Monday Morning, October 25, 1999

Organic Electronic Materials Topical Conference
Room 616/617 - Session OE+EM+FP-MoM

Organic Devices

Moderator: A. Kahn, Princeton University

8:20am **OE+EM+FP-MoM1 Invited Paper***, **C.W. Tang,*** Eastman Kodak Company **INVITED**

NO ABSTRACT SUBMITTED.

9:00am **OE+EM+FP-MoM3 Ultrafast Electron Relaxation in Excited, DCM Doped Alq Films***, **K. Read,*** University of Michigan*; H.S. Karlsson,* Royal Institute of Technology, Sweden*; M.M. Murnane, H.C. Kapteyn,* University of Michigan*; R. Haight,* IBM T.J. Watson Research Center

Electrons photoexcited into the lowest unoccupied molecular orbital (LUMO) of Alq (tris(8-hydroxyquinoline)aluminum) films doped with DCM (4-dicyanomethylene-2-methyl-6-p-dimethylaminostyryl-4H-pyran) have been studied using excite-probe laser photoemission. DCM doping, achieved by co-evaporation with Alq, is an important means of color tuning and enhancing Alq organic LED emission. In addition, DCM doped Alq films have been shown to lase at low photoexcitation thresholds. A detailed understanding of the involved relaxation mechanisms is beneficial to both applications. Using 3.14 eV excite, and 26.7 eV probe, 100 femtosecond laser pulses, we have observed the LUMO decay rate over the first 175 picoseconds, during which time diffusion is insignificant, and all dynamics occur in the absence of electron transport. We have found that the LUMO population fits to a model wherein the majority of the excitation rapidly transfers from the Alq to the DCM and decays via stimulated emission in the DCM, concentration quenching in the DCM, and bimolecular singlet-singlet annihilation in both the Alq and the DCM. Increasing either the DCM doping percentage, or the excitation intensity, is seen to significantly enhance the early, fast processes. The occupied to unoccupied molecular orbital energy gap shrinks as a function of excite-to-probe delay, in accordance with the expected energy relaxation within the excited states. Pure DCM yields a correspondingly smaller energy gap, and rapid LUMO decay. Analyzing the LUMO decay mechanisms allows an improved understanding of the functions served by DCM doping of Alq films.

9:20am **OE+EM+FP-MoM4 Unoccupied Molecular Orbitals in Organic Electroluminescent Materials Studied by Femtosecond Harmonic Photoemission***, **H.S. Karlsson,*** Royal Institute of Technology, Sweden*; K. Read,* University of Michigan*; R. Haight,* IBM T.J. Watson Research Center

We have studied the lowest unoccupied molecular orbital (LUMO) in three organic electroluminescent materials using pump-probe harmonic photoemission based on a femtosecond laser system. The energy gap between the LUMO and the highest occupied molecular orbital (HOMO) in thin films of the blue-light-emitting molecules bis(2-methyl-8-quinolinolato)(para-phenyl-phenolato)aluminum (BAlq) and 1,4-bis(2,2-diphenylvinyl)biphenyl (DPVBi) was established and compared with the green-light-emitting molecule tris(8-hydroxyquinoline)aluminum (Alq). We have also studied the LUMO decay characteristics for the three materials and relate the differences in decay times to the morphology of the evaporated thin films. The effect on the electronic structure of the organics induced by deposition of metallic overlayers will also be shown and discussed.

9:40am **OE+EM+FP-MoM5 Femtosecond Charge Transfer Processes in Organic Molecular Heterostructures***, **A.J. Mäkinen**, S. Schoemann, Y. Gao,* University of Rochester*; M.G. Mason, A.A. Muenter,* Eastman Kodak Company*; A.R. Melnyk,* Xerox Wilson Center for Research & Technology

The charge transfer (CT) process in organic semiconductor heterostructures is an important problem for applications such as photoreceptors and light-emitting devices. The operation of a photoreceptor structure is based on a CT process at the interface of a charge generator layer and a charge transport layer. We have investigated such a structure formed by vacuum grown thin films of two organic molecules, N,N'-diphenethyl-3,4,9,10-perylenetetracarboxylic-diimide (DPEP) and N,N'-diphenyl-N,N'-(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine (TPD), with femtosecond time-resolved photoemission spectroscopy (TR-PES). By measuring the lifetimes of the excited electron states in the mixtures and in the bilayer structures of these molecules, and by recording the UPS spectra of the films we are able to determine the time-scale and the energy regime for the CT process. Our results show that the CT takes place in less than 10 fs between the DPEP and the TPD molecules. We also demonstrate the significance of the film interface in separating the charges upon CT.

