

## Organic Electronic Materials Topical Conference Room 327 - Session OE+EM-MoM

### Organic Thin Film Devices I: Light Emitters

**Moderator:** A. Kahn, Princeton University

8:20am **OE+EM-MoM1 Polymers for Optoelectronics**, *N. Peyghambarian*, University of Arizona **INVITED**

Tailoring of organic molecules and polymers has enabled the recent development of multifunctional materials such as photorefractive polymers and organic electroluminescent materials. This talk will review: (i) the development of thermally stable photorefractive polymers with infrared and their application to imaging through scattering media using holographic time-gating techniques; (ii) the fabrication of photorefractive polymer-dispersed liquid crystals; (iii) the demonstration of ultra-bright electroluminescent devices using new Al-based cathodes; (iv) the fabrication of micro-pixel arrays of organic light-emitting devices for displays; (v) the demonstration of optically pumped organic laser structures based on conjugated polymers.

9:00am **OE+EM-MoM3 High Efficiency Three Color Stacked Organic Light Emitting Devices**, *P.E. Burrows*, *G. Parthasarathy*, *G. Gu*, *S.R. Forrest*, Princeton University; *T. Zhou*, Universal Display Corporation **INVITED**

Vacuum deposited organic light emitting devices (OLEDs) based on "small molecule" organic semiconductors have demonstrated adequate efficiency and lifetime for commercial monochrome flat panel display applications. For full color display applications, vertically stacked OLEDs (SOLEDs) offer increased resolution and aperture ratio over conventional, side-by-side patterned pixels. The SOLED consists of separate red, green and blue elements grown in a vertical stack by sequential vacuum deposition. The elements emit light co-axially through semi-transparent electrodes enabling any combination of three colors to be emitted from the entire area of the device. In this paper we present recent improvements in the color, efficiency and operating voltage of SOLEDs. A typical SOLED is a 13 layer device comprised of organic semiconductors, metal oxides and metal thin films. Understanding and controlling microcavity effects in the stacked device is therefore essential to generate a pixel with well separated and adequately saturated colors. We present an analytical model of weak microcavity effects in SOLEDs and apply the results to fabricate a three color pixel with minimal directionality and good color separation. We also discuss a highly transparent, metal-free cathode which defeats the microcavity effects by reducing reflections within the stack.

9:40am **OE+EM-MoM5 Excited-State Electronic Structure of Conjugated Polymers and Oligomers: Characterization of the Luminescence and Two-Photon Absorption Properties**, *J.L. Brédas*, University of Mons-Hainaut, Belgium **INVITED**

Conjugated polymers and oligomers present remarkable semiconducting and nonlinear optical properties. They can for instance be incorporated as the active element in new generations of organics-based field-effect transistors, light-emitting diodes, or photovoltaic cells; much work is also devoted to designing chromophores with enhanced second-order or third-order optical response. In this talk, we discuss the results of correlated quantum-chemical calculations aimed at characterizing the electronic structure of these excited states that are responsible for the luminescence and nonlinear optical properties. We focus on poly(phenylenevinylene) and its derivatives; these polymers are widely exploited in polymer-based light-emitting diodes. We describe the nature of the lowest singlet excited states involved in the absorption and emission processes. We then discuss the major influence of interchain interactions; by considering poly(phenylenevinylene) chains carrying different substituents, we show that some combinations lead to exciton transfer (which is good for luminescence) and others to charge transfer (which is good for photovoltaics). The second (brief) part of the talk deals with the design of novel donor-acceptor phenylenevinylene oligomers which display unprecedented two-photon absorption cross-sections. Some examples of potential applications will be briefly described.

10:20am **OE+EM-MoM7 Gain, Amplified Spontaneous Emission and Lasing in Semiconducting Polymers**, *M.D. McGehee*, *R. Gupta*, *E.K. Miller*, *A.J. Heeger*, University of California, Santa Barbara **INVITED**

Because of the high absorption coefficients, the high density of chromophores, and the Stokes-shifted luminescence, luminescent semiconducting polymers have potential as low threshold laser media.

Optically pumped amplified spontaneous emission has been demonstrated in submicron films of  $\frac{1}{4}$ -conjugated polymers as the active materials. Resonant structures appropriate for photopumped lasers include microcavities, distributed feedback (DFB) substrates, and whispering gallery mode micro-discs and micro-rings. Photopumped stimulated emission and lasing have been observed in a growing number of highly luminescent polymers with emission wavelengths that span the visible spectrum. Progress in the areas of polymer lasers will be reviewed and the possibility of electrically pumped diode lasers (fabricated from semiconducting polymers) will be explored.

11:00am **OE+EM-MoM9 XPS and AFM Investigation of Stability Mechanism of tris-(8-hydroxyquinoline) Aluminium Based Light-Emitting Devices**, *Q.T. Le*, *F.M. Avendano*, *E.W. Forsythe*, *L. Yan*, *Y. Gao*, University of Rochester; *C.W. Tang*, Eastman Kodak Company

Stability is an essential issue in the application of organic light-emitting devices (OLEDs). We have investigated the indium tin oxide (ITO) surface for operated and un-operated OLEDs that consist of ITO/phenyl-diamine (NPB)/tris-(8-hydroxyquinoline) aluminium (Alq@sub 3@)/Mg:Ag with NPB thickness varied from 0 to 300 Å using X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM) techniques. The ITO surface was exposed by removing the organic and metal layers with dichloromethane, an organic solvent in which NPB and Alq@sub 3@ are highly soluble. Electroluminescence (EL) characterization demonstrates that the NPB layer substantially enhanced the stability. XPS analysis shows that for the device made without NPB and after 90 hours of operation, there exists an insoluble organic material on the ITO surface. This organic material is not observed on the ITO of un-operated cells nor of the operated NPB-containing devices. Lateral force AFM also shows a striking difference between the ITO surface of devices with and without NPB after operation. The XPS and AFM results suggest that the organic residue is the degradation product of Alq@sub 3@ that act as quenching sites at the ITO/Alq@sub 3@ interface, which may lead to the early failure of the single layer devices. This work was supported in part by DARPA DAAL 0196K0086 and NSF grant DMR-9612370.

