

Organic Electronic Materials Topical Conference Room 616/617 - Session OE+EM+AS-TuM

Interfaces and Characterization of Organic Thin Films

Moderator: Y. Gao, University of Rochester

8:20am **OE+EM+AS-TuM1 Electronic Properties of Organic Semiconductor Interfaces**, *I.G. Hill*, Princeton University; *C. Shen*, Princeton University, US; *D. Markiewicz*, *J. Schwartz*, *A. Kahn*, Princeton University **INVITED**

The alignment of molecular energy levels at the interfaces of organic semiconductor films plays a critical role in determining organic light emitting device (OLED) efficiencies. At a metal/semiconductor interface, the positions of the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO respectively) relative to the metal Fermi level determine the barriers for charge injection into the organic. At organic/organic heterointerfaces, the relative alignment of the HOMO and LUMO levels of the two organics determines whether charges will flow freely across the interface or result in charge accumulation. It is now widely accepted that vacuum levels do not, in general, align at metal/organic interfaces,^{1,2} implying that techniques such as ultraviolet photoelectron spectroscopy (UPS) and internal photoemission must be used to determine barrier heights. Vacuum levels do align at the majority of organic/organic heterointerfaces, with a few notable exceptions.³ Using UPS, we have studied a variety of both metal/organic and organic/organic interfaces with the goal of understanding the origin of, and therefore ways to control, the interface dipoles which result in vacuum level discontinuities. The results of these studies will be discussed with an emphasis on our attempts to understand the roles of surface modifying procedures, such as oxygen plasma treatment of indium tin oxide (ITO), on improving device performance. ¹H. Ishii and K. Seki, IEEE Trans. Electr. Devices 44, 1295, (1997) ²I.G. Hill, A. Rajagopal and A. Kahn, Appl. Phys. Lett., 73, 662, (1998). ³I.G. Hill and A. Kahn, Proceedings of SPIE, Organic Light-Emitting Materials and Devices II, 3476, 168, (1998).

9:00am **OE+EM+AS-TuM3 Photoemission Characterization of Al/Alq@sub 3@ and Al/LiF/Alq@sub 3@ Interfaces**, *L. Yan*, *Q.T. Le*, *Y. Gao*, University of Rochester; *M.G. Mason*, *C.W. Tang*, Eastman Kodak Company

We have investigated the interface formation of Al on tris-(8-hydroxyquinoline) aluminium (Alq@sub 3@) and Al on LiF/Alq@sub 3@ using X-ray and ultraviolet photoemission spectroscopy (XPS and UPS). We observed significant modifications of O1s, N1s and Al2p core level spectra as Al was directly deposited on the Alq@sub 3@ surface. The Alq@sub 3@ features in the UPS spectra were also quickly destroyed. In contrast, a dramatically different behavior was observed for Al on the LiF/Alq@sub 3@ interface. With only 5Å of LiF deposited on the Alq@sub 3@ surface as a buffer layer, the reaction between Al and Alq@sub 3@ is significantly suppressed. A well-defined gap state is formed. The Alq@sub 3@ features in UPS shift to higher binding energies but remain easily recognizable. Both the core level spectra and the gap state suggest that the Alq@sub 3@ anion is formed in the presence of Al and LiF.

9:20am **OE+EM+AS-TuM4 Charge Injection vs. Chemical State of Electrode Surfaces in Metal/Alq@sub 3@/Metal Structures**, *C. Shen*, Princeton University, US; *I.G. Hill*, *A. Kahn*, Princeton University

The effect of the deposition sequence on the electrical behavior of metal-organic interfaces is an important issue in the context of multiple layer organic light emitting devices (OLED). Metals deposited on organics generally lead to more extensive interface chemistry, and have been reported to produce different electrical behavior, than organics deposited on metals. To address this issue, we investigate the interface chemistry, electronic structure and electrical transport in nominally symmetric Mg:Ag/8-hydroxyquinoline aluminum(Alq@sub 3@)/Mg:Ag structures fabricated and tested in ultra-high vacuum and under controlled atmosphere. We perform detailed X-ray photoemission spectroscopy measurements which confirm that the metal-organic chemical reaction and interdiffusion are different at the Mg-on-Alq@sub 3@ interface than at the Alq@sub 3@-on-Mg interface. We also show, however, that the chemical state of the bottom electrode surface plays a major role in the device electrical behavior. The Mg:Ag/Alq@sub 3@/Mg:Ag structure built in ultra-high vacuum leads to symmetric top and bottom electron injection, whereas controlled oxidation of the bottom metal surface leads to a two-order-of-magnitude lower bottom contact injection. These results fully

explain earlier results obtained for devices made under "standard" conditions, i.e. in moderate 10⁻⁵ Torr vacuum. A similar study of the Al/Alq@sub 3@/Al structure is under way and will be reported as well at the conference.