10:00am **OE+EM+FP-MoM6 A Comparison of Organic Light-Emitting Devices Using Transient Current-Transient Voltage, Transient Brightness-Transient Voltage, and Transient Brightness-Transient Current Analysis***, **B.J. Norris**, J.F. Wager,* Oregon State University*; J. Liu, Y. Yang,* University of California, Los Angeles

Four types of organic light-emitting devices (OLEDs) are compared using transient current-transient voltage [i(t)-v(t)], transient brightness-transient voltage [b(t)-v(t)], and transient brightness-transient current [b(t)-i(t)] analysis.@footnote 1@@footnote 2@ These analysis methods consist of obtaining the instantaneous brightness [b(t)], current [i(t)], and voltage [v(t)] of the device under test when it is subjected to a bipolar, piecewise-linear applied voltage waveform and then plotting these quantities parametrically. The four types of OLEDs considered are: two types of green OLEDs and a blue OLED, provided by the Eastman-Kodak Co., and a polymer light-emitting device (PLED) fabricated at the UCLA. The OLEDs are dual-layer heterostructures, involving an electron transport layer (ETL) and a hole transport layer (HTL). In contrast, the PLED is a single-layer device. The ETL and HTL capacitances of heterostructure OLEDs can be estimated from b(t)-i(t) curves. The b(t)-v(t) curves allow the conduction current to be estimated. Perhaps the most interesting aspect of this study is the existence of a small bump in the retrace portion of i(t)-v(t) curves of heterostructure OLEDs, which is not observed in single-layer PLEDs. This bump is ascribed to the removal of accumulated holes at the ETL/HTL interface. Hole accumulation at the ETL/HTL interface of OLED heterostructures is manifest as hysteresis in b(t)-v(t) curves. @FootnoteText@ @footnote 1@B. J. Norris, J. P. Bender, and J. F. Wager, "Steady-State Transient Voltage-Transient Current Characterization of OLEDs," SID Digest, in press. @footnote 2@ B. J. Norris, "Characterization of Organic Light-Emitting Devices," MS Thesis, Oregon State University, 1999.

10:20am **OE+EM+FP-MoM7 Organic and Polymer Transistors: Device Physics, Functional Blocks, and Circuits***, **A. Dodabalapur**, B.K. Crone, Y.Y. Lin, J.A. Rogers, S. Martin, R. Sarpeshkar, Z. Bao, W. Li, H.E. Katz, V.R. Raju,* Bell Laboratories, Lucent Technologies **INVITED**

This presentation will begin with a description of the basic physics of typical organic and polymer transistors and the factors which determine and influence the apparent mobility. The transient characteristics organic transistors with sub-microsecond switching speeds will be described. The integration of organic light emitting diodes and transistors is promising for emissive displays. We have developed designs for 'smart' pixels in which an analog circuit consisting of 6-7 transistors drives each LED. The simulated and experimental characteristics of such pixels will be presented. The development of air-stable n-channel organic transistors led to our demonstrating the first organic complementary circuits. The design considerations and characteristics of organic complementary circuits with > 100 transistors will be described. The noise properties of organic transistors and their use in gas sensors will be described.

11:00am **OE+EM+FP-MoM9 Sub-microsecond Switching of n and p-Channel Organic Field Effect Transistors***, **B.K. Crone**, A. Dodabalapur, Z. Bao, W. Li,* Lucent Technologies, Bell Laboratories

Steady state and transient electrical characteristics are presented for p-channel (@alpha@,@omega@-dihexyl quinquethiophene) and n-channel (copper hexadecaflourophthalocyanine) organic field effect transistors. The structure of the transistor is as follows. The gate electrode is a doped silicon wafer with a thermal oxide gate oxide. Gold source and drain contacts are evaporated and photolithographically defined on the oxide, and finally the active organic film is evaporated. The transistors measured had channel length of 4 µm and width 250 µm. Field effect carrier mobilities are determined for both the steady state and transient response using a simple model for the saturated drain current. The steady state mobility and threshold voltage were determined by a linear fit to the square root of the saturated drain current versus gate voltage. Steady state mobilities of 1.5x10@super -2@cm@super 2@/Vs for the p-channel and 3x10@super -2@cm@super 2@/Vs for the n-channel were measured. Transient mobilities were determined using the same model for the saturated drain current and the threshold voltage obtained in the steady state case. Transient mobilities were higher, 3x10@super -2@cm@super 2@/Vs for the p-channel and 1.5x10@super -1@cm@super 2@/Vs for the n-channel devices. The transient responses showed switching times less than 1 µsec for both p and n-channel devices.