11:20am **OE+EM-MoM10 A Comparison of the Change in the Valence Electronic Structure of p-sexiphenyl Thin Films upon Doping with K and Cs**, *N. Koch*, Technische Universität Graz, Austria; *J.-J. Pireaux*, *L.M. Yu*, Facultés Universitaires Notre-Dame de la Paix, Belgium; *R.L. Johnson*, Universität Hamburg, Germany; *G. Leising*, Technische Universität Graz, Austria

Thin films of the electroactive conjugated material para-sexiphenyl (6P) were doped with potassium and cesium under ultra-high vacuum conditions. The changes in the valence electronic structure of 6P upon increasing dopant exposure were followed with synchrotron ultraviolet photoelectron spectroscopy (UPS), and are compared subsequently. For doping with Cs, new occupied electronic states are only found in the energy gap at 5.8 and 3.6 eV (with respect to the vacuum level); they lie well below the Fermi level, and can be interpreted to negative bipolaron states in 6P. The experimental findings are different when doping with K; for very low doping levels, a finite density of valence states (DOVS) is observed at the position of the Fermi-level E@sub F@. Higher doses of K lead to a shift of E@sub F@ closer to the vacuum level, and out of the DOVS. This observation could be interpreted in terms of a polaron to bipolaron transition of the charged species of 6P with progressive doping. But also a different interpretation will be proposed, in a manner that bipolarons are formed from the beginning of the doping experiment.

## Organic Electronic Materials Topical Conference Room 327 - Session OE+EM-MoA

### Organic Thin Film Devices II: Transistors and Transport

Moderator: P.E. Burrows, Princeton University

2:00pm **OE+EM-MoA1 Organic Thin Film Transistors**, *T.N. Jackson*, The Pennsylvania State University **INVITED**

Over the past several years the performance of organic thin-film transistors (OTFTs) has improved dramatically and it now appears likely that they will find application in displays or other low-cost large-area electronic applications. Small molecule materials such as oligothiophenes and oligoacenes have shown the most progress. When deposited by thermal evaporation onto substrates held at elevated temperature these materials often form thin films with strong molecular ordering; such ordering may be important for obtaining large field-effect mobility and other desirable electrical characteristics. In particular, pentacene thin films deposited at a few Å/s onto substrates held at 50 - 100 °C typically have micron-sized grains, and OTFTs using pentacene as the active layer have demonstrated field-effect mobility as large as 1.5 cm<sup>2</sup>/V-s, current on/off ratio larger than 10<sup>8</sup>, near zero threshold voltage, and subthreshold slope less than 1 V/decade; all these characteristics are similar to those typically observed for a-Si:H thin film transistors (TFTs). Polymeric semiconducting materials are also of interest since they may offer a simple path to solution-processable devices. Thin films of these materials can often be solvent cast which leads to films that are less well-ordered than evaporated small molecule films; however, field-effect mobility near 0.05 cm<sup>2</sup>/V-s has been demonstrated for alkyl-substituted soluble polythiophenes. In addition to all-organic applications, OTFTs show promise for integration with a-Si:H TFTs. The field-effect mobility of p-channel OTFTs and n-channel a-Si:H TFTs are similar and integrated organic/a-Si:H devices can provide a simple complementary circuit technology.

2:40pm **OE+EM-MoA3 Fast Electronic Transport in Organic Molecular Solids**, *N. Karl*, Universität Stuttgart, Germany **INVITED**

The fundamental aspects of electronic charge transport in organic solids will be reviewed and some specific features of this class of materials highlighted. Examples of appropriate measurement techniques - such as time-of-flight (TOF), field effect transistor (FET), and surface acoustoelectric travelling wave (SAW) techniques - as well as of characteristic results - such as magnitude, temperature dependence and anisotropy of intrinsic charge carrier mobilities - will be presented. While ample basic knowledge has been gained from well-defined ultrahigh purity single crystals, where mobilities of several hundred cm<sup>2</sup>/V-s could be reached (see e.g. ref. 1), understanding of the electronic properties of organic thin films is often unsatisfactory. Different kinds and degrees of structural disorder, residual foreign molecules, and a sensitivity to accidental doping by ambient donor or acceptor molecules (such as e.g. O<sub>2</sub>) frequently not only lead to ill-defined irreproducible or nonstationary properties but also to slow transport. Sample preparation under well-controlled conditions and careful sample characterization by sensitive methods of structural and trace impurity chemical analysis are the prime prerequisite not only for further progress in fundamental research, but also for the development of innovative applications. Needless to say that proper selection of material parameters, such as sufficient stability and specific molecular architecture-based functions, is necessary for designing promising molecular-electronic systems, but the complementary aspect of efficient charge carrier transport, which is a superordinated consideration in most applications, may necessitate optimization compromises. @FootnoteText@ @footnote 1@ "Organic Semiconductors" in: Landolt-Börnstein (New Series) Group III, Vol.17i, pp 106-218 (Springer-Verlag, Berlin, New York 1985).

3:20pm **OE+EM-MoA5 Soluble and Processable Oligothiophenes and Analogues as Semiconductors for Thin Film Transistors**, *W. Li, H.E. Katz, A.J. Lovinger, K.R. Amundson*, Bell Laboratories, Lucent Technologies

There has been rapid progress in the synthesis and fabrication of organic semiconductors for field effect transistors (FETs) useful for plastic-based electronics. Conjugated oligomers, such as oligothiophenes and their derivatives, have been shown to be effective semiconducting layers for FETs. We and others have utilized these compounds primarily as vapor-deposited solid films. Recently, our investigation has been extended to liquid phase fabrication of organic FETs. We have synthesized a series of

soluble and processable oligothiophenes and related compounds. Thin film FETs cast from solutions of these compounds showed both high field-effect mobilities (ca. 0.03 cm<sup>2</sup>/V-s) and relatively high on/off current ratios (>10<sup>3</sup>). We find that the film continuity and field-effect mobility are strongly dependent on solvents and dielectric substrates used as well as other casting conditions. Detailed synthetic routes and transistor characteristics, as well as approaches to devices with higher on/off ratios will be presented.

