Wednesday Afternoon, November 17, 2004

Surface Science
Room 213B - Session SS+OF-WeA
Contacts to Molecules and Molecular Films

Moderator: G.G. Malliaras, Cornell University

2:00pm **SS+OF-WeA1 Electron Transport at Interfaces and Junctions: Understanding Molecular Electronics***, **X.-Y. Zhu,*** University of Minnesota **INVITED**

Charge transport at or across molecule-electrode interfaces is central to the operation of a wide variety of molecule-based electroic devices. The critical charge transporting interfaces in most systems are buried interfaces which are not readily accessible to conventional structural or spectroscopic probes. For any given device, two critical questions are: (1) What is the structural and chemical nature of the molecules at the buried interface before or during operation? (2) How is the electrical conductance across an interface related to physical properties such as electronic energy level alignment and charge redistribution? This talk will attempt to address both questions from spectroscopic measurements and to demonstrate that such a spectroscopic view is of critical importance in achieving a quantitative understanding of moleular electronics.

2:40pm **SS+OF-WeA3 The Influence of Chemical Coupling Groups on the Electronic Structure of Conjugated Self-Assembled Molecular Monolayers***, **S.W. Robey**,* NIST*; C.D. Zangmeister,* NIST, US*; R.D. Van Zee,* NIST

The performance of conjugated molecular systems in electronic applications, either for organic light emitting diodes (OLED's) and field effect transistors, or in more speculative applications proposed for molecular electronics, depends critically on coupling at the molecule-electrode interface. Interactions at this interface determine the alignment of the contact Fermi level with the transport levels in the molecular system, which in turn controls charge injection into the molecular @pi@ levels. Using one-and two-photon photoemission to access occupied and unoccupied levels, we have examined the influence of the metal-molecule coupling chemistry on the Fermi level alignment and electronic structure in the prototypical "molecular wire", 4,4'-(ethynylphenyl)-1-benzenethiol system on Au. Photoelectron spectroscopies reveal an increase in the binding energies (relative to the Fermi level of Au) for the C @sigma@ and @pi@ derived valence levels and the C (1s) core level upon substitution of the isocyanide coupling for thiol. No spectral changes are observed, however, in the region of the molecular @pi@ levels important for transport. Optical absorption measurements also reveal no change in optical band gap. These results indicate that substitution of the isocyanide linking chemistry for thiol based chemistry leads to a large shift, by ~ .5 eV, of E@sub f@ away from the highest occupied level in the molecule, but little modification of the extended @pi@ molecular electronic structure. The interaction at the Au-thiol-OPE interface will be compared and contrasted with the Au-isocyanide-OPE interface in terms of bonding and charge transfer effects and contact made to RAIRS and transport data for related systems.

3:00pm **SS+OF-WeA4 Mechanical and Charge Transport Properties of Self Assembled Organic Monolayers***, **I. Ratera**, J.Y. Park, J. Chen, A. Liddle, D.F. Ogletree, M. Salmeron,* Lawrence Berkeley National Laboratory

We are interested in measuring and correlating electronic and mechanical properties of molecules. We will report our progress in the fabrication of insulating test substrates with embedded coplanar metallic nanoelectrodes. In this manner a monolayer of molecules can bridge two electrodes and be accessible to an AFM or STM tip. This approach may lead to a better understanding the nature of the molecule - electrode contact. The use of AFM with conducting tips provides the ability to vary the load on the nano-contact and also opens the way for exploring electron transfer as a function of molecular deformation. Initial results will be presented on the influence of mechanical stress on the structural and electrical properties of self-assembled alkylthiols on gold surfaces as a function of the chain length and tip pressure.

3:20pm **SS+OF-WeA5 Electronic Properties of Interfaces between Organic Semiconductors and Metals***, **M. Knupfer,*** Leibniz Institute for Solid State and Materials Research Dresden, Germany **INVITED**

The electronic properties and the energy level alignment of interfaces between organic semiconductors and metals have been studied using photoemission spectroscopy in the valence as well the core level region. Different contrubutions to the frequently observed interface dipoles are discussed. In particular, the role of a reduction of the metal workfunction in comparison to clean, uncovered surfaces and image charge screening will be addressed. Furthermore, there are several examples where a charge transfer is observed at the interface, in particular for technologically relevant cases, which is essential for the understanding of charge transport acroos the corresponding interface.