Organic Electronic Materials Topical Conference
Room 616/617 - Session OE+EM+FP-MoA

Transport and Nanostructures in Organic Films

Moderator: E. Umbach, Universität Würzburg, Germany

2:00pm **OE+EM+FP-MoA1 Generation and Transport of Charge Carriers in Conjugated Polymers**, *V.I. Arkhipov,* ***H. Baessler****, S. Barth, C. Im, D. Hertel, B. Schweitzer,* Philipps Universität, Germany **INVITED**

Upon photoexcitation of conjugated polymers, such as ladder-type polyphenylene (LPPP) and substituted PPVs, both geminately bound electron-hole pairs and free charge cariers are generated. Evidence for geminate pair production in LPPP comes from electric field assisted delayed fluorescence. Intrinsic free charge carrier generation occurs via on-chain dissociation of vibrationally hot singlet excitations. Motion of positive charge carriers has been studied involving time of flight experiments. From the hole mobility in a sieres of substituted PPV as a function of temperature and electric field it will be concluded that transport is disorder controlled as it is in molecularly doped polymers. An exception of this rule is hole transport in LPPP. The question of intra versus inter chain transport will briefly be addressed. This work was supported by the Deutsche Forschungsgemeinschaft (Sonderforschungsbereich 383) and the Stiftung Volkswagenwerk.

2:40pm **OE+EM+FP-MoA3 Resistance of Individual Molecular Semiconductor Grains Measured by Conducting Probe Atomic Force Microscopy**, ***T.W. Kelley****, C.D. Frisbie,* University of Minnesota

Continued interest in organic electronics has underscored the need for better understanding of transport mechanisms in polycrystalline films of organic semiconductors. We are employing conducting probe atomic force microscopy (CP-AFM) to measure the electrical resistances associated with individual grains and grain boundaries in thin films of @alpha@-sexithiophene (6T). These measurements focus on single 6T grains that are several microns in length and width and 1 - 6 molecular layers (2-14 nm) in thickness. The 6T grains are vacuum deposited onto insulating substrates with lithographically patterned gold electrodes. A Au-coated AFM probe is used to image each grain, including any crystal defects, and to subsequently make point-contact electrical measurements at particular positions on the grain. Current-voltage (I-V) curves are recorded at each position as a function of probe-electrode separation. From these data, we estimate tip-grain contact resistance and conductivity of each grain. In general, we show that CP-AFM is a powerful approach to exploring the effects of microstructure on conductivity in organic semiconductor films.

3:00pm **OE+EM+FP-MoA4 Self-Assembled, Template-Based Nanolithography**, ***S.R. Cohen****, R. Maoz, E. Frydman, J. Sagiv,* Weizmann Institute of Science, Israel

The versatility of our recently developed technique@footnote 1@ for scanning probe microscope (SPM)-based, non-destructive nanolithography on an organized organic monolayer template is demonstrated here. By building on, rather than destroying the organic "resist", consisting of an ordered self assembled monolayer (SAM), it is possible to construct complex 3 dimensional structures which can ultimately lead to device formation. In the first step, applying a bias voltage between a conductive SPM tip and a silver thiolate-based monolayer surface site leads to "activation" of that site by the tip. The second step, deposition of metal (silver) from solution by interaction with an enhancing solution which specifically deposits silver on these sites, leads to in-situ formation of metallic features with sub-micron resolution. These features are chemically bound to the surface-altered monolayer, and comprise a three-dimensional structure of surface-bound silver. The fabrication of conducting nanowires is demonstrated, which could be extended to device or nanocircuit formation. The formation of complex, three-dimensional structures with order determined by the underlying monolayer has been demonstrated. Considering that the surface template exhibits molecular order, this technique has the potential of creating molecular-scale devices, using standard ambient application of SPM, and solution chemistry. @FootnoteText@ @footnote 1@ R. Maoz, S.R. Cohen, and J. Sagiv, Adv. Mater. 11, 55 - 61 (1999).

3:20pm **OE+EM+FP-MoA5 Fabrication of Organic Microstructures Using Soft Lithography**, ***G. Whitesides,*** Harvard University **INVITED**