3:40pm **OE+EM-MoA6 Field Effect Conductance of 1-6 Monolayer Thick Crystals of Organic Semiconductors**, *E.L. Grannstrom, T.W. Kelley, C.D. Frisbie*, University of Minnesota

We describe two types of field effect measurements on organic semiconductor single crystals that are as thin as a single molecular layer. In these studies, crystals of the semiconductors pentacene or sexithiophene are grown by vacuum sublimation onto SiO<sub>2</sub>, ranging in thickness from 1-6 monolayers with lengths and widths on the order of a micron. In one experiment, individual crystals are contacted with source and drain electrodes fabricated by electron-beam lithography; heavily doped Si underneath the SiO<sub>2</sub> serves as a gate electrode. Field effect conductance and carrier mobility are measured as a function of temperature (30-300 K) and the number of discrete molecular layers in the crystals. We find that measurements on these thin crystals are extremely sensitive to carrier trapping and offer a potential approach to dynamic recording of the effects of individual trapping events on source-drain current. A second experiment uses a conducting atomic force microscopy (AFM) probe as a positionable source or drain contact to crystals contacted by a fixed electrode at the other end. @footnote 1@ This configuration allows variation of the source-drain separation and estimation of the organic-metal contact resistance. Resistances associated with defects, e.g., a single grain boundary between adjacent crystals may also be measured. In general, the conjunction of AFM imaging methodology with transport measurements facilitates correlation of transport properties with specific, well-defined organic semiconductor structures. @FootnoteText@ @footnote 1@Loiacono, M. J.; Grannstrom, E. L.; Frisbie, C. D. J. Phys. Chem. B 1998, 102, 1679.

4:00pm **OE+EM-MoA7 Charge Injection and Transport in Organic Films**, *D.K. Murti*, Xerox Research Centre of Canada, CANADA

Charge injection and transport is important in many diverse organic electronic devices. For example, electroluminescent devices for display and organic photoreceptors for digital printers depend on injection and transport. In this presentation, the primary focus will be on the organic photoreceptor. Organic photoreceptors consist of a metal film with layers of organic photoconductor and molecularly doped polymers. Charge injection and transport at metal-phthalocyanine interfaces and phthalocyanine-molecularly doped polymer interfaces will be discussed in this presentation. In the photoinduced discharge technique, the surface is initially corona-charged and then followed by discharge of the surface potential with photogenerated carriers that are injected from phthalocyanine and transported in the tetraphenylbenzidine (TPD) doped polycarbonate film. Photoinduced discharge measurements indicate that photogenerated holes can be injected from phthalocyanine into TPD without charge trapping. Hole mobility and the electric field dependence were measured with the time-of-flight technique. In this technique, the drift of a sheet of holes injected from the phthalocyanine film is time-resolved; the transit time is determined in order to calculate the hole mobility at an applied electric field. Hole mobility showed dependence on the electric field with a mobility of about 1x10<sup>-5</sup> cm<sup>2</sup>/V-s at an electric field of 1x10<sup>4</sup> V/cm. Kelvin probe was used to determine the contact potential difference and changes in the work function of phthalocyanine and TPD. The relative work functions of phthalocyanine and TPD are 5.2 eV and 4.7 eV respectively based on Kelvin probe measurements. This indicates no barrier for hole injection as observed by photodischarge techniques.

4:20pm **OE+EM-MoA8 Localized Growth and Electrical Characterization of Polypyrrole on Temperature Programmed Microhotplates**, *C. Kendrick, R.E. Cavicchi, S. Semancik*, National Institute of Standards and Technology

Arrays of microhotplates fabricated at CMOS foundries have been post-processed to realize suspended, heatable structures that have previously allowed localized deposition of SnO<sub>2</sub> by thermally activated CVD. @footnote 1@ This work presents an electrochemical, self-lithographic technique for the growth of polypyrrole on the micromachined platforms and a study of the effect of rapid heating/cooling cycles on film conductivity during gas exposure. Electropolymerization was performed in a sealed flow cell containing Ag-pseudoreference and Pt-counter

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electrodes mounted directly on the chip package and filled with a solution of acetonitrile, 0.1M LiClO<sub>4</sub>, and 50mM pyrrole. Optical microscopy indicates that polypyrrole growth begins on the Au-plated microhotplate contacts and expands laterally, forming a continuous film. The effects of NO<sub>x</sub>, NH<sub>3</sub>, CO, H<sub>2</sub>, and methanol vapors on film resistance have been measured for different film dopings and temperature schedules. The highest sensitivities are found for the strongly oxidizing and reducing gases NO<sub>x</sub> and NH<sub>3</sub>, respectively, where resistance changes have been shown to be caused by changes in carrier concentration brought about by a weak charge transfer interaction between adsorbates and the film. We show that resistance changes ( $\Delta R/R_0$ ) due to 100ppm NO<sub>x</sub> exposure can be increased from ~15% at 25°C to ~30% when periodically pulsing the sensor to 150°C. A similar increase in sensitivity is observed for periodic heating during exposure to NH<sub>3</sub>. Information on analyte adsorption rates and dynamics can also be extracted from the transient resistance characteristics observed between temperature pulses.

@FootnoteText@  
@footnote 1@S. Semancik, R. E. Cavicchi, K. G. Kreider, J. S. Suehle, and P. Chaparala, Sensors and Actuators B 34, 209 (1996).

