### Thursday Morning, October 5, 2000

### Organic Films and Devices Room 313 - Session OF+EL+SS-ThM

### **Organic Thin Films**

8:20am OF+EL+SS-ThM1 Highly Ordered Layers of Large Conjugated @pi@-systems on Cu(111): A Novel Preparation Method, G. Beernink, K. Weiss, A. Birkner, Ruhr-Universität Bochum, Germany; F. Dötz, K. Müllen, Max-Planck-Institut für Polymerforschung, Germany; C. Wöll, Ruhr-Universität Bochum, Germany

With regard to applications in molecular electronics and the fabrication of nanoelectronic devices, polycyclic aromatic hydrocarbons (PAH), e.g. the graphite segment hexa-peri-hexabenzocoronene (HBC), have recently received considerable attention. For such large PAHs, however, the low solubility in organic or polar solvents and the rather large sublimation temperatures make the application of the commonly used deposition methods, namely adsorption from solution or evaporation in a vacuum system (CVD, OMBE) difficult or even impossible. In this work, we present a direct way to synthesize one particular polycyclic aromatic hydrocarbon, namely hexa-peri-hexabenzocoronene (HBC) by using a surface as a template. A modified precursor molecule, 1,2,3,4,5,6-Hexakis(4dodecyloxyphen-1-yl)benzene (HPB), which is not planar, is evaporated on a Cu(111) surface. Heating of the substrate leads via thermally induced cyclodehydrogenation to the product HBC, which is characterized by XPS, X-ray absorption spectroscopy (NEXAFS) and STM. The NEXAFS-data directly demonstrate the formation of flat, graphite-like segments which interact only weakly with the substrate, whereas the STM data reveal a high of lateral order.

#### 8:40am OF+EL+SS-ThM2 The Effect of Conjugation Length on the Frontier Orbital Position of Oligothiophene Derivatives at Metal-organic Interface, *A.J. Makinen, I.G. Hill,* Naval Research Laboratory; *T. Noda, Y. Shirota,* Osaka University, Japan; *Z.H. Kafafi,* Naval Research Laboratory

We report an ultraviolet photoelectron spectroscopy (UPS) study of a novel family of end-substituted oligothiophene derivatives with a varying conjugation length, BMA-nT (n=1-4), where n indicates the number of thiophene rings. These new oligothiophene derivatives are thermally and morphologically stable, and unlike unsubstituted oligothiophenes, which undergo luminescence quenching due to the polycrystalline nature of their solid films, the thiophene derivatives form amorphous films. The BMA-nT compounds show luminescence from the blue (n=1) to the orange (n=4), and additionally they posses hole-transport properties making them attractive materials for organic light-emitting diodes (OLEDs). The UPS results show that the position of the highest occupied molecular orbital (HOMO) of the end-substituted oligothiophenes at the metal-organic interface is dependent on the number of thiophene rings present, i.e. the effective conjugation length of the molecule. We will discuss this property and its implications in the context of carrier injection in an OLED.

#### 9:00am OF+EL+SS-ThM3 Electronic Properties of @pi@-Conjugated Organic Molecular Semiconductor Interfaces, A. Kahn, Princeton University INVITED

Metal/organic interfaces are central to a number of organic-based devices. Their electronic structure and chemistry control charge injection. Modeling these interfaces requires an accurate knowledge of the injection barriers, i.e. the position of the transport levels with respect to the metal Fermi level, and of the role of interface chemical reactions. This talk reviews our latest results obtained via direct and inverse photoemission and scanning tunneling spectroscopy on metal interfaces with five organic materials (PTCDA, CuPc, Alg@sub 3@, @alpha@-NPD, @alpha@-6T) of interest for light emitting device and TFT applications. We present the first accurate picture of the transport levels in these materials, levels which are generally unknown because of the strongly correlated nature of molecular solids. The transport gap is found to be significantly larger, i.e. by the exciton binding energy, than the optical gap usually used to describe interface and bulk molecular level diagrams. The exciton binding energy ranges from 0.4eV to 1.4 eV in the materials investigated. Furthermore, we present a detailed and systematic investigation of molecular level alignment at interfaces of organic thin films deposited on a series of metals with different work function. These demonstrate that one of three mechanisms is involved in the formation of the dipole barriers generally observed at such interfaces: (1) lowering of the metal work function by the molecules; (2) electron transfer from the metal to the organics; (3) chemical bonding. Knowledge of the transport gap, interface level alignment mechanisms and interface chemistry leads to a more accurate description of these organic interfaces. Work supported by the MRSEC program of the National Science Foundation (DMR-9809483).

