Organic Electronic Materials Topical Conference
Room 327 - Session OE+AS+EM-TuM

Organic Thin Film Interfaces

Moderator: J.L. Brédas, University of Mons-Hainaut, Belgium

8:20am **OE+AS+EM-TuM1 UV Photoemission Study of Interfacial Electronic Structures of Organic Materials*, K. Seki,*** *E. Ito, H. Oji, K. Sugiyama, D. Yoshimura, Y. Ouchi, H. Ishii,* Nagoya University, Japan **INVITED**

The energy level alignment at organic/inorganic and organic/organic interfaces is a fundamental issue for understanding interfacial phenomena of organic-based electronic devices. Using UV photoemission spectroscopy (UPS), we have investigated the electronic structure and energy level alignment at the interfaces of various organic films on metal substrates prepared in ultrahigh vacuum (UHV). The observed results clearly demonstrated that the traditional picture which assumes vacuum level alignment at the interfaces is not valid: the vacuum level of organic layer is shifted from that of metal electrode. We report here our recent effort on the examination of the vacuum level shift at organic/metal, and organic/organic interfaces. At most organic/metal interfaces so far studied, downward shifts of vacuum level were observed (i.e. the vacuum level of organic layer is below that of the metal). At acceptor/metal interface, upward shift was often observed, depending on metal electrode. From the relation between the observed shift and the work function of the metal, we discuss the possible origins of the vacuum level shift such as the polarization of organic molecule by image effect, charge transfer, and mid-gap state. We will also present the results of 'sexiphenyl(6P) on metal' and 'metal on 6P' by UPS, X-ray photoemission (XPS), and metastable atom electron spectroscopy (MAES). At organic/organic interface such as Alq@sub 3@(tris(8-hydroxyquinolino)aluminum) /TPD(N-N'-diphenyl-N-N'-(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine), the observed vacuum level shift was less than 0.1eV, leading to an apparent applicability of the traditional model. However, finite shift of 0.2 eV was observed at donor/acceptor interface such as TTN(tetrathianaphthacene)/TCNQ(tetracyanoquinodimethane) due to electron-transfer.

9:00am **OE+AS+EM-TuM3 Electronic Structure of Molecular Organic Semiconductor Metal Interfaces*, A. Kahn,*** *I.G. Hill,* Princeton University

It is now well known that the traditional assumption of vacuum level alignment at metal-organic semiconductor interfaces is incorrect.@footnote 1,2@ Large interface dipoles shift the vacuum level at the interface by more than 1 eV in some cases. The electron injection barrier therefore cannot be reliably estimated as the difference between the metal work function and the organic electron affinity. Furthermore, it has been found that the magnitude of this barrier varies significantly with the metal work function on some organic materials, and not at all on others. To illustrate these properties, we present a comprehensive investigation of metal-organic semiconductor interfaces. Many of these interfaces have been studied both in the organic on metal and metal on organic systems, which in general are not equivalent. The metals studied range in work function from 3.7 eV (Mg) to 5.2 eV (Au). The organic materials studied include the hole transport materials, PTCDA and @alpha@-NPD, the electron transport material Alq@sub 3@, and the cathode interface material, CBP. Using ultraviolet photoelectron spectroscopy, we have measured the relative positions of the metal Fermi level and the organic HOMO, as well as the offset of the vacuum level at each interface. We show that the dependence of the barriers on the metal work function is very small with PTCDA and Alq@sub 3@, and increases with @alpha@-NPD and CBP. All of these organic-metal pairs exhibit substantial interface dipoles which compensate for the restricted range of interface Fermi level positions. Implications for contact performances are discussed. @FootnoteText@ @footnote 1@H. Ishii and K. Seki, IEEE Trans. on Elect. Dev., 44, (1997) 1295. @footnote 2@I. G. Hill, A. Rajagopal, A. Kahn and Y. Hu, Submitted to Appl. Phys. Lett.