# Monday Evening Poster Sessions, November 2, 1998

## Organic Electronic Materials Topical Conference Room Hall A - Session OE-MoP

### Organic Electronic Materials Poster Session

#### OE-MoP1 Photoelectron Spectroscopic Studies of Interfaces Between Metals and CBP, I.G. Hill, A. Kahn, Princeton University

A mixture of Mg and Ag is traditionally used as a low work function electron injecting contact in small molecule organic light emitting devices (OLEDs). Thin cathode interface layers of aromatic diamines, such as 4,4'-N,N'-dicarbazolyl-biphenyl (CBP), have recently been shown to increase the electron injection efficiency of Ag cathodes. @footnote 1@ The resulting devices are more stable than traditional structures utilizing reactive MgAg cathodes, and have comparable efficiencies. The role of the aromatic diamine interface layer is unclear. We have investigated the interfaces between CBP and Mg, Ag and Au using ultraviolet photoemission spectroscopy. Each interface was studied by depositing the organic on the metal, and by depositing the metal on the organic. The two methods produced inequivalent interfaces, except in the case of Au/CBP. We have measured the Fermi level/HOMO offset, and estimated the electron injecting barriers at each of these interfaces. The electron injection barrier was 0.5 eV for Mg, 0.6 eV for Ag and 1.2 eV for Au. This variation with the metal work function is quite strong, when compared to PTCDA and Alq@sub 3@. @footnote 2@ The discontinuity of the vacuum level at the interface, caused by the formation of an interface dipole layer, was also measured. The barriers to electron injection from Mg and Ag are comparable in magnitude, and surprisingly large, considering the performance of devices using these contacts. The evolution of the UPS spectral shape with overlayer thickness indicates a rough morphology in the cases of Ag and Mg on CBP. This qualitatively supports the suggestion that a rough interface may lower the barrier to electron injection and improve contact efficiencies. @footnote 3@ @FootnoteText@ @footnote 1@H. Kanai, S. Ichinosawa and Y. Sato, *Synthetic Metals*, 91, (1997) 195. @footnote 2@I. G. Hill, A. Rajagopal, A. Kahn and Y. Hu, Submitted to *Appl. Phys. Lett.* @footnote 3@Y. Yang, E. Westerweele, E. Zhang, P. Smith and A. J. Heeger, *J. Appl. Phys.*, 77, (1995) 694.

#### OE-MoP2 Ultraviolet and X-ray Photoemission Spectroscopy Characterization of Base and Acid Treated Indium Tin Oxide for Organic Device Applications, F.A. Nüesch, E.W. Forsythe, Y. Gao, University of Rochester

Because of its transparency and high conductivity, indium tin oxide (ITO) electrodes are ideal for optoelectronic device applications. Its ability to inject charges into organic solids, however, depends strongly on the interface properties. The effective ITO workfunction can be modified by a surface treatment such as plasma cleaning and chemical treatments. Here, we report the ultraviolet and X-ray photoemission spectroscopy (UPS, XPS) of chemically modified ITO using acids and bases. The UPS results confirm the presence of a dipole layer at the base treated ITO surface, with a vacuum level decrease of more than 1 eV. Current-voltage characteristics of tris-(8-hydroxyquinoline) aluminum (Alq) films sandwiched between the treated oxide electrode and a metallic counter electrode are in agreement with the workfunction shifts obtained by the UPS measurements. From XPS results, we will report the surface composition of the ITO films. In addition to base treatments, we will report UPS and XPS results for acid treated ITO and correlate these results with device transport measurements. The construction of thin dipole layers on the ITO substrate is a promising technique to modify the effective work function of ITO and improve the overall organic LED performance.

#### OE-MoP3 Investigation of the Growth Mode of Phenylamine (NPB) on Indium Tin Oxide, F.M. Avendano, E.W. Forsythe, Y. Gao, University of Rochester; C.W. Tang, Eastman Kodak Company

Since the first report on Organic Light Emitting Devices (OLED)@footnote 1@ there has been much interest for their potential applications as flat panel displays. In these devices charge carriers are injected into the organic layers across the interfaces and the electrode/organic interface characteristics have a strong effect on the device efficiency. Among these characteristics, the morphology of the anode(Indium Tin Oxide) strongly affects the device stability@footnote 2@ as revealed by the presence of microshorts in I-V curves. We study the growth mode of N,N-bis-(1-naphthyl)-N,N-diphenyl-1,1-biphenyl-4,4-diamine (NPB) on Indium Tin Oxide (ITO)/Glass substrates using Atomic Force Microscopy (AFM) and Lateral Force Microscopy (LFM). The addition of LFM to AFM allows us to

clearly distinguish the features due to NPB or ITO. The study was performed as a function of the ITO morphology and NPB thickness. In order to modify the ITO surface morphology a series of processing steps were applied reducing the roughness more than three times as compared to the as received ITO. Next, NPB was deposited with thickness of 5, 15, 30 and 150Å onto the flat and as received ITO. At 5Å of NPB on the flat ITO, AFM/LFM pictures reveal the formation of NPB islands. These islands start to coalesce at a thickness of 15Å. At 30Å of NPB on flat ITO the film exhibits some pinholes which are no longer present at 150Å of NPB on flat ITO. The NPB films grown onto as received ITO show ITO features at the thickness of 5, 15, and 30 Å of NPB and the roughness of the NPB film is an order of magnitude bigger as compared to the NPB grown onto flat ITO. These ITO features present in the NPB film grown onto as received ITO may have detrimental effects on device performance as a consequence of microshorts. @FootnoteText@ @footnote 1@C. W. Tang and S. A. Van Slyke, *Appl. Phys. Lett.* 51, 913 (1987) @footnote 2@F. M. Avendano, E. W. Forsythe and Yongli Gao. The American Physical Society, March 1998.

