

## Electronic Materials and Processing Room 309 - Session EM+SS-WeM

### Contacts to Organic and Molecular Devices

Moderator: Y. Roichman, Princeton University

8:20am **EM+SS-WeM1 Energy Level Alignment at Interfaces in Organic Semiconductor Devices**, *K. Demirkan, A. Mathew, S. Vaidyanathan, Z.I. Niazimbetova, H. Christian-Pandya, M.E. Galvin, R.L. Opila*, University of Delaware

Poly-phenylene vinylene based organic semiconductor polymers and oligomers were studied using X-ray Photoelectron Spectroscopy (XPS) and Ultraviolet Photoelectron spectroscopy (UPS). Valence bands and highest occupied molecular orbitals (HOMOs) (with respect to Fermi level) for these organic structures were determined. Due to the high electron withdrawing property of the oxadiazole moiety, polymers, which have a higher oxadiazole density, are found to have lower energy levels. Using optical absorbance spectra, the lowest unoccupied molecular orbitals (LUMO) for some of the organic semiconductor materials were estimated and the basic energy level diagrams were established with respect to the underlying electrode. The valence band spectra of the polymers spin coated on different substrates did not show any substantial variation except for shifts in the entire spectra. In the Mott-Schottky limit, the energy difference between the electrode Fermi level and the HOMO of the organic layer is expected to follow the work function of the electrode. The interface slope parameter, a measure of the change in HOMO-Fermi level difference as a function of electrode work function, was found to vary between 0.4 and 0.9. These values are intermediate to Mott-Schottky and Fermi level pinning. We will explain the interface slope parameter in light of the interfacial dipole and charge neutrality level at organic/metal interfaces.

8:40am **EM+SS-WeM2 Towards Molecular Electronic Circuitry: Selective Deposition of Metals on Patterned Self-Assembled Monolayer Surfaces**, *C. Zhou, G. Nagy, A.V. Walker*, Washington University in St. Louis

We have developed a robust method by which to construct complex two- and three- dimensional structures based on controlling surface chemistry. This work has important applications in molecular and organic electronics, sensing, biotechnology, photonics and other technologies. Our method is extensible to many different types of materials, easily parallelized, affords precise nanoscale placement and is fully compatible with photolithographic fabrication processes. The method is based on the deposition of metals on UV-photopatterned self-assembled monolayers (SAMs). To demonstrate the method we have selectively vapor-deposited Mg on a patterned -CH<sub>2</sub>sub 3@/-COOH terminated alkanethiolate surface. The deposited metal penetrates through the -CH<sub>2</sub>sub 3@ SAM to the Au/S interface while reacting with the -COOH terminal group and accumulating on top of the other SAM.

9:00am **EM+SS-WeM3 Interface Disorder and Charge Injection into Organic Semiconductors**, *M.A. Baldo, B.N. Limketkai*, MIT **INVITED**

In this talk, we examine the effect of structural disorder at the injection interface on the current-voltage (IV) characteristics of organic semiconductors. We find that structural disorder at the injection interface creates energetic disorder, which in turn may dominate the IV characteristics of these materials. We will describe the effects of interfacial disorder on charge injection in several model systems: flat metal electrodes, rough metal electrodes, and highly conductive polymer electrodes. Disorder is most important at interfaces with relatively small energetic barriers between the metal and semiconductor.

9:40am **EM+SS-WeM5 Modelling Inhomogeneities of Organic Device Contacts: Organic Film Growth on Nanostructured Surfaces**, *M.G. Ramsey, B. Winter, S. Surnev, G. Koller, F.P. Netzer*, Karl-Franzens-University Graz, Austria

In this contribution the growth, geometric and electronic structure of sexiphenyl films grown on clean Cu(110) and mesoscopically patterned Cu(110)-(2x1)O will be presented. The results highlight the effects of the atomic and nanometric substrate structure on the growth and electronic level alignment of active organic films. Scanning tunnelling microscopy (STM) reveals that on the clean Cu the molecules align parallel to each other and are highly mobile in one surface direction. By monolayer coverages a complete layer forms reminiscent of a smectic liquid crystal phase. Despite the lack of strict long range order the molecules align in

strings with a periodicity determined by intermolecular interactions, while the periodicity between the strings is determined by the substrate periodicity. In contrast when the substrate is covered with a half monolayer of oxygen the molecules appear not to wet the surface and, apart from at defects, are not visible in STM. On the mesoscopically patterned Cu(110)-(2x1)O (stripes of clean and oxygen covered surface with a periodicity of ~ 7 nm) the molecules first appear at the Cu-CuO boundaries and then grow preferentially on the clean Cu stripes. Growth and electronic structure on the three basic substrate situations are also followed by angle resolved ultraviolet photoemission spectroscopy (ARUPS). These results highlight the problems of imaging such wide band gap materials with STM and indicate that the 6P does in fact wet the Cu(110)-(2x1)O and that the visibility of the molecule is dependent on charge transfer states in the gap. These ARUPS results will also be discussed in terms of the electronic level alignment on inhomogeneous surfaces where large band offsets between molecules on different regions occur.