## 9:40am OF+EL+SS-ThM5 Effect of Alkyl Substituents on the Adsorption of Thienylenevinylene Oligomers on the Si(100) Surface, *B. Grandidier, J.P. Nys, D. Stievenard, C. Krzeminski, C. Delerue,* IEMN/ISEN, France; *P. Blanchard, J. Roncali,* IMMO Universite d'Angers, France

Conjugated thiophene-based oligomers are subject to intense research activity due among others to their potential use as molecular wires in future molecular electronic devices. As microelectronics technology is based on the use of silicon substrates, there is an increasing need to connect these organic molecules to the existing silicon technology. Due to the low intrinsic solubility of the rigid conjugated chains, the synthesis of the longuest chains required the substitution of alkyl chains to the thiophene ring in order to increase the solubility. Whereas such a substitution has limited effect on the electronic structure of the oligomers, it exerts a strong effect on the interactions of the molecules with their physical and chemical environment. The adsorption of unsubstituted and substituted thienylenevinylene oligomers on the Si(100) surface has been investigated using scanning tunneling microscopy. The mode of substitution of the thiophene ring exerts a strong influence on the adsorption configurations and the images of the oligomer based on 3,4dihexyl thiophene are highly voltage dependent. We discuss the influence of the alkyl chains on the adsorption process and on the appearance of the molecules in the STM images.

10:00am OF+EL+SS-ThM6 Growth of Films of Thiophene Oligomers by Seeded Supersonic Beams to Improve Control on their Quality and Properties, *S. lannotta*, *T. Toccoli*, *A. Boschetti*, CeFSA - Research Center CNR-ITC for the Physics of Aggregates, Italy; *P. Milani*, INFM - Universit@aa a@ di Milano, Italy; *S. Ronchin*, INFM - Universit@aa a@ di Trento, Italy; *A. Podest@aa a@*, INFM - Universit@aa a@ Bicocca, Italy

The growing interest in pi-conjugated organic molecular materials and polymers, driven by wide potential technological impact in electronics and photonics, still faces severe limitations. Applications would be much more favored by improving control on morphology and structure in the solid state. Standard growth methods are based on the self-assembling of the molecules resulting more or less affected by the interaction with the substrate. Very often the resulting films show an inadequate ordering. These problems become severe as the thickness increases over a few monolayers. Fully considering the major role played by the initial state of the molecules at early stages of growth, we approached the problem combining a supersonic free jets that permit to control kinetic energy, momentum and flux with a UHV deposition apparatus. We perform the deposition and simultaneously control the initial state of the seeded organic molecules by varying the parameters of the supersonic expansion (dilution, temperature of the source, form and diameter of nozzle, etc) [P. Milani and S. Iannotta, Synthesis of Nanophase Materials by Cluster Beam Deposition, Springer, Berlin (1999)]. We have prepared a series of films of alpha guaterthiophene that are then characterized by optical measurement, TM-AFM and X-ray diffraction. We report an overall strong evidence of an unprecedented control on morphology, structure and optical response that correlate well to the beam's parameters. PL spectra at low temperature show the vibronic molecular structure very well resolved depending on the initial state of the oligomer in the beam. Films, several hundreds nm thick, show a high degree of ordering with surface morphologies characterized by layered structures of molecular height. Xray diffraction confirms the high degree of ordering induced by the growth from highly supersonic beams. Correlation between morphology, degree of ordering and the optical response of these films will be discussed.