#### OE-MoP4 Second-Harmonic-Generation Spectroscopy and Hyper-Rayleigh Scattering in Langmuir Films of C60 and its Derivatives, E.D. Mishina, T.V. Misuryaev, A.A. Nikulin, Moscow State University, Russia; V.R. Novak, Institute of Physical Problems, Russia; Th. Rasing, University of Nijmegen, The Netherlands; O.A. Aktsipetrov, Moscow State University, Russia

We report here the results of experimental studies by second-harmonic-generation (SHG) spectroscopy and hyper-Rayleigh scattering (HRS) of thin Langmuir films of C60 and C60-derivatives: C60-tetracyanoethylene oxide derivative (C60[CN]) and C60-indopane derivative (C60[ind]). Langmuir technique allows to fabricate thin films with controlled thickness with monolayer resolution and ordering the molecules within the layer, while the SHG probe provides a reliable diagnostic tool for such films. For the SHG measurements the output of a Ti:Sapphire laser in the range of the fundamental wavelength of 710-800 nm is used. SHG spectroscopic studies showed that, depending on the nature of organic group, the modification of C60 molecules can either increase (for C60[CN]) or decrease (for C60[ind]) the SHG intensity in thin fullerene films, while the general character of the spectra remains unchanged. The obtained results can be interpreted as due to the following two mechanisms: nonuniform broadening of resonances due to fluctuations, that is also revealed in absorption spectra; breaking of the inversion symmetry of C60 molecules by the organic "grafts" resulting in appearance of dipole hyperpolarizability and its interference with the quadrupole hyperpolarizability of C60 "cage". Hyper-Rayleigh scattering allowed us to get information about the structural and statistical properties of these systems. In particular, the modification of C60 molecules with the [CN] "graft" does not noticeably change the structure of the Langmuir films: for both C60 and C60[CN] monolayer samples have a disordered island-like structure, whereas the multilayer C60 and C60[CN] samples indicate their more regular structure. The modification of C60 molecules with the [ind]-"graft" significantly increases homogeneity of the monolayer samples. In all films the characteristic spatial scale of in-plane fluctuations of the HRS sources has been estimated.

#### OE-MoP5 Structure and Properties of the System of Nanometer-scale Quantum Wells Fabricated by the Incorporation of Organic Molecules in Sol-gel SiO@sub 2@ Glass, J. Perez-Bueno, Univ. Autonoma de Queretaro, Mexico; L.L. Diaz-Flores, Inst. Tecnológico de Saltillo, Mexico; F.J. Espinoza-Beltran, CINVESTAV-IPN, Mexico; R. Ramirez-Bon, Universidad de Sonora, Mexico; Y.V. Vorobiev, J. Gonzalez-Hernandez, CINVESTAV-IPN, Mexico

Organic molecules of the colorants (like Fast Green, Brilliant Black, Tartrazine, etc.) were encapsulated in SiO@sub 2@ glass derived by the solution-gelatinization process. The doping organic material in a power form was added to the initial solution, and after its solidification and annealing the colored glass was obtained containing the molecules of the colorants within the vitreous matrix. The optical and photoacoustic absorption as well as the photoluminescence excitation and emission spectra reveal the existence of sets of the discrete energy levels in these systems. The levels separation were determined by the structure of the colorant's molecule and the percentage of doping. The quantum mechanical description of the system is given considering the organic molecules as the two-dimensional or circular potential wells, depending on the molecular structure. The finite depth of the wells is taken into account by introduction of the periodic boundary conditions, which essentially influences the calculated energy spectra. The dependence of the spectra upon the colorant concentration is explained on the basis of the perturbation theory and, in itself, confirms the importance of the account of the finite depth of the potential wells. The theory was a reasonable

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agreement with the experiment. The results obtained demonstrate that the sol-gel technology gives a simple and cheap method of fabrication of a system of the nanometer-scale potential wells with a set of the energy levels which could be regulated by the structure of the doping molecules and their concentration.

**OE-MoP6 Structures and Growth of Monolayers of 4-methyl-4'-mercaptobiphenyl on Au(111): The Role of the Molecular Backbone,** *T.Y.B. Leung*, Princeton University; *P. Eisenberger*, Columbia Earth Institute; *F. Schreiber*, Max-Planck-Institut für Metallforschung, Germany; *P. Schwartz*, Princeton University; *A. Ulman*, Polytechnic University; *G. Scoles*, Princeton University

We present the results of a comprehensive diffraction study of monolayers of 4-methyl-4'-mercaptobiphenyl assembled on Au(111) [abbreviated as mbp]. Two phases of different density are observed. The diffraction patterns suggest that a low-density phase can be comprised of molecules assembling in rows with their molecular axes parallel to the surface. A second, high-density phase is thought to be composed of a hexagonal arrangement of molecules, which are aligned along the surface normal. We denote the low-density phase as the "striped" phase and the high-density phase as the "hexagonal" phase. Although the striped phase and the hexagonal phase are also observed in monolayers of n-alkanethiol on Au(111) [abbreviated Cn], interesting differences have been found. Apart from the structural differences, annealing experiments show that both phases of mbp are more thermally stable than the phases of Cn. In addition, the growth behaviour of mbp is investigated and different growth protocols have been attempted. Unlike the case of Cn where the hexagonal phase can be grown reliably and reproducibly, the hexagonal phase of mbp has only been observed a few times. We will address the role of the molecular backbone in the self-assembly process of thiol on gold, based on the disparities in the structures, the thermal behaviour, and the growth behaviour between mbp and Cn.

## 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 Naphthyl-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 naphthyl-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@sup -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.