9:20am **OE+AS+EM-TuM4 Interface Dipoles and Band Bending in Organic Semiconductor Interfaces*, R. Schlaf,*** *M.W. Nelson, P.G. Schroeder, B.A. Parkinson,* Colorado State University*; P.A. Lee, K.W. Nebesny, N.R. Armstrong,* University of Arizona

The fast paced development in the field of organic light emitting diodes (OLED) and thin film transistors (OTFT) has sparked intense efforts to determine the electronic structure at organic interfaces and to understand the rules governing it. Photoemission spectroscopy (PES) measurements offer direct information about the HOMO alignment, interface dipole and band bending at such interfaces. We performed multistep growth experiments with insitu PES characterization on a variety of organic/organic, organic/inorganic semiconductor and organic/conductor interfaces. We used combined X-ray and UV photoemission spectroscopies (XPS, UPS) which allow the separate determination of the band bending across the interface. This procedure, which is well established in the field of inorganic semiconductor heterojunctions, allows the measurement of HOMO alignment and interface dipoles with high precision. High precision results from avoiding the problem of the superposition of substrate and overlayer emissions in UP-spectra where elaborate curve fitting procedures are needed to distinguish between band bending and HOMO alignment. Our measurements indicate that band bending and interface dipoles play a significant role in the electronic structure at these interfaces similar to effects known from inorganic semiconductor interfaces. The interface dipoles are discussed in terms of quantum and structural dipoles caused by tunneling of charge carriers and permanent molecular dipoles at the interface.

9:40am **OE+AS+EM-TuM5 Molecular Level Offsets at Organic Semiconductor Heterojunctions*, I.G. Hill,*** *A. Rajagopal, A. Kahn,* Princeton University

Organic light emitting devices typically consist of two or more organic layers between hole and electron injecting contacts. The interface between the two organics can provide a barrier to either holes or electrons, which may increase device efficiency by reducing the leakage current through the device (leakage current does not contribute to light production). Most of the exciton formation and subsequent light emission occurs near this interface because of the resulting high carrier densities. Knowledge of the relative positions of the organic highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular (LUMO) orbitals at the interface is required to predict the transport or blocking characteristics for holes and electrons, respectively. The assumption of vacuum level alignment at organic heterojunctions is usually used to predict the size of carrier injection barriers, but it has been shown that this model breaks down at organic-metal interfaces.@footnote 1@ We have addressed the validity of this assumption by performing the most comprehensive direct measurement of the HOMO-HOMO offsets at key organic-organic interfaces using ultraviolet photoelectron spectroscopy. Five molecular solids are considered: PTCDA, @alpha@-NPD, Alq@sub 3@, CBP and CuPc. In general, the assumption of a common vacuum level at the interface was found to be valid. A few heterojunctions, such as PTCDA/Alq@sub 3@ and @alpha@-NPD/Alq@sub 3@, do show substantial discontinuities of the vacuum level, however, indicating the formation of an interface dipole.@footnote 2@ The molecular level offsets are discussed in terms of the Fermi level positions observed at interfaces between these organics and various metals. @FootnoteText@ @footnote 1@H. Ishii and K. Seki, IEEE Trans. on Elect. Dev., 44, (1997) 1295. @footnote 2@A. Rajagopal, C. I. Wu and A. Kahn, J. Appl. Phys., 83, (1998) 2649.

10:00am **OE+AS+EM-TuM6 Interface Analysis of Naththyl-substituted Benzidine Derivative and tris-8(hydroxyquinoline) Aluminum Using Ultraviolet and X-Ray Photoemission Spectroscopy*, E.W. Forsythe,*** *V.-E. Choong,* University of Rochester*; C.W. Tang,* Eastman Kodak Company*; Y. Gao,* University of Rochester