9:40am **OE+EM+AS-TuM5 Investigation of the Electronic Structure of Organic Schottky Contacts with Photoemission Spectroscopy: Discrimination Between Interface Dipole, HOMO Offset, Band Bending and Charging Related Spectral Shifts**, *R. Schlaf*, *G.P. Kushto*, *L.A. Crisafulli*, *C.D. Merritt*, *Z.H. Kafafi*, US Naval Research Laboratory

We have determined the electronic structure of several organic Schottky contacts formed between the organic luminescent semiconductor tris (8-hydroxyquinolino) gallium (Gaq@sub 3@) and the metals Al, Mg, Ag, Au, and Pt. The investigated interfaces were prepared by vapor deposition of Gaq@sub 3@ on in-situ deposited metal films or thin sputtered high purity metal foils in a multi step growth procedure. Before growth and after each Gaq@sub 3@ deposition step the samples were characterized in situ using a combination of x-ray and ultraviolet photoemission spectroscopies (XPS, UPS). UPS was used to measure the highest occupied molecular orbital (HOMO) positions and interface dipoles, while XPS was used to determine the band bending (bulk charge redistribution) at the interface. In addition, simultaneous measurements of the high binding energy cutoff of the XP- and UP-spectra allowed the determination of the onset of charging phenomena observed at around 100Å Gaq@sub 3@ film thickness. Our results demonstrate that both, charging and band bending effects, may result in strong shifts of the PES spectra which need to be carefully evaluated in order to accurately determine the orbital line-up and the dipole at the interface. Our experiments suggest that the investigated organic Schottky contacts have large interface dipoles due to the chemisorption of the first organic layer in contact with the metal surface. All investigated interfaces also exhibit strong band bending in the organic layer, which strongly depends on the work function difference between Gaq@sub 3@ and the particular metal in contact.

10:00am **OE+EM+AS-TuM6 Examination of Band Bending at Organic Semiconductor / Metal Interfaces Studied by Kelvin Probe Method**, *H. Ishii*, *N. Hayashi*, *E. Ito*, *K. Seki*, Nagoya University, Japan

How the energy levels of an organic semiconductor and a metal electrode align at the interface between them is a critical and basic issue for understanding organic electronic devices. So far, Mott-Schottky (MS) model has been applied for the estimation of the electronic structure at organic/metal interfaces. In the model, vacuum level alignment is assumed right at the interface, while the Fermi level alignment is achieved through band bending in space charge layer. In order to examine the validity of this model, the film-thickness dependence of the location of the vacuum level of TPD (N,N'-bis(3-methylphenyl)-N,N'-diphenyl-[1,1'-biphenyl]-4,4'-diamine) on various metals (Au, Cu, Ag, Mg and Ca) were measured by Kelvin probe method in ultrahigh vacuum (UHV). At all the interfaces, an abrupt shift of the vacuum level was observed within 1 nm thickness, while further deposition of TPD up to 100 nm led to no change of the location of the vacuum level. These results indicate that the possible space charge layer is much thicker than 100 nm in UHV. The observed relation between the vacuum level shift and the work function of the metals suggests that (1) the Fermi level of TPD is located around the midgap in UHV condition and that (2) the Fermi level alignment is achieved only at TPD/Cu,Ag,Mg interfaces, not by band bending but by dipole layer formation right at the interface. These findings clearly demonstrate the invalidity of MS model for organic / metal interfaces in UHV. The results for the interface between Alq@sub 3@ (tris(8-hydroxyquinolino)aluminum) and metal will be also presented.

10:20am **OE+EM+AS-TuM7 Schottky Energy Barriers and Charge Injection at Metal/Organic Interfaces**, *I.H. Campbell*, Los Alamos National Laboratory; *B.K. Crone*, Lucent Technologies; *R.L. Martin*, *D.L. Smith*, Los Alamos National Laboratory; *C.J. Neef*, *J.P. Ferraris*, University of Texas, Dallas **INVITED**

We present independent measurements of metal/organic Schottky energy barriers and their charge injection characteristics in metal/organic/metal structures. The Schottky energy barriers were measured using internal photoemission and built-in potential techniques. The Schottky energy barriers to a poly (p-phenylene vinylene) based polymer (MEH-PPV) and to Alq were measured for a variety of metals with work functions ranging from 2.7 eV (Sm) to 5.6 eV (Pt). For MEH-PPV we find good agreement with the ideal Schottky model. In contrast, for Alq we find that the ideal Schottky picture is not applicable and that electron injecting contacts are pinned about 0.6 eV below the electron conducting states. The charge injection characteristics of these contacts were investigated by measuring

the current-voltage characteristics of single carrier structures. The dependence of the current-voltage characteristics on the Schottky energy barrier is quantitatively described by a device model which includes charge injection, transport and space charge effects in the structure. For Schottky barriers less than about 0.3 eV the current in the structure is space charge limited and the contact is ohmic. Finally, we present results using organic self-assembled monolayers to manipulate the metal/organic Schottky energy barrier and to control charge injection into the organic material. The monolayers are used to insert a thin (1 nm) dipole layer between the metal contact and the organic material. Depending upon the orientation of the dipole layer the Schottky energy barrier may be increased or decreased and the corresponding charge injection properties degraded or enhanced.