# Tuesday Morning, November 3, 1998

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, ellipsometry, 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 oligomer 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. Mäkinen, S. Xu, S. Diol, A.R. Melnyk, D.A. Mantell, M.G. Mason, A.A. Muentner, 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 crystallinity 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

## Organic Electronic Materials Topical Conference Room 327 - Session OE+BI+EM-TuA

### Organic Thin Film Growth

**Moderator:** N. Karl, Universität Stuttgart, Germany

**2:00pm OE+BI+EM-TuA1 Structural Characterization of Organic Overlayers Physisorbed on the Surface of Self-Assembled Monolayers (SAMs) of Alkanethiols on Au(111), P. Schwartz, D.J. Lavrich, M.C. Gerstenberg, G. Scoles, Princeton University**

**INVITED**

We have been able to grow well-ordered crystalline monolayers of alkanethiols, and multilayers of dodecane on the surface of alkanethiol SAMs by exposing the surface of the c(4x2) phase of the SAM to the appropriate amount of flux at carefully controlled temperatures. Low energy atomic diffraction shows that all but one of the overlayers proved to be considerably more ordered than the underlying c(4x2) surface as judged by the specular and diffraction peak intensities. While the surfaces of the dodecane overlayers have the same structure whether grown on a C@sub 11@SH or C@sub 10@SH c(4x2), monolayers of C@sub 10@SH on a C@sub 10@SH c(4x2) surface were distinctly different from and of higher quality than monolayers of C@sub 11@SH on a C@sub 11@SH c(4x2) surface. Debye Waller measurements reveal that, besides improving the overall order of the surface, an overlayer has a stiffer surface than the underlying c(4x2) that supports it. Temperature Programmed Desorption experiments have shown that, although the adsorption energy of organic molecules on a gold surface is much greater than that of the bulk heat of vaporization, the adsorption energy of an overlayer on an organic substrate is similar to the bulk value of the overlayer substance as soon as the metal-overlayer distance is greater than 5 Å. To the best of our knowledge, this is the first time that, making use of the great surface specificity of low energy atomic scattering, organic monolayers are structurally characterized after adsorption on an organic substrate of different structure.

**2:40pm OE+BI+EM-TuA3 Influence of Lattice Misfit on Morphology of Vanadyl-Phthalocyanine Epitaxial Thin Films and Their Growth Mechanisms, S. Nakao, H. Hoshi, K. Ishikawa, H. Takezoe, Tokyo Institute of Technology, Japan**

In organic molecular beam epitaxy (MBE) process, the lattice matching condition has been considered not so critical for the epitaxial growth because of the weak interaction between organic molecules and substrates. In fact, however, the morphology of the MBE films depends on the species of substrates. Hence the systematic study for the parameters affecting the MBE growth is required. In this paper, we first demonstrate the influence of lattice misfit on the morphology of vanadyl-phthalocyanine (VOPc) MBE films on alkali-halide (AH) substrates. Substrates with continuously varied lattice constants were prepared by using KCl/KBr mixed crystals, supplying the positive and negative lattice misfit. The domain size of the VOPc MBE film becomes larger as the lattice misfit becomes smaller. This fact indicates that the lattice misfit plays an important role in organic MBE processes and the smooth large domain could be grown under the zero-misfit condition. We also discuss the growth mechanism in the same system. The reflection high energy electron diffraction (RHEED) study showed that the lattice of the VOPc films is commensurate with that of the substrate in spite of large lattice misfit up to 5%, and then rapidly relaxes to the stable lattice constant independent of lattice misfit. More detailed study of the growth process clarified that the process takes two steps; The 2-dimensional (2-D) tetragonal lattice grows at first and the 3-D monoclinic domains nucleate and grow from the edge of the first layer when the first layer reaches a certain height defined by the lattice misfit. This two-step growth process is thought to be typical in MBE growth of VOPc on AH substrates.

**3:00pm OE+BI+EM-TuA4 Preferential Orientation of Copper Phthalocyanine Molecular Columns on Vicinal Si(001)-(2x1)-H, M. Nakamura, JRCAT-ATP, Japan; T. Matsunobe, Toray Research Center, Inc., Japan; H. Tokumoto, JRCAT-NAIR, Japan**

Fabrication of Pc films on silicon substrates has an advantage in terms of having electrical interfaces with silicon devices. Furthermore, it is a great scientific interest to study organic film growth on various atomically controlled surfaces utilizing well established methods to prepare clean silicon surfaces with a chemical passivation by hydrogen. In our previous work, @footnote 1@ we investigated the molecular arrangement of CuPc films on atomically flat Si(001)-(2x1)-H. Atomic force microscopy (AFM) showed that the molecular column laid parallel to the surface, and the

orientational angle between the column and the substrate directions was around 17°. The angle was also supported by molecular mechanics (MM) simulations using simple atom-atom van der Waals potentials. The results suggested that the CuPc crystals were placed so as to make the linear corrugation of the surface parallel to the substrate H rows, although their periods were still incommensurate with each other. In this work, we therefore used vicinal Si(001)-(2x1)-H as substrates which contain atomic steps of approximately 4 nm period to further control the in-plane orientation. A continuous film of which thickness was distributed within 16.5±2.5 molecular layers was grown at 60°C. 90% of the molecular columns in the film were estimated to be aligned to across the step rows by observing a frictional force image. The preferential orientation is considered to be due to a kind of artificial surface lattices which are formed with the striped 'effective contact area' between the rigid Pc crystals and the vicinal surfaces. Detailed discussions and optical property of the films will be presented. @FootnoteText@ @footnote 1@M. Nakamura and H. Tokumoto, Surf. Sci. 398 (1998) 143.

