

Contacts to Organic Materials Topical Conference Room 318/319 - Session OM-MoA

Contacts to Molecules and Molecular Films (II)

Moderator: D.R.T. Zahn, Technische Universität Chemnitz, Germany

2:00pm OM-MoA1 Characterization of Organic-Metal and Organic-Organic Interfaces, *J.L. Bredas*, Georgia Institute of Technology **INVITED**

In organics-based (opto)electronic devices, organic/metal and organic/organic interfaces play a key role in determining the device performance. Here, we focus first on the interface dipole present at organic-on-metal interfaces. The origin of this dipole is rationalized from the results of a joint experimental and theoretical study based on the interaction between pi-conjugated molecules and transition metal surfaces. It is found that the interface dipole formed at the organic/metal interface can be divided into two contributions: (i) the first corresponds to the "chemical" dipole induced by a partial charge transfer between the organic layers and the metal upon chemisorption of the organic molecules on the metal surface; and (ii) the second relates to the change in metal surface dipole due to the modification of the metal electron density tail that is induced by the presence of the adsorbed organic molecules. In a second part, we investigate the electronic structure of metal-on-oligomer and organic/organic interfaces.

2:40pm OM-MoA3 The Role of Charge Neutrality Level in Molecular Level Alignment at All-organic Heterojunctions, *W. Gao, A. Kahn*, Princeton University

Alignment of molecular levels at organic-organic (OO) heterojunctions controls charge injection and transport in multilayer organic devices. Because of weak intermolecular interaction and absence of free charges, vacuum level alignment is often observed at heterojunctions between intrinsic (undoped) molecular films. We present here the first experimental evidence that an alignment mechanism based on the charge neutrality level of the molecular semiconductor becomes important when one of the interface constituents is doped. Our direct and inverse photoemission (UPS, XPS, IPES) investigation focuses on interfaces between hole transport layers (HTL) and electron transport layers (ETL). We use the strong electron acceptor F@sub 4@-TCNQ to p-dope the HTLs. We show that, unlike at metal-organic (MO) interfaces, molecular levels and energy barriers across the interfaces are not strongly anchored and shift with respect to each other upon doping of the HTL. The shift is accompanied by the formation of an interface dipole, the size of which depends on the constituents of the heterojunction. The key result is that the Fermi level position in the gap of the undoped ETL remains fixed and independent of the HTL when the HTL is doped. This important observation suggests that the introduction of charges and of electronic states at the interface in the gap of the HTL and ETL via doping results in a pinning of the Fermi level at or near a specific energy level, tentatively related to the charge neutrality level of the organic material. W. Gao and A. Kahn, Appl. Phys. Lett., (in press) W. Gao and A. Kahn, Organic Electronics 3, 53 (2002).

3:00pm OM-MoA4 Au/CuPc Interface: A Photoemission Investigation, *L. Lozzi, S. Santucci*, INFN and University of L'Aquila, Italy; *S. La Rosa*, Sincrotrone Trieste SCpa, Trieste, Italy

Copper phthalocyanine (CuPc) are deeply investigated for many different applications as thin films. One of the most promising application is the fabrication of photovoltaic cells, in which the CuPc film is the active part. Au is a widely used metal for metallic contact, in particular for organic photovoltaic cells, because of its high work function. In this study we will show our results on the investigation of the interface between CuPc and Au by means of photoemission. We have deposited, by means of thermal evaporation in ultra high vacuum conditions, very thin Au films on a 70 nm thick CuPc film and we have investigated both core levels and valence band features as a function of the Au thickness. We have used different photon energies (from X-ray to UV) to investigate surface and in depth properties. Moreover we have performed high spatial resolution photoemission experiments (Spectromicroscopy beamline at Elettra Synchrotron Radiation Center, spatial resolution about 0.5@micron@) to investigate the homogeneity of the Au film on the organic film. The evolution of the Au 4f spectrum, as a function of the Au film thickness shows indicates the formation of gold cluster. Comparing the valence band acquired using low photon energy with those using X-ray photons, it is evident that these clusters are dispersed inside the organic

film. No evident variations are observed in the core levels of the CuPc elements. The spatially resolved photoemission spectra do not show any difference of the valence band spectra as a function of the position and also the images, acquired looking at different energies of the valence band, showed a very high homogeneity of the deposition, although the CuPc surface is quite rough. P. Peumans and S.R. Forrest, Appl.Phys.Lett. 79, 126 (2001) S.B. Di Censo, S.D. Berry, and E.H. Hartford Jr., Phys.Rev.B38, 8465 (1988).