11:00am OE+EM+AS-TuM9 Interfacial Electronic Structures between p-Sexiphenyl and Metals Studied by Electron Spectroscopies, E. Ito, H. Oji, H. Ishii, Y. Ouchi, K. Seki, Nagoya University, Japan

Recently, organic electroluminescent (EL) devices have attracted much attention in relation to application to flat panel display. In order to understand the charge injection mechanism in such devices, the energy level alignment at the interfaces between organic films and metal electrodes is of crucial importance. In this study, we investigated electronic structures at the interfaces between p-sexiphenyl (6P) and a metal (Au or Mg) by ultraviolet photoelectron spectroscopy (UPS), metastable atom electron spectroscopy (MAES), and X-ray photoelectron spectroscopy (XPS). MAES is an extremely surface sensitive method because the excitation source is metastable atoms which can not penetrate into a sample. The abrupt shift of the vacuum level by 6P deposition on the evaporated metal film (Au or Mg) was observed in the UPS spectra. MAES spectrum of 6P on Au with the thickness of 0.3nm is almost similar with that of 20nm thick 6P film. This suggests that the flat-lying 6P molecules uniformly covered Au substrate. We also measured the spectra of Au on 6P/Au. Even when Au was evaporated with the thickness of 50nm, the spectral feature of 6P dominates in the MAES spectra, suggesting that Au does not cover completely with the 6P film, while the core level peak of Au gradually increased in XPS spectra with deposition of Au. Similar trend was also observed for Mg deposited on 6P/Mg. These results indicate the diffusion of Au into 6P film, leading to formation of the intermixing region. In the system of Au on 6P film, we observed downward shift of the energy levels with irradiation of UV-light (the excitation source of UPS), probably due to the photovoltaic effect. These results show the formation of the different interface between the 6P/metal and the metal/6P.

11:20am OE+EM+AS-TuM10 A Photoemission Investigation of Interfaces of poly(2, 5-diheptyl-1,4-phenylene-alt-2,5-thienylene) with an oligomer (p-sexiphenyl) and a Metal - Calcium, A. Rajagopal, Univ. Notre-Dame, Belgium; N Koch, Tech. Univ. Graz, Austria; J Ghijsen, Univ. Notre-Dame, Belgium; K. Kaeriyama, Kyoto Inst. of Tech., Japan; R.L Johnson, Univ. Hamburg, Germany; G. Leising, Tech. Univ. Graz, Austria; J.J. Pireaux, Univ. Notre-Dame, Belgium

Poly(2, 5-diheptyl-1,4-phenylene-alt-2,5-thienylene) (PDHPT) is a blue light emitting conjugated polymer with a band gap of ca. 3 eV, and is a promising candidate as an active material in organic light emitting diodes. The interface of this polymer with a) a blue light emitting oligomer (sexiphenyl- 6P), and with b) a low work function cathode material, calcium (Ca) have been investigated using both ultraviolet and x-ray photoelectron spectroscopy (UPS and XPS). Both 6P and PDHPT have a band gap of ca. 3 eV, as well as similar ionization potentials, and this makes the interface an interesting one. A systematic study of the in-situ growth of 6P on PDHPT allows the estimation of the relative positions of the HOMOs and the vacuum levels. We find that the HOMO of PDHPT is below that of 6P, and there is a vacuum level offset of 0.3 eV suggesting charge transfer from 6P to PDHPT. In the case of metal-PDHPT interface, Ca was deposited in extremely small steps in-situ, and both XPS and UPS data were recorded after each subsequent deposition. Contrary to what can be predicted based on calculations and experiments on similar systems, namely phenylenes and thiophenes, we propose that Ca forms covalent bonds with the polymer. The consequences of these experimental findings will be discussed within the context of LEDs.

11:40am OE+EM+AS-TuM11 A Photoelectron Study of Chemically Treated Indium Tin Oxide Surface and Its Reactivity with Phenyl-Diamine, Q.T. Le, F. Nuesch, E.W. Forsythe, L.J. Rothberg, Y. Gao, University of Rochester

We report on the effect of various treatments by base and acid solutions on the work function of indium tin oxide (ITO). Ultraviolet and x-ray photoelectron spectroscopy (UPS and XPS) were used to measure the work function and chemical composition, respectively, of the processed

ITO surface. The results indicate that the magnitude of the work function shift is highly dependent on the nature of the solution. In contrast, for the same solution, the concentration of the solution appears to have little effect on the work function shift. In addition, the interface formation between processed ITO and N,N'-bis-(1-naphthyl)-N,N'-diphenyl-1,1'-biphenyl-4,4'-diamine (NPB) using XPS and UPS is presented. The reactivity of the treated ITO surfaces versus NPB is compared with the case of plasma-treated sample. The low current onset obtained from the single-layer devices based on acid-treated ITO can be attributed to the low energy barrier for hole injection at the ITO/hole-transporting material interface. This work was supported in part by DARPA DAAL 0196K0086, NSF Grant DMR-9612370, and the Swiss National Science Foundation.

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