**3:20pm OE+BI+EM-TuA5 Long Range Crystalline Order for Thin Films of an Organic Salt Grown by Low Pressure Organic Vapor Phase Deposition, M. Deutsch, S.R. Forrest, M.C. Gerstenberg, Princeton University; H.F. Gossenberger, V.S. Ban, PD-LD Inc.**

There is a growing interest in new organic materials with large second-order hyperpolarizabilities,  $\beta$ , for use in nonlinear optical (NLO) devices. In particular, small organic-molecule salts can exhibit very large  $\beta$ , due to their non-centrosymmetric crystal structure. The organometallic charge-transfer salt DAST is an ideally suited material for NLO device applications, having a large electro-optic (EO) coefficient and low dielectric constants, which eventuate in a high figure of merit. Thin films of DAST with very long-range structural ordering were grown by organic vapor phase deposition (OVPD). In this technique vapor transported precursors of the stilbazole and methyl-tosylate combine on a substrate in the heated zone of a low pressure, hot wall reactor. This method enables the stoichiometric growth of polar, multiple-component compounds with highly incongruent vapor pressures, which cannot be otherwise deposited by vacuum evaporation. The DAST films were grown on amorphous TiO<sub>2</sub> substrates, which was pre-sputtered on thermally oxidized [111] Si wafers. The films exhibit very long-range structural ordering, limited only by substrate size. The strong azimuthal dependence of the relative second harmonic generation (SHG) efficiencies, together with polarized microscopy studies indicate that the structural ordering extends typically ~2 cm across the substrate surface. Using x-ray diffraction we have identified the films as consisting of the SHG-active crystalline phase of DAST belonging to the monoclinic space group Cc, with a well-defined [001] orientation with respect to the substrate normal. Such very long-range crystalline order is a prerequisite for realizing high-performance, low-loss NLO devices.

**3:40pm OE+BI+EM-TuA6 Control of Self-Assembled Monolayer Film Structure and Properties, P.S. Weiss, L.F. Charles, L.A. Bumm, T.D. Dunbar, D.L. Allara, The Pennsylvania State University**

Scanning tunneling microscopy (STM) has been used to investigate self-assembled film formation of molecules in single and varied compositions of alkanethiols on Au(111). While the average surface composition of these films typically reflects that of the deposition solution, STM is used to determine the position and motion of these molecules on the surface. We also use STM to measure electron transport through these molecules to ascertain the roles of chain length and chemical contact with the substrate. We discuss how spacer molecules such as adamantanethiol (C10H15SH) can be used to isolate other molecules for such studies. Our investigation of this system shows that ordered films can be produced from such molecules for this purpose. Unlike alkanethiolate films, this produces structural domain boundaries and other defects that do not involve significant conformation relaxation. In our studies we focus on the modification of self-assembled surfaces to tailor the films to our needs. Our growing abilities to control the placement of molecules within these films are presented.

**4:00pm OE+BI+EM-TuA7 Growth, Modification, and Control of the Structures of Mixed Composition Organic Monolayers, T.D. Dunbar, The Pennsylvania State University; T.P. Burgin, J.M. Tour, The University of South Carolina; D.L. Allara, L.A. Bumm, The Pennsylvania State University**

Control of the molecular-scale structure of multi-component self-assembled of organic thiols on Au(111) can be achieved by selecting a combination of deposition and processing techniques. These include competitive adsorption (growth) and subsequent exchange (modification). The effects of this processing on the molecular-scale structure have been



# Tuesday Afternoon, November 3, 1998

studied by conventional and AC scanning tunneling microscopy. Lateral epitaxy has been observed where a growing domain of one molecular species is grafted onto an existing crystalline lattice of a different molecular species with no lattice mismatch. In other examples, the limited substrate access afforded by structural defects in the films has been utilized to insert single molecules for further use or study. We also use these mixed composition monolayers to gain insight into the mechanism by which these films can be imaged and the extent to which organic molecules conduct. By analyzing images and local spectra of isolated and aggregated molecules, we can determine the extent to which neighboring molecules contribute to these processes. We believe that none of the structures we obtain are equilibrium structures. We discuss relevant considerations for stabilizing the nanometer-scale structures created.

**4:20pm OE+BI+EM-TuA8 A Grazing Incidence X-ray Diffraction Study of the Organic-Organic Interface for PTCDA Films Grown on Self-assembled Monolayers of Thiols on Gold, M.C. Gerstenberg,** Princeton University; *F. Schreiber*, Max-Planck-Institut für Metallforschung, Germany; *P. Fenter*, Argonne National Laboratory; *T.Y.B. Leung*, *S.R. Forrest*, *G. Scoles*, Princeton University

We present results from a grazing incidence X-ray diffraction study of 3,4,9,10 perylenetetracarboxylic dianhydride (PTCDA) films deposited on self-assembled monolayers (SAMs) of either decanethiols or 1,6 hexanedithiols on Au(111). The aim is to study the effect of changes at the organic-organic interface on the in-plane ordering of PTCDA and the SAM. Changing the number of chemisorbed Sulphur (S) atoms in the layer between the PTCDA and the metallic substrate is of interest in view of the importance of the charge injecting properties of the organic-inorganic interface in organic semiconductor devices. PTCDA is one of the most thoroughly studied van der Waals epitaxial systems. It has previously been shown that under non-equilibrium growth conditions (high incident flux of PTCDA and low substrate temperature) PTCDA layers order parallel to the Au(111) substrate with a well-defined in-plane structure in registry with the underlying substrate. Under the same conditions our first measurements have indicated an unaltered PTCDA in-plane ordering on both thiol SAMs. However, the orientation of the PTCDA in-plane structure changes with respect to the Au surface in both cases. No change in the ordering of the thiols was observed as the PTCDA was deposited. The confined full coverage c(4x2) layer of decanethiols melts at higher temperatures than the unconfined SAM. With melting, the order of the SAM was lost and was not fully recovered upon cooling. However, no significant change was seen in either the out-of-plane or in-plane scattering of PTCDA.

**4:40pm OE+BI+EM-TuA9 The Adsorption of azo Compounds on Si(001), M.D. Ellison,** R.J. Hamers, University of Wisconsin, Madison

Recent investigations have demonstrated that unsaturated organic compounds can bond to the Si(001) surface by interaction of the C=C bond with the Si=Si dimers, forming a 4-member Si@sub 2@C@sub 2@ ring at the interface. We have investigated whether analogous reactions can be used to link azo bonds (N=N) to the Si(001) surface using XPS, FTIR, STM, and ab initio calculations. The experimental evidence indicates that the unsaturated N=N bond reacts with a Si=Si dimer in an analogous fashion to a [2+2] cycloaddition reaction, forming a 4-member Si@sub 2@N@sub 2@ ring. Although the thermal [2+2] reaction is forbidden by symmetry considerations, this and other studies have shown the reaction of unsaturated bonds with the Si(001) surface to be quite facile. The facility and selectivity of this reaction reveals the potential of azo compounds to be used in creating ordered organic layers on a Si(001) surface.