3:20pm OM-MoA5 XPS and HRSEM Studies on the Interfaces of Au/CuPc vs. Au/FCuPc, *X. Yu, T.E. Madey*, Rutgers, The State University of New Jersey

Ultrathin films of Au have been grown on both copper phthalocyanine (CuPc) and copper hexadecafluorophthalocyanine (FCuPc) samples at room temperature (RT). These are model systems for metal contacts on organic semiconductors. X-ray photoelectron spectroscopy (XPS) measurements, corresponding to various average Au film thicknesses (from 0.3 to 3.0 Å), show that Au deposited on CuPc does not react, but for Au on FCuPc there is evidence for possible charge transfer from Au atoms to the four aromatic rings of FCuPc. Annealing the films at 125°C for one hour enhances charge transfer at the interfaces of Au/FCuPc, while it does not cause any chemical reactions at the interfaces of Au/CuPc. High-resolution field emission scanning electron microscopy (HRSEM) was employed to examine the nucleation and growth of Au (average thicknesses from 5 to 180 Å) on CuPc and FCuPc films at room temperature. Au grows in an island mode on four types of samples CuPc (RT), CuPc (125), FCuPc (RT), and FCuPc (125) in the initial stages of Au deposition (average thicknesses from 5 to 15 Å). The number in the parentheses is the temperature of substrates (in degrees Celsius) during CuPc or FCuPc deposition. Au atoms tend to form bigger clusters with a lower cluster density on CuPc surfaces than on FCuPc surfaces. This may indicate a lower diffusivity for Au on FCuPc than on CuPc, perhaps because of a stronger interaction between Au and FCuPc. These observations support our results from XPS studies. The onset of percolation occurs at a Au thickness of 90 Å for Au/CuPc (RT) and Au/CuPc (125), and 90 Å for Au/FCuPc (RT) and Au/FCuPc (125). A continuous and hole-free Au film is formed at a thickness of 180 Å.

3:40pm OM-MoA6 A Combined Photoemission Spectroscopy and Scanning Probe Microscopy Study of Organic Charge Injection Layer / Metal Interfaces, *A.J. Mäkinen, J.P. Long, N.J. Watkins, Z.H. Kafafi*, Naval Research Laboratory

The electronic structure of organic/metal interfaces was investigated using photoemission spectroscopy in combination with scanning probe microscopy. Organic films of copperphthalocyanine (CuPc) and 6T were vacuum-deposited onto a single-crystal Au(111) substrate step-by-step, and ultraviolet and x-ray photoemission spectroscopies (UPS and XPS) were performed on the sample, together with scanning probe microscopy (SPM), at each step. By correlating different organic film structures revealed by SPM measurements with the corresponding electron energy spectra measured with UPS and XPS, we have been able to gain insights into how the frontier orbital character and position evolve with the organic film growth on the Au substrate. Since CuPc/Au and 6T/Au interfaces serve as model systems for similar structures responsible for charge injection and transport in many organic electronic devices, such as organic light-emitting diodes and photovoltaics, the results of this investigation will be useful for the characterization of such systems.

4:00pm OM-MoA7 Electronic Structures of Al/Liq/Alq Interfaces Studied by Photoemission Spectroscopy, *Y. Park*, Korea Research Institute of Standards and Science, Korea; *J. Lee*, Samsung Advanced Institute of Technology, Korea; *J.W. Choi*, KRISS, Korea; *M. Han*, University of Seoul, Korea

Lithium quinoate (Liq) has recently been attracting a good deal of attention for a cathode interlayer material in organic light-emitting devices (OLEDs) as it showed electron injection performance as good as most commonly used LiF. Using X-ray and UV photoemission spectroscopy (XPS & UPS) techniques, we studied the evolution of the electronic structures at Al/Liq/Alq interface as it is formed in ultrahigh vacuum condition. The valence region spectra taken with UPS showed that the HOMO peaks move to higher binding energy (relative to Fermi level, E_F) as Liq is deposited on Alq interface. This indicates that the deposition of Liq caused density of states inside the HOMO-LUMO gap although its intensity is too weak to be observed clearly with UPS. The total amount of the peak movement is ~ 1.8 eV comparable to the value for

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LiF (~1.9 eV). We believe this shift of Fermi level (relative to vacuum level) toward LUMO level is principal cause of the observed improvement in device performance. The evolution of XPS peaks during the interface formation is very similar to the case of LiF and there is no appreciable direct chemical reaction when Liq was initially deposited on Alq@sub 3@. We further discuss the possible origins of the observed HOMO peak movement.