#### 10:20am OF+EL+SS-ThM7 Scanning Tunneling Microscopy/Spectroscopy Investigation of the Organic Molecules PTCDA and HBC on Au(100), *T. Fritz*, *M. Toerker*, *H. Proehl*, *F. Sellam*, *K. Leo*, TU Dresden, Institut fuer Angewandte Photophysik, Germany

Highly ordered organic thin films on gold single crystals have been investigated by Scanning Tunneling Microscopy (STM) and Scanning Tunneling Spectroscopy (STS) at room temperature. The organic dye molecule perylene-tetracarboxylic-dianhydride (PTCDA) has been deposited as submonolayer coverage on Au(100). I-V-spectroscopy at fixed tip-sample-separations has been performed alternately on the PTCDA islands and on uncovered areas of the Au(100) surface. The corresponding normalized derivatives of these I-V-curves have then been compared to inverse photoelectron spectroscopy data known from literature, indicating resonant tunneling via the lowest unoccupied molecular orbital. As a

# Thursday Morning, October 5, 2000

second molecule peri-hexabenzocorone (HBC), also deposited on Au(100), has been investigated. The Au(100) surface has been fully covered by a few monolayers thick, highly ordered HBC film. The normalized derivatives of I-V-curves measured on these films show a pronounced local maximum at a negative voltage of about -1.4 V. By comparison with ultraviolet photoelectron spectroscopy (UPS) measurements of HBC on Au(111) we can show that this peak in the tunneling spectroscopy plot is due to resonant tunneling via the highest occupied molecular orbital of HBC.

# 10:40am OF+EL+SS-ThM8 STM, AFM, & Electrochemical Investigations of Squaraine Thin Films, *M.E. Stawasz*, *N. Takeda, B.A. Parkinson*, Colorado State University

Squaraines are a class of organic photoconductors which have found industrial use in photoreceptors of laser printers and xerographic devices. as well as in ablative optical recording material. They have also been investigated for their nonlinear optical characteristics as well as their ability to sensitize large-bandgap semiconductors in photoelectrochemical solar cells. Central to its various uses and characteristics is the squaraine molecules' ability to form organized aggregates, both in solution and in the solid state. Few studies have been done, however, to relate the molecular structure of squaraines to the structure of the aggregates that spontaneously form in thin films. We report STM and AFM data which unambiguously determines thin film/monolayer aggregate structure for a series of hydroxylated and non-hydroxylated dialkylamino-phenyl squaraines with varying alkyl tail lengths deposited on HOPG. Results show that alkyl tail length significantly affects squaraine aggregate structure while the presence or absence of hydroxyl groups does not. Electrochemical investigations of the redox behavior of squaraine thin films using HOPG as the working electrode were also performed. Remarkable redox behavior was observed suggesting a structural change in the squaraine aggregate state upon oxidation. In addition, the effect of electrolyte anion and film thickness on the redox behavior of squaraines was observed, thus providing additional insight into the charge transfer abilities of the squaraine film in the direction normal to the substrate surface.

11:00am OF+EL+SS-ThM9 Work Function Modification and Surface Chemistry of Indium Tin Oxide with Organosilane Self Assembled Monolayers, J.A. Chaney, Naval Research Laboratory; F. Farzad, Geo-Centers, Inc. and Naval Research Laboratory; C.S. Dulcey, R. Shashidar, P.E. Pehrsson, Naval Research Laboratory