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 Heeger, A.J.: OE+EM-MoM7, 1  
 Hill, I.G.: OE+AS+EM-TuM3, 6; OE+AS+EM-TuM5, 6; OE-MoP1, 4  
 Hoshi, H.: OE+BI+EM-TuA3, 8

### — I —

Ishii, H.: OE+AS+EM-TuM1, 6  
 Ishikawa, K.: OE+BI+EM-TuA3, 8  
 Ito, E.: OE+AS+EM-TuM1, 6

### — J —

Jackson, T.N.: OE+EM-MoA1, 2  
 Johnson, R.L.: OE+EM-MoM10, 1

### — K —

Kahn, A.: OE+AS+EM-TuM3, 6; OE+AS+EM-TuM5, 6; OE-MoP1, 4  
 Karl, N.: OE+EM-MoA3, 2  
 Katz, H.E.: OE+EM-MoA5, 2  
 Kelley, T.W.: OE+EM-MoA6, 2  
 Kendrick, C.: OE+EM-MoA8, 2  
 King, D.E.: OE+AS+EM-TuM11, 7  
 Koch, N.: OE+EM-MoM10, 1  
 Kosterin, A.: OE+AS+EM-TuM9, 7

### — L —

Lavrich, D.J.: OE+BI+EM-TuA1, 8  
 Le, Q.T.: OE+EM-MoM9, 1  
 Lee, K.: OE+AS+EM-TuM8, 7  
 Lee, P.A.: OE+AS+EM-TuM4, 6  
 Leising, G.: OE+EM-MoM10, 1  
 Leung, T.Y.B.: OE+BI+EM-TuA8, 9; OE-MoP6, 5  
 Li, W.: OE+EM-MoA5, 2  
 Lovinger, A.J.: OE+EM-MoA5, 2

### — M —

Makinen, A.J.: OE+AS+EM-TuM10, 7  
 Mantell, D.A.: OE+AS+EM-TuM10, 7  
 Mason, M.G.: OE+AS+EM-TuM10, 7  
 Matsunobe, T.: OE+BI+EM-TuA4, 8  
 McGehee, M.D.: OE+EM-MoM7, 1  
 Melnyk, A.R.: OE+AS+EM-TuM10, 7  
 Miller, E.K.: OE+EM-MoM7, 1  
 Mishina, E.D.: OE-MoP4, 4  
 Misuryaev, T.V.: OE-MoP4, 4  
 Muentzer, A.A.: OE+AS+EM-TuM10, 7  
 Murti, D.K.: OE+EM-MoA7, 2

### — N —

Nakamura, M.: OE+BI+EM-TuA4, 8  
 Nakao, S.: OE+BI+EM-TuA3, 8  
 Nebesny, K.W.: OE+AS+EM-TuM4, 6  
 Nelson, M.W.: OE+AS+EM-TuM4, 6  
 Nikulin, A.A.: OE-MoP4, 4  
 Novak, V.R.: OE-MoP4, 4

Nüesch, F.A.: OE-MoP2, 4

### — O —

Oji, H.: OE+AS+EM-TuM1, 6  
 Ouchi, Y.: OE+AS+EM-TuM1, 6

### — P —

Parkinson, B.A.: OE+AS+EM-TuM4, 6  
 Parthasarathy, G.: OE+EM-MoM3, 1  
 Perez-Bueno, J.: OE-MoP5, 4  
 Peyghambarian, N.: OE+EM-MoM1, 1  
 Pireaux, J.-J.: OE+EM-MoM10, 1  
 Plank, R.V.: OE+AS+EM-TuM8, 7

### — R —

Rajagopal, A.: OE+AS+EM-TuM5, 6  
 Ramirez-Bon, R.: OE-MoP5, 4  
 Rasing, Th.: OE-MoP4, 4

### — S —

Schlaf, R.: OE+AS+EM-TuM4, 6  
 Schreiber, F.: OE+BI+EM-TuA8, 9; OE-MoP6, 5  
 Schroeder, M.J.: OE+AS+EM-TuM7, 7  
 Schroeder, P.G.: OE+AS+EM-TuM4, 6  
 Schwartz, P.: OE+BI+EM-TuA1, 8; OE-MoP6, 5

Scoles, G.: OE+BI+EM-TuA1, 8; OE+BI+EM-TuA8, 9; OE-MoP6, 5

Seki, K.: OE+AS+EM-TuM1, 6  
 Semancik, S.: OE+EM-MoA8, 2  
 Stadniychuk, H.: OE+AS+EM-TuM9, 7  
 Sugiyama, K.: OE+AS+EM-TuM1, 6

### — T —

Takezoe, H.: OE+BI+EM-TuA3, 8  
 Tang, C.W.: OE+AS+EM-TuM6, 6; OE+EM-MoM9, 1; OE-MoP3, 4  
 Tokumoto, H.: OE+BI+EM-TuA4, 8  
 Tour, J.M.: OE+BI+EM-TuA7, 8

### — U —

Ulman, A.: OE-MoP6, 5

### — V —

Vohs, J.M.: OE+AS+EM-TuM8, 7  
 Vorobiev, Y.V.: OE-MoP5, 4

### — W —

Wei, Y.: OE+AS+EM-TuM8, 7  
 Weiss, P.S.: OE+BI+EM-TuA6, 8

### — X —

Xu, S.: OE+AS+EM-TuM10, 7

### — Y —

Yan, L.: OE+EM-MoM9, 1  
 Yoshimura, D.: OE+AS+EM-TuM1, 6  
 Yu, L.M.: OE+EM-MoM10, 1

### — Z —

Zhou, T.: OE+EM-MoM3, 1