4:20pm **OM-MoA8 Direct Observation of the Evolution of the Molecular Orbital Energy Levels of a Silole Derivative as a Function of Magnesium Deposition**, *N.J. Watkins, A.J. Mäkinen*, Naval Research Laboratory; *Y. Gao*, University of Rochester; *M. Uchida*, Chisso Corporation, Japan; *Z.H. Kafafi*, Naval Research Laboratory

The electronic structure of the interface formed by Mg deposition onto 2,5-bis(6-(2,2-bipyridyl))-1,1-dimethyl-3,4-diphenyl silacyclopentadiene (PyPySPyPy) was investigated using ultraviolet photoemission, inverse photoemission, and X-ray photoemission spectroscopies. PyPySPyPy is of interest due to its high electron mobility. In addition, organic light-emitting diodes (OLEDs) using this silole derivative in the electron injection/transport layer exhibit very low operating voltages. Upon deposition of Mg onto PyPySPyPy a shift of the occupied molecular orbital energy level structure to higher binding energy, away from the Fermi level, was observed and accompanied by the appearance of two new levels within the energy gap of PyPySPyPy. These new levels have been assigned to a charge transfer complex between Mg and PyPySPyPy. At high Mg coverage, the shift in the lowest unoccupied molecular orbital can be correlated with the formation of "metallic-like" Mg clusters. The impact of these results on charge injection at the Mg metal contact in an OLED structure will be discussed.

4:40pm **OM-MoA9 Band Alignment on Patterned Surfaces**, *G. Koller, F.P. Netzer, M.G. Ramsey*, Karl-Franzens University, Austria

An important parameter for the function of organic electronic devices is the barrier to charge injection which is controlled by the interface dipole. This is determined by the details of the interaction of the first layer of molecules with the contact material. In reality the interface is not perfectly homogeneous and thus local differences in band alignment are to be expected although not necessarily observable with standard area averaging techniques. In this contribution we explore the local variation in band alignment on a nanoscopically patterned substrate surface by investigating the growth of bithiophene films, from sub-monolayer to multilayer coverages, with angle resolved UV-photoemission and workfunction measurements. The substrate used was the oxygen reconstructed Cu(110) surface. This surface reconstructs to form a mesoscopically patterned surface consisting of alternating stripes of clean Cu(110) and passive Cu(110)-(2x1)O, with stripe widths in the range of several nanometers depending on oxygen exposure. The bonding interaction of the probe molecule bithiophene is very different on the two surfaces resulting in band alignment differences of 1 eV for films grown on these surfaces. On the Cu(111)-(2x1)O striped surface for coverages of bithiophene up to two monolayers, the photoemission spectra is a result of the superposition of spectra offset by this difference in band alignment clearly indicating local differences in the charge injection barrier. However, beyond two monolayers the valence band spectra clearly indicate a single emitting species whose energy position is determined by the average interface dipole. The results thus show that inhomogeneities of the substrate surfaces will lead to local differences in the charge injection barrier which are invisible to area averaging techniques if the molecular film thickness are greater than the lateral dimensions of the inhomogeneities. Acknowledgments: Supported by the Austrian Science Foundation SFB Electroactive Materials

5:00pm **OM-MoA10 A General Soft Contact Evaporation Method for Molecule-Based (Opto) Electronic Devices**, *H. Haick, J. Ghabboun, D. Cahen*, Weizmann Institute of Science, Israel

Hybrid devices, in which molecular functionality is used to influence the characteristics of established electronic devices, but that do not require electronic charge transfer through the molecules, is an alternative approach to more established ones to molecule-based electronics. It is worth pursuing because of stability issues and the ability to use established technology as much as possible at this stage of molecule-based electronics. One such hybrid approach is based on controlling electronic properties of semiconductor devices by placing molecules, whose dipole can, synthetically, be changed systematically, at the device interface. Because mostly one can not insert molecules into a ready-made device interface, constructing such device structures requires device completion by making

a solid electrical contact to a surface with the organic molecules on it. This is problematic because a process such as thermal evaporation or sputtering easily damages the molecules, especially molecules that have sensitive functional groups exposed. Earlier we overcame this by successful use of soft, alternative methods. Still, the clear technological advantages of vacuum evaporation led us to search for ways to adapt this method to meet the challenge. The result, which we will present here is Indirect, Collision-Induced, Cooled Evaporation (ICICE), with which we prepared, among others, GaAs/molecule/Au diodes. ICICE decreases drastically the temperature and, thus, the kinetic energy of the evaporated particles/atoms arriving at the surface and assures that irradiation emitted from the crucible does not reach the modified samples. Based on TOF SIMS, XPS, STM and (I-V) electrical measurements, we find that ICICE provides intimate contacts without damaging the (~ 1-3 nm wide monolayer of) organic ligands and their functional groups. This is best expressed by the clear molecular effect on the resulting Au/GaAs barrier heights; they vary with the functionality of the adsorbed molecules. To understand the limiting steps for contacting by means of metal evaporation, we compared results obtained in our experimental system with ICICE, and another popular one, known as Direct Evaporation Under Cryogenic Cooling (DEUCC). While, indeed use of the DEUCC mode leaves the organic ligands beneath the metal contacts, it does damage their functional groups. This finding, for which we will present an explanation, has very significant implications as it shows that while the often-used criterion of absence of shorts in metal/molecule/metal junctions is indeed a necessary condition for successful contacting molecules, it is not a sufficient one. We thank the Israel Ministry of Science (Eshkol fellowship to HH and tashtyoth project and the Israel Science Foundation (Jerusalem) for partial support.

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