the National Science Foundation Division of Chemistry-MSN and Division of Materials Research DMR-05-20471.

4:20pm **SS1-ThA8 Donor-to-Acceptor Core-level Shift in Molecular Blend/Metal Interfaces.** *P. Borghetti, A. El-Sayed*, Material Physics Center (MPC), Spain, *E. Goiri*, Donostia International Physics Center (DIPC), Spain, *C. Rogero*, MPC, Spain, *L. Floreano*, CNR-IOM, Lab Nazionale TASC, Italy, *D. Mowbray, J.L. Cabellos-Quiroz*, DIPC, Spain, *Y. Wakayama*, International Center for Materials Nanoarchitectonics (WPI-MANA), Japan, *A. Rubio*, Univ. del País Vasco, Spain, *J.E. Ortega*, Univ. del País Vasco, Spain, *D.G. De Oteyza*, DIPC, Spain

Self assembled donor-acceptor complexes on metallic electrodes are at the heart of novel organic optoelectronic applications such as solar cells. In these devices, the organic/metal interface is of fundamental importance, since it defines the charge injection barrier that determines the ultimate device performance. Despite the dramatic progress of the organic electronic field so far, the ability to accurately model and predict the electronic properties at interfaces is still inadequate, thereby hampering the translation of organic thin film growth into an established technology. One of the key issues is how the molecule/metal interaction plus the intermolecular interactions affect the energy-level alignment, i.e., how do the Highest Occupied Molecular Orbital, HOMO, and the Lowest Unoccupied Molecular Orbital, LUMO, align with respect to the metal Fermi energy. However, the HOMO and LUMO alignment is not easy to elucidate in complex multi-component, molecular/metal systems. Here we demonstrate that core-level photoemission from donor-acceptor/metal interfaces can straightforwardly and transparently determine molecular level alignment. We focus on 2D crystalline networks, and carry out a systematic investigation over a number of donor-acceptor/metal systems. In particular, we use Au(111), Cu(111) and Ag(111) as substrates, perfluorinated copper-phthalocyanine ($F_{16}CuPc$) and perfluoropentacene (PFP) as aromatic acceptors, and copper-phthalocyanine (CuPc) and pentacene (PEN) as electron donors. For each combination, XPS spectra show a characteristic binding energy shift in core-levels as a function of molecular donor/acceptor ratio, irrespectively of the molecule or the metal. Such shift reveals how the level alignment at the molecule/metal interface varies as a function of the donor-acceptor stoichiometry in the contact blend. We also show that the energy level alignment is barely affected by donor-to-acceptor charge transfer, and majorly determined by the electron potential created by donor (high attractive potential) or acceptor (low attractive potential) molecules in their vicinity, i.e., by the average change in work function.

4:40pm **SS1-ThA9 Morphology of Submonomolecular Layers of PTCDI-C8 on (16x2) Reconstructed Si(110).** *K. Lament, P. Mazur, S. Zuber, W. Kaminski, A. Ciszewski*, University of Wrocław, Poland

Organic nanostructures on semiconductor surfaces offer a variety of applications in modern electronic such as light emitting diodes, transistors, solar cells, etc. In most cases well-ordered interfaces are required. Therefore interest in interfaces between organic molecules and inorganic semiconductors surface and the phenomenon of self-organization is still increasing. The growth of thin molecular films with a commensurate structural relationship to the substrate needs substrates that exhibit template

structure into which the molecules can be locked. We apply STM, STS, XPS, UPS, and LEED techniques to study adsorption of PTCDI-C8 (N, N'-Dioctyl-3,4,9,10-perylenedicarboximide) on Si(110). The adsorbate of an average thickness from a fraction of monomolecular layer (ML) up to 1.3 ML was vapor deposited on (16x2) reconstructed surface of n-type, Sb-doped substrate. The reconstruction, typical for clean Si(110) surface, shows a stripe-like structure with alternately spaced lower and higher terraces lying along the [-112] and [1-12] directions. The distance between adjacent raised stripes is about 5 nm and the width of the stripes is about 0.2 nm.

We have found out that the PTCDI-C8 molecules are bound to the surface through oxygen atoms. We have measured the changes of electron affinity of the surface as a function of the average adsorption layer thickness. We were able to observe single molecules of the adsorbate for the layers of the thickness up to 0.6 ML. For these coverage values template effect of the substrate on the PTCDI-C8 ad-layer structure is clearly visible. The molecules form chains along the [-112] and [1-12] directions of the substrate. Conclusions are drawn concerning the chain structure and, with the help of model calculations, the topography of adsorption site for a single molecule in the chain.