10:00am **EM+SS-WeM6 The Influence of Alkyl Side-chains and Charge-Transfer Complex Formation on Sexithiophene/Metal Interface Energetics**, *S. Duhm, H. Glowatzki*, HU-Berlin, Germany; *R.L. Johnson*, Hamburg University, Germany; *J.P. Rabe, N. Koch*, HU-Berlin, Germany

The energy level alignment at metal/organic interfaces is a key issue for improved performance of novel organic (opto-) electronic devices. In certain cases, solution-based processing of organic materials (i.e., spin-coating, ink-jet printing) is preferred over vacuum sublimation. Frequently, alkyl side-chains are attached to the conjugated moieties for improved solubility. In order to investigate the influence of alkyl side-chain addition on interface energetics, we studied interfaces formed between the organic molecules sexithiophene (6T) and @alpha@.@omega@-dihexylsexithiophene (DH6T) and the metal surfaces Ag(111) and polycrystalline Au with ultraviolet photoelectron spectroscopy (UPS). Samples were prepared by sublimation of the organic substances on clean metal surfaces in ultrahigh vacuum. Interestingly, we observed significantly lower hole injection barriers (0.2 - 0.4 eV) for DH6T on the metal surfaces than for 6T. We propose that the mechanism responsible for our observations is closely related to the "electron push-back effect" at metal/organic interfaces. Furthermore, the influence of molecular orientation will be discussed. Additionally, we demonstrate that the hole injection barrier at interfaces between 6T (DH6T) and metals can be further reduced by the formation of charge transfer complexes comprising tetrafluoro-tetracyanoquinodimethane (F4-TCNQ).

10:20am **EM+SS-WeM7 Top-contact Junctions for Molecules Electronics: Nano-transfer Printing**, *K. Ojima*, Osaka University, Japan; *K. Nakamatsu*, University of Hyogo, Japan; *Y. Otsuka, T. Matsumoto*, Osaka University, Japan; *S. Matsui*, University of Hyogo, Japan; *T. Kawai*, Osaka University, Japan

Recently, nanotransfer printing (nTP) attracts an attention as a method of producing the electrode. The electrode fabricated by nTP give the solutions for the problems of bottom contact-type electrode because electrodes are fabricated directly on the substrate after the deposition of molecules. In the previous reports, the nTP process needed chemical modification for the substrate in order to obtain well adhesiveness between the electrode and the substrate. This requirement has been serious limitation to fabricate molecular-scale devices. We have developed a nTP process for molecular devices without any modifications of substrate surfaces and evaluated the electrical properties of the electrodes fabricated by nTP. The use of the release agent enables us to print electrodes without any surface modification and heating the substrate. A test pattern of gold electrodes formed by the nTP on a DNA spread SiO<sub>2</sub>/Si substrate was examine by AFM. We found that the resistivity of a line of gold electrode is nearly equal to that of bulk gold. We also examined the electric contact between the electrodes and molecules using Kelvin force microscopy (KFM) under applying bias voltage to the electrode/molecules junctions. We will present the images of electric potential distribution for the junctions.

10:40am **EM+SS-WeM8 Orbital Alignment and Chemical Interaction at Macro-Molecular Contacts**, *M.M. Beerbom, B. Lagel, J.P. Magulick, A.J. Cascio, R. Schlaf*, University of South Florida

Our experiments aim at the determination of the chemical and electronic structure of interfaces between macro-molecules and inorganic materials to determine charge injection barriers across the interfaces, the electronic structure of the highest occupied molecular orbitals (HOMO), and the chemical interaction between the materials in contact. Photoemission spectroscopy (PES) was used in combination with multi-step in-situ

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deposition of macro-molecular materials on inorganic substrates. PES characterization between deposition steps yields a sequence of spectra allowing the determination of the orbital line-up. Multi-step deposition was achieved using either a unique electrospray thin film deposition system, or a glove-box based deposition procedure. This allowed the fabrication of pure and non-contaminated interfaces suitable for PES measurements. Results from a series of experiments on poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV),<sup>1</sup> ribonucleic acid (RNA)<sup>2</sup> and L-cysteine (amino acid)<sup>3</sup> interfaces will be presented. The electronic and chemical structure of these interfaces will be discussed as well as the measurement technique.<sup>1</sup> N. Dam, M.M. Beerbom, J.C. Braunagel and R. Schlaf: "Photoelectron Spectroscopic Investigation of In-Vacuum Prepared Luminescent Polymer Thin Films Directly From Solution", *J. Appl. Phys.* 97(pp.024909 (2005)).<sup>2</sup> N. Dam, B.V. Doran, J.C. Braunagel and R. Schlaf: "Charge injection barriers at a ribonucleic acid/inorganic material contact determined by photoemission spectroscopy", *J. Phys. Chem.* 109(2), pp.748-756 (2005).<sup>3</sup> M.M. Beerbom, R. Gargagliano and R. Schlaf: "Determination of the Electronic Structure of Self-Assembled L-cysteine/Au Interfaces Using Photoemission Spectroscopy", *Langmuir Articles ASAP*, (2005).