Attachment of organosilane SAM's with monomers having different dipole magnitude and direction may permit control of the work function (@PHI@) of indium tin oxide (ITO) substrates used in OLED's. However, reliable measurement of @DELTA@@PHI@ requires reproducible control of the environmental conditions. In this work, ITO substrates were treated with SAM's having different head and attachment groups and then inserted into an ultra high vacuum (UHV) chamber. The SAM/ITO work function was measured using an in-vacuo Kelvin probe calibrated with a graphite standard. Surface chemistry was probed by high resolution electron energy loss spectroscopy (HREELS), and electronic structure was investigated by energy loss spectroscopy (ELS). The SAM-modified surfaces usually had lower work functions (@PHI@ = ~4.8-5.3 eV), than bare, oxygen-plasma treated ITO (@PHI@ = ~5.3 eV). The SAM monomers had either one or three Si-OCH@sub 2@CH@sub 3@ units for attachment to the ITO surface. Trifunctional SAM's gave higher @PHI@ values than monofunctional SAM's. The HREELS of monofunctional SAM/ITO showed structure which may be attributable to bending modes. These modes were more intense than on the trifunctional counterpart, possibly due to tighter binding of the latter with ITO. Most SAM modified surfaces showed significant deviation in @PHI@ with time and temperature (up to 200°C), suggesting that adsorption of ambient gasses, even in UHV, affects the SAM/ITO system. However, the work function of some SAM's with hydrophobic head groups was apparently unaffected by adsorption. Differences in the band edge transitions of clean ITO vs. SAM/ITO indicate electronic interactions between the SAM and substrate.

11:20am OF+EL+SS-ThM10 Effect of Fluoride Layer Insertion on the Electronic Structures of Al/Organic Interfaces@footnote 1@, Y. Park, Korea Research Institute of Standards and Science, Korea; D. Kim, Hallym University, Korea; S. Cho, O. Kwon, G. Lee, Korea Research Institute of Standards and Science, Korea; F. Cho, Chonnam National University, Korea We have investigated the electronic structures of interfaces between Al and tris-(8-hydroxyquinoline)aluminum (Alq@sub 3@), which is a prototypical organic electroluminescent (EL) material. It has been well known that the insertion of alkali metal fluoride, such as LiF, greatly

enhances the EL performance and the origin of such behaviors have been controversial. We used photoelectron spectroscopy techniques including Xray and UV photoelectron spectroscopy (XPS and UPS) as well as resonant photoemission (RPES) to probe the electronic structure change caused by the insertion of thin layer of various alkaline and alkaline earth metal fluorides between Al and Alq@sub 3@. As previously known, the presence of LiF layer enhanced gap-state formation, but even without the LiF layer, Al deposition significantly alters the electronic structures of Alq@sub 3@. While the insertion of CsF layer showed clear enhancement of the gap states, it was much less obvious for CaF@sub 2@ layer. For both materials, the RPES showed very weak resonant enhancement when excited with photons with the energy near Cs and Ca core level absorption edge. We report similar measurements for various other fluoride materials and discuss their implications. @FootnoteText@ @footnote 1@ This work was supported in part by MOST of Korea through National Research Laboratory Program and Atomic-scale Surface Science Research Center.

11:40am OF+EL+SS-ThM11 Interface of Aluminum and Poly(vinylidene fluoride with Trifluoroethylene) Copolymer, B. Xu, C.N. Borca, S. Ducharme, A.V. Sorokin, P.A. Dowben, University of Nebraska, Lincoln; V.M. Fridkin, S.P. Palto, N. Petukhova, S.G. Yudin, Institute of Crystallography, Russia

The interface between aluminum and crystalline copolymer thin films of vinylidene fluoride (70%) with trifluoroethylene (30%) [PVDF-TrFE] has been studied. The ratio of carbon 1s and aluminum 2p core level photoemission peak intensities changes little with increasing emission angle, even after deposition of 5 Å aluminum on the surface of PVDF-TrFE. This indicates that the distribution of aluminum atoms in the copolymer film is quite uniform in the near surface region and that the interface is not abrupt. The contributions to the C 1s core level shift ~1eV to lower binding energy, while the relative ratio of the intensity of C 1s peaks changes, provides further evidence for changes in screening with aluminum doping within the polymer film. The XRD data also shows the crystalline structure of the copolymer film can be deformed with aluminum doping, if the polymer film is annealed.