5:00pm **SS1-ThA10 Passivation of Metallic Al Surface with Monolayer Organic Adsorbates.** *T. Yamada, R. Sato*, RIKEN, Japan, *K. Watanabe*, Science University of Tokyo, Japan, *M. Kawai*, The University of Tokyo, Japan

We performed a surface-scientific investigation on adsorption of hydrocarbon thiols and fluorocarbon thiols on clean aluminum (111) in order to realize passivation of metallic Al towards air oxidation. Passivation of Al surfaces with oxide-free ultimately thin layers, that is, molecular monolayers, is a prerequisite in nanofabrication with Al entities, such as planar nano-patterned devices and nano-particles. We newly surveyed the adsorption of organic thiol molecules to form densely-packed monolayers, which are suitable for blocking O_2 gas molecules. We found hydrocarbon thiols can readily adsorb on clean Al(111) and form monolayers at room temperature by exposure to vapor from liquid ($n-C_nH_{2n+1}SH$, ($n \leq 12$)) or by sublimation ($(n-C_nH_{2n+1}SH$, ($n > 12$)) and 4-biphenylthiol). The hydrocarbon parts were proven to be intact after adsorption by the electron spectroscopies (XPS and vibrational analysis by HREELS). The SH species was not detected vibrationally, indicating that S is anchoring the hydrocarbon part on Al. Blocking of O_2 oxidation of Al substrate was effective in the O_2 pressure range below 10^{-5} Torr. At higher pressures ranging up to 1000 Torr, a multilayer of Al_2O_3 was formed underneath the organic monolayer, even for $n-C_{18}H_{37}SH$ monolayer. The ability to block O_2 oxidation was remarkably enhanced by curing these organic monolayers with electron beam. We irradiated a shower of 100 eV electron ($\sim 1 \text{ mC cm}^{-2}$) onto these monolayers, and the rate of Al substrate oxidation decreased to less than one tenth of that of the clean Al(111) in the atmospheric pressure of O_2 . It was seen that the irradiation of electron beam introduces unsaturated C-C bonds with a nearly complete loss of C-H bonds from the monolayer, both from alkane and aromatic thiols. A quasi-graphitic monolayer is anticipated to be formed by electron irradiation. The thickness of this layer is ~ 1 nm. The electron-bombarded monolayers of this type exhibited a substantial robustness towards oxidation in ambient O_2 . [1,2] Linear fluoroalkane thiols, $n-C_nF_{2n+1}C_2H_4SH$ ($n=4,8$), form monolayers at room temperature with a full coverage smaller than the alkanethiols. When the adsorption process was made at substrate temperatures higher than 100°C , the uptake of carbon exceeded the monolayer amount of the precursor molecule, and substantial loss of F from the adlayer was observed. The adlayer seemed to be composed of polymerized fluorohydrocarbon, and exhibited a substantial strength against oxidation. These robust monolayers will bring about a better utility of metallic Al in nanotechnology in general. [1] S. Nomura et al., *Chem. Lett.* **39** (2010) 1297. [2] T. Yamada, Japan Patent Application 2011-168725.

5:20pm **SS1-ThA11 Selenium: The Better Anchor Group for Self-Assembled Monolayers (SAMs) on Gold?** *A. Terfort*, University of Frankfurt, Germany, *M. Zharnikov*, University of Heidelberg, Germany, *P. Cyganik*, Jagiellonian University, Poland

Self-assembled monolayers (SAM) became a very powerful tool in the materials sciences, biochemistry, and engineering. In particular SAMs of thiolates are renowned for their ease of formation, their stability and their high order. Nevertheless, not all thiols can form densely packed monolayers and for some cases even the best thiolate monolayers are not well ordered enough.

Based on the idea that a softer anchoring atom would fit better to the soft gold atoms (according to Pearson's HSAB principle), we prepared a number of selenium-containing precursors and studied their assembly on gold (and in some cases on silver). Data obtained by surface infrared spectroscopy, different photo-electron spectroscopies, and STM hint on the formation of very stable monolayers with improved order. [1-4]

In this talk we will present the preparation methods for the starting materials and the respective monolayers, give details on the surface characterisation, and offer explanations for the superior behaviour of the selenolate SAMs.

References

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- [4] Shaporenko, A.; Müller, J.; Weidner, T.; Terfort, A.; Zharnikov, M. *J. Am. Chem. Soc.* **129**, 2232-2233 (2007)

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