4:00pm **SS+OF-WeA7 Energy Level Alignment at Organic Interfaces: Interface Induced Gap States and Charge Neutrality Levels***, **T.U. Kampen**,* Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany

The energy level alignment at organic interfaces determines the efficiency of charge injection into organic films. Quite often the vacuum level alignment rule has been used to determine the energy level alignment at organic interfaces. Here, barrier heights can simply be calculated using the ionisation potentials or electron affinities of semiconductors materials and work functions of metals. For organic interfaces a conclusion has been reached that in general the vacuum levels do not align. At intimate, abrupt, and defect free interfaces of inorganic semiconductors interface induced gap states are the primary mechanism determining the energy level alignment. These interface states derive from the bulk states and their character changes across the band gap from more acceptor-like closer to the conduction band to predominantly donor-like nearer to the valence band. The branch point where the character changes has the significance of a charge neutrality level. This work shows that the concept of interface induced gap states may also be applied to organic interfaces. The charge neutrality levels of PTCDA, DiMe-PTCDI, and CuPc are found to be 1.96 eV, 1.93 eV, and 0.51 eV above the HOMO, respectively.

4:20pm **SS+OF-WeA8 Work Function and Charge Distribution XPS Study of Molecular Layers Self-Assembled on Gold***, H. Cohen, **S. Ray**, R. Naaman,* The Weizmann Institute of Science, Israel

Substrate-overlayer charge transfer frequently imposes considerable changes on the properties of self-assembled (SA) monolayers. The study of space charge distribution across molecular layers is targeted here, using XPS in a slightly modified setup, capable of in-situ work-function evaluation. Fine differentiation between chemical and electrical information across dipolar layers is demonstrated. Intra-molecular charge transfer is found to take place in part of the systems, giving rise to a directional flip of the dipole moment on the nanometer scale.

4:40pm **SS+OF-WeA9 Influence of Electrode Contamination on @alpha@-NPD/Au Hole-injection Barriers***, **A.S. Wan**, J.H. Hwang, A. Kahn,* Princeton University

Processing for OLEDs and other organic devices often involves exposure of surfaces and interfaces to nominally controlled atmosphere (e.g. N@sub 2@) or even ambient conditions. A model system for studying barriers built under such "practical" conditions, as opposed to barriers built on ultra-clean substrates prepared under ultra-high vacuum (UHV) conditions, is the interface between Au and @alpha@-NPD, a standard hole- transport material for OLEDs. In this work, we investigate the effect of ambient exposure of polycrystalline Au surfaces on the hole-injection barrier using ultraviolet photoemission spectroscopy (UPS) and I-V measurements. We compare @alpha@-NPD layers grown in UHV on: i. Au as-loaded, exposed to air; ii. Au cleaned by Ar@super +@ sputtering; iii. fresh Au deposited in UHV. Conventional wisdom is that the higher the work function of the contact metal, the lower the hole-injection barrier. However, our UPS studies unambiguously show that the injection barrier is 0.5-0.6 eV lower for Au exposed to air, which has a work function of 4.7-4.9 eV, than for clean Au (sputtered or UHV deposited), which has a work function of 5.3-5.4 eV. The vacuum level shift, or dipole barrier, (down from Au to organic) is 0.3 eV for the former and 1.3 eV for the latter. I-V measurements on Au/@alpha@-NPD/Au devices made on clean vs. "dirty" Au show several orders of magnitude increase in injection from "dirty" Au, entirely consistent with the changes in barriers measured in UPS. The large differences in dipole and injection barriers are attributed to the layer of contamination (consisting primarily of carbon) on the air- exposed Au, which lowers the work function of the metal and decouples the interface molecules from the Au atoms. Mechanisms based on disruption of interface bonding and/or metal-induced states will be discussed.

5:00pm **SS+OF-WeA10 Time-Evolution and Stability of Metal-Molecule Contacts**, *G. Nagy, **A.V. Walker**,* Washington University in St. Louis

Understanding the nature of metal-molecule interactions is important for many technologies, including organic and molecular electronics. It has already been demonstrated using vapor-deposited metals on self-assembled monolayers (SAMs) that many interactions are possible, ranging from destruction of the SAM to organometallic formation to penetration through the SAM to the Au/S interface. We apply time-of-flight secondary ion mass spectrometry (TOF SIMS) experiments and density functional theory (DFT) calculations to investigate the time-evolution and the energetics of vapor-deposited metallic contacts. As model systems we are employing vapor-deposition of copper on alkanethiolate SAMs with -CH3, -OCH@sub 3@, -COOH, -OH and -COOCH@sub 3@ terminal groups. We observe at room temperature that vapor-deposited Cu on -COOH and -OCH@sub 3@ SAMs initially both penetrates to the Au/S interface and forms a weak complex with the terminal group. However, Cu at the vacuum interface is not stable in the long term and slowly penetrates through the monolayer. We demonstrate that the stability of metal-molecule contacts is dependent on a number of factors including the strengths of the metal-metal and the metal-molecule interactions and the rate of penetration through the monolayer, which itself is dependent on the diffusion of the SAM molecules on the Au substrate.

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