The interface energy level alignment is a decisive factor in producing highly efficient organic light emitting diodes (OLEDs). We have studied the interface between naththyl-substituted benzidine derivative (NPB) and tris-8-(hydroxyquinoline) aluminum (Alq), a prototypical system used in OLEDs. The combination of ultraviolet photoemission and x-ray photoemission spectroscopy (UPS, XPS) allows us to distinguish contributions from NPB and Alq and obtain a detailed picture of the interface formation. The NPB coverages were deposited onto a 150 Å thick Alq film prepared insitu at 1x10@super -9@ Torr. The Alq and NPB HOMO levels are -1.7 eV and -1.4 eV, relative to the Fermi level, respectively. From the UPS difference spectrum, the gradual modification of the HOMO levels of NPB and Alq are revealed. The Alq HOMO level increases from -1.7 eV in the bulk to -1.8 eV with 2 Å of NPB. Likewise, the NPB HOMO level increases from -1.1 eV for the 5 Å coverage to -1.4 eV with 55 Å of NPB. The increases observed for the Alq and NPB HOMO levels are consistent with the vacuum level shift as well as the observed core level shifts from XPS. Further, the XPS results show no chemical interactions at the interface. This observed local interface formation region may contribute additional traps and energy barriers for carrier transport across the Alq/NPB interface. This work was supported by DARPA DAAL01-96-K-0086 and NSF DMR-9612370.

10:20am **OE+AS+EM-TuM7 Vapor Deposition Polymerization of 4-fluorostyrene and Pentafluorostyrene**, ***B. Bartlett,*** *L.J. Buckley, D.J. Godbey,* Naval Research Laboratory*; M.J. Schroeder,* U.S. Naval Academy

Solventless deposition of thin, uniform dielectric films is of considerable interest and importance in the microelectronics industry, due to increasing wafer sizes and environmental concerns. This work demonstrates a solvent-free method for atmospheric pressure chemical vapor deposition polymerization of thin dielectric films on a variety of substrates, including Si, Mo, Pt, and Cu. The films are characterized using transmission FTIR, and XPS. Depth profiling is performed using XPS, elipsometry, and step profilometry. Film growth is found to be independent of substrate, and proceeds with an activation energy of 15 kcal/mol between 450K and 500K. Films are shown by GPC (gel permeation chromatography) to consist of low molecular weight polymer and oligimer species (between 3 and 165 repeat units). AFM analysis indicates that the RMS thickness variation along the surface is < 0.2%, verifying film uniformity.

10:40am **OE+AS+EM-TuM8 Growth and Characterization of Polyaniline Thin Films on Metal Substrates**, *K. Lee, R.V. Plank,* ***J.M. Vohs***, University of Pennsylvania*; Y. Wei, N.J. DiNardo,* Drexel University

Polyaniline (PANI) thin films have potential for use as conductive layers in organic-based electronic devices. In a series of experiments, the near-surface sensitivity of High Resolution Electron Energy Loss Spectroscopy (HREELS) was used to probe interfacial and thin film properties of insulating and conducting forms of PANI grown on metal surfaces. PANI was deposited on Ag, Cu, and Au surfaces by evaporative-deposition in vacuum using an emeraldine source and from solution. The fully-resolved vibrational spectra and electronic excitation spectra of PANI films as a function of thickness and modes of preparation reveal clear trends regarding film quality and conductivity upon doping. Specific interface interactions observed in the vibrational spectra at the outset of growth of ultrathin vapor-deposited PANI correlate with increased ordering and an oxidation state similar to the starting emeraldine powder. A relatively high (microscopic) conductivity is indicated by the observation of a split-off far-IR plasmon loss upon HCl doping; this has been compared to the bulk (macroscopic) conductivity of similarly prepared films. In contrast, thicker vapor deposited and solution cast films exhibit a greater degree of branching and lower conductivities. Studying the evolution of polymer thin film properties from the polymer-substrate interaction to the polymer surface demonstrates a general approach with great potential, and the data suggests several aspects of preparation and modification to better control the properties of PANI films in particular.

11:00am **OE+AS+EM-TuM9 Tapping Mode Near-Field Scanning Optical Microscopy of Molecular Crystals and Thin Films**, ***H. Stadniychuk***, *A. Kosterin, C.D. Frisbie,* University of Minnesota

We describe near-field optical imaging experiments to probe fluorescence and birefringence in molecular crystals and polymeric thin films. These experiments utilize a near-field microscope that employs tapping mode feedback to scan the sample underneath a cantilevered optical fiber probe, facilitating imaging of soft organic samples. In one set of studies, we have focussed on fluorescence and transmission imaging of 30-400 nm thick crystals of tetracene grown by vacuum sublimation onto transparent substrates. These well-defined crystals are excellent samples for investigating quantitative aspects of near-field imaging, and we seek to determine the spatial extent of the near-field by quantifying the relationship between fluorescence intensity and crystallite thickness. A second set of studies exploits polarization modulation techniques to investigate birefringence from thin films of polymers, such as polyethylene oxide. A key aspect of these investigations is comparison of the near-field birefringence images with birefringence images obtained by confocal microscopy. This comparison facilitates understanding of contrast mechanisms in near-field characterization of organic thin films.