11:00am **EM+SS-WeM9 Self-assembled Monolayers with Reactive Endgroups: Studies of Inorganic-Organic Interfaces and the Initiation of Top Contact Formation**, A. Dube, M. Sharma, A.S. Killampalli, J.R. Engstrom, Cornell University

Self-assembled monolayers (SAMs) have attracted considerable interest over the past several years in the field of molecular electronics. In such applications two interfaces become important, and understanding the formation of both is critical to effectively making use of SAMs in these devices. While formation of the bottom contact is a well studied area, the formation of top contacts is an immature field. We have been examining the reactions of transition metal coordination complexes, such as  $Ti[N(CH_3)_2]_4$  and  $Ta[N(CH_3)_2]_5$ , with SAMs possessing different head group chemistries [e.g.,  $RSiCl_3$  on  $SiO_2$ , R-(thiophene) on Au] and endgroup functionalities (e.g.,  $-CH_3$ ,  $-NH_2$  and  $-OH$ ) in order to develop an understanding of interface and contact formation. In this presentation we will highlight our most recent work that includes the self-assembly and reactions of functionalized molecular wires (thiophenes with conjugated ethynyl-phenylene backbones) adsorbed on Au using in situ angle resolved x-ray photoelectron spectroscopy (ARXPS). Here we find that the saturation density of the SAM increases from  $\sim 2.1$  to  $3.4 \times 10^{14}$  molecules/cm<sup>2</sup> as the length of the conjugated backbone is roughly doubled. More importantly, these layers, which possess an isopropylamine endgroup, react via ligand exchange with  $Ti[N(CH_3)_2]_4$  even at  $-50^\circ C$ , forming a structure that has a Ti:SAM stoichiometry of  $\sim 1:2$ . ARXPS shows conclusively that these Ti coordination complexes bond with the SAMs exclusively at the isopropylamine group, and can seed additional deposition of the top contact. We will discuss the importance of these and other results concerning what they say about designing an effective means to make top contacts to molecular monolayer structures.

11:20am **EM+SS-WeM10 Observation of Interface Gap-State between Pentacene Molecules and Gold Metal by Scanning Tunneling Spectroscopy**, Y.J. Song, S.H. Kim, Y. Kuk, K. Lee, J. Yu, Seoul National University, Korea

Pentacene has been studied widely as a candidate for an organic thin film transistor (OTFT) because of its high mobility, and easy processing on various substrates. It has been pointed out that interface states work as scattering centers and results in poorly reproduced potential barriers for various metal contacts in the transport measurement. In this work, we investigated the electronic structure of a single pentacene molecule adsorbed on Au(100) surface with one dimensional spatially-resolved scanning tunneling spectroscopy (1D SR-STs) to map position-dependent local density of states (LDOS).<sup>1</sup> In the geometry of metal-pentacene-metal transport measurement with a single crystal or a thin film pentacene, the molecule is positioned as if it flat on the contact metal. This geometry can be achieved by adsorbing the molecule on a metal substrate. Au(100) surface was chosen since it offers both near-hexagonal and square symmetry, depending on a location of the (5x20) reconstruction. We measured SR-STs at various sites on the Au(100)-(5x20) surface. Unlike previously observed spectroscopy results on an insulator surface,<sup>2</sup> two dominant features are clearly resolved in the HOMO-LUMO gap of the spectroscopy: 1) Au surface state peaks of which

energy level is position independent, and 2) a HOMO derived gap state which depend on the registry of the pentacene molecule on the substrate. We expect that these gap states work as a scattering center and change the barrier height between metal contact and organics in the transport measurement. A density functional theory (DFT) calculation confirms our observation. <sup>1</sup> Jinhwan Lee, H. Kim, S.-J. Kahng, G. Kim, Y.-W. Son, J. Ihm, H. Kato, Z. W. Wang, T. Okazaki, H. Shinohara and Young Kuk, *Nature* (London) 415, 1005 (2002).<sup>2</sup> Jascha Repp, Gerhard Meyer, Sladjana M. Stojkovic', Andre' Gourdon and Christian Joachim, *Phys. Rev. Lett.* 94, 026803 (2005)

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