### **Author Index**

— B — Beernink, G.: OF+EL+SS-ThM1, 1 Birkner, A.: OF+EL+SS-ThM1, 1 Blanchard, P.: OF+EL+SS-ThM5, 1 Borca, C.N.: OF+EL+SS-ThM11, 2 Boschetti, A.: OF+EL+SS-ThM6, 1 - C -Chaney, J.A.: OF+EL+SS-ThM9, 2 Cho, E.: OF+EL+SS-ThM10, 2 Cho, S.: OF+EL+SS-ThM10, 2 — D — Delerue, C.: OF+EL+SS-ThM5, 1 Dötz, F.: OF+EL+SS-ThM1, 1 Dowben, P.A.: OF+EL+SS-ThM11, 2 Ducharme, S.: OF+EL+SS-ThM11, 2 Dulcey, C.S.: OF+EL+SS-ThM9, 2 — F — Farzad, F.: OF+EL+SS-ThM9, 2 Fridkin, V.M.: OF+EL+SS-ThM11, 2 Fritz, T.: OF+EL+SS-ThM7, 1 — G — Grandidier, B.: OF+EL+SS-ThM5, 1 -H -Hill, I.G.: OF+EL+SS-ThM2, 1

Bold page numbers indicate presenter

-1lannotta, S.: OF+EL+SS-ThM6, 1 <u> - к -</u> Kafafi, Z.H.: OF+EL+SS-ThM2, 1 Kahn, A.: OF+EL+SS-ThM3, 1 Kim, D.: OF+EL+SS-ThM10, 2 Krzeminski, C.: OF+EL+SS-ThM5, 1 Kwon, O.: OF+EL+SS-ThM10, 2 -L-Lee, G.: OF+EL+SS-ThM10, 2 Leo, K.: OF+EL+SS-ThM7, 1 -M-Makinen, A.J.: OF+EL+SS-ThM2, 1 Milani, P.: OF+EL+SS-ThM6, 1 Müllen, K.: OF+EL+SS-ThM1, 1 -N-Noda, T.: OF+EL+SS-ThM2, 1 Nys, J.P.: OF+EL+SS-ThM5, 1 - P --Palto, S.P.: OF+EL+SS-ThM11, 2 Park, Y.: OF+EL+SS-ThM10, 2 Parkinson, B.A.: OF+EL+SS-ThM8, 2 Pehrsson, P.E.: OF+EL+SS-ThM9, 2 Petukhova, N.: OF+EL+SS-ThM11, 2 Podest@aa a@, A.: OF+EL+SS-ThM6, 1 Proehl, H.: OF+EL+SS-ThM7, 1 — R — Roncali, J.: OF+EL+SS-ThM5, 1 Ronchin, S.: OF+EL+SS-ThM6, 1 — S — Sellam, F.: OF+EL+SS-ThM7, 1 Shashidar, R.: OF+EL+SS-ThM9, 2 Shirota, Y.: OF+EL+SS-ThM2, 1 Sorokin, A.V.: OF+EL+SS-ThM11, 2 Stawasz, M.E.: OF+EL+SS-ThM8, 2 Stievenard, D.: OF+EL+SS-ThM5, 1 - T -Takeda, N.: OF+EL+SS-ThM8, 2 Toccoli, T.: OF+EL+SS-ThM6, 1 Toerker, M.: OF+EL+SS-ThM7, 1 -w-Weiss, K.: OF+EL+SS-ThM1, 1 Wöll, C.: OF+EL+SS-ThM1, 1 -x -Xu, B.: OF+EL+SS-ThM11, 2 - Y -Yudin, S.G.: OF+EL+SS-ThM11, 2