11:20am **OE+AS+EM-TuM10 Morphology and Relaxation Dynamics in Thin Organic Films Probed by Femtosecond Time-Resolved Photoemission Spectroscopy**, ***A.J. Makinen***, *S. Xu, S. Diol, A.R. Melnyk, D.A. Mantell, M.G. Mason, A.A. Muenter, Y. Gao,* University of Rochester

We have studied for the first time the lifetimes of the excited electron states of thin N,N'-bis(phenethyl)-perylene-3,4:9,10-bis(dicarboximide) (DiPe)films, prepared in situ, using femtosecond time-resolved photoemission spectroscopy. DiPe is an organic compound similar to photoreceptor materials widely used in many imaging applications. By controlling the evaporation conditions, we have been able to grow films of different morphologies, and found that the relaxation dynamics depends on the morphology. We have investigated two distinct films characterized by very different absorption spectra. We have found that for the film with absorption maximum at 500 nm, a typical lifetime is 45 fs at 2.1 eV above the molecular HOMO level. For the other film with absorption maximum at 630 nm, the relaxation rate is almost twice as fast, resulting a lifetime of 25 fs at the same energy. We attribute the extremely short lifetimes to a rapid charge transfer reaction from the high energy sites to the low energy sites. This mechanism is further enhanced by the presence of disorder, which prevents the conservation of crystal momentum in the films. The dependence of the lifetimes on the morphology can be explained by the difference of crytallinity of the films, which affects the density of states and the localization of the excited electrons.

11:40am **OE+AS+EM-TuM11 XPS and ISS Studies of Cu Deposited onto Acid-terminated Self-Assembled Monolayers**, ***L.S. Dake***, *D.E. King, A.W. Czanderna,* National Renewable Energy Laboratory

Metal/self-assembled monolayer (SAM) systems serve as models for more complex metalized polymers. Often the adhesion of metals to polymers is a problem, and the metal/polymer interface can be the critical weak link in such a system. We have studied the interactions of Cu deposited onto an acid-functionalized (COOH) SAM surface to improve our understanding of the fundamental metal/organic interactions. We are interested in the chemical interactions of the Cu with the SAM surface, the growth mode of the deposited metals, and the penetration of the metal. Copper deposited onto SAMs with different organic functional endgroups exhibits a wide range of behavior ranging from no surface interaction and rapid penetration (for methyl-terminated SAMs) to weak interactions followed by slow penetration (for methyl-ester terminated SAMs). In this work, we have characterized the interactions of Cu with a carboxylic acid-functionalized alkanethiol SAM, using XPS to examine the chemical interactions, and a combination of XPS and ISS to deduce the growth mode and penetration rate of the deposited Cu. Of particular interest is whether a chemical reaction with the acid surface suppresses penetration, and if there is a limit to the amount of Cu that penetrates the SAM. We find that small amounts of Cu react with the acid surface group, whereas the rest of the Cu penetrates beneath the SAM. Considerable amounts of Cu (10 nm or more) will diffuse beneath the SAM layer, despite the presence of small amounts of reacted Cu at the surface. The penetration rate depends strongly on the deposition rate, with much more rapid penetration occurring at deposition rates of 0.1 nm/min or less. Cooling the sample during Cu deposition, and more rapid Cu deposition rates result in slower or even completely suppressed penetration of the Cu through the SAM layer. This work was performed under DOE contract DE-AC36-83CH10093 @FootnoteText@ After Aug. 1, address for Dr. L. S. Dake is Susquehanna University, Selinsgrove, PA 17870-1001

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