Chemistry, with stimulus from biology, is beginning to develop a range of new concepts for fabrication of microsystems: these include self-assembly, non-covalent synthesis, microprinting, micromolding, microfluidic patterning, microelectrochemistry, and related techniques designed to make it possible to design complicated structures having electrical, optical, biological or magnetic functionality and to replicate these systems efficiently. These concepts suggest approaches to fabrication that are substantially different from photolithography in their areas of application. The phrase "soft lithography" encompasses one core set of techniques for replication. The techniques included in soft lithography include the formation of self-assembled monolayers, the patterning of these monolayers using microcontact printing, the fabrication of structures inside small channels using microfluidic methods, and the fabrication of small (< 50 nm) polymer structures using transfer molding and replica molding. The adjective "soft" in the phrase "soft lithography" refers to the elastomeric stamps or molds that are important in many of these techniques, and to the properties of organic materials in general. These techniques may use photolithography, but normally primarily during the step that fabricates the master. This talk will outline progress in this area: from homogeneous self-assembled monolayers (SAMs) to transistors, and from molecular self-assembly to the self-assembly of macro-scale objects. Areas of application in which soft lithography is promising include 3-D fabrication and pattern transfer to non-planar surfaces, large-area patterning, low-cost additive fabrication, rapid prototyping (especially of microanalytical and microfluidic systems), fabrication of systems where control of surface chemistry is crucial (e.g., cell biology) and fabrication of MEMS. Key problems are defect densities, distortions in the elastomeric masks/stamps/molds, and fabrication requiring multiple registered levels of fabrication. Reviews: "Soft Lithography" Xia, Y. and Whitesides, G. M., Angew. Chem. Intern. Ed. Engl. 1998, 37, 550-575. "Soft Lithography" Xia, Y. and Whitesides, G. M., Annu. Rev. Mater. Sci. 1998, 28, 153-184.

4:00pm **OE+EM+FP-MoA7 Electron Beam Patterning of Amine-Functionalized Self-Assembled Monolayers**, ***C.K. Harnett****, K.M. Satyalakshmi, M.G. Metzler,* Cornell University*; D.R. Medeiros,* IBM T.J. Watson Research Center*; H.G. Craighead,* Cornell University

Amine-functionalized self-assembled monolayers form a hydrophilic surface that can strongly attach other materials. Examples of materials that have been selectively deposited on patterned amine monolayers include nanoparticles,@footnote 1@ metals, fluorescent molecules, and biological cells.@footnote 2@ Nanopatterning of reactive monolayers is therefore of great practical interest. We have studied electron-beam patterning of 3-aminopropyltriethoxysilane (APTS) and other self-assembled monolayers. Submicron features that are difficult to achieve with UV lithography or microcontact printing are accessible with electron beams. Exposed patterns are examined with lateral-force microscopy (LFM) to determine pattern quality vs. electron dose. At 20 kV, a dose of 300 µC/cm@super 2@ is required to produce continuous 1-micron lines. Results from several electron energies will be presented, with the goal of using these monolayers in a low-energy (1-2 kV) electron-beam lithography system. Exposed areas are analyzed with grazing angle IR spectroscopy to determine possible exposure mechanisms. Subsequent deposition of metals, and use of protection-group chemistry to produce a tone-reversed pattern, will also be discussed. @FootnoteText@ @footnote 1@ T. Vossmeyer, S. Jia, E. Delonno, M. R. Diehl, S.-H. Kim, X. Peng, A. P. Alivisatos, J. R. Heath, Journal of Applied Physics 84, 3664-3670 (1998) @footnote 2@ C. S. Dulcey, J. H. Georger, V. Krauthammer, D. A. Stenger, T. L. Fare, J. M. Calvert, Science 252, 551-554 (1991).

4:20pm **OE+EM+FP-MoA8 Liquid Crystal Imprinting: A New Method for Preparing Uniformly Oriented Thin Films**, ***D.L. Patrick,*** Western Washington University

A new synthetic strategy is presented for preparing nanostructured thin films possessing macroscopically-uniform organization. The method is based on the use of a thermotropic nematic liquid crystal (LC) solvent, which serves a growth medium for deposition of material onto a suitable substrate. Application of a magnetic field results in the formation of an oriented film whose directionality can be controlled externally. The method has been used to prepare several organic monolayer systems in which the orientation of the films' molecular constituents is highly controlled. We show that orientational order at the solid-fluid interface originates during film nucleation, and that the alignment mechanism is based on anisotropic anchoring interactions between surface adsorbates and the LC solvent. Details of the relationship between molecular-scale surface structure and bulk LC ordering were studied by combining scanning tunneling microscopy and polarized optical measurements of uniformly oriented cells. LC fluids exhibit anisotropic anchoring interactions with most crystalline surfaces, indicating that the method may be applicable to the synthesis of films and layered materials using a wide range of molecular and supramolecular building blocks.

4:40pm **OE+EM+FP-MoA9 Electro-Patterning of Conjugated Polymer Films on Conducting Surfaces Using the Precursor Polymer Approach***, R.C. Advincula,* University of Alabama at Birmingham, US*; S. Inaoka,* University of Alabama at Birmingham*; **D. Roitman**,* Hewlett-Packard Laboratories

Recently, a novel method of depositing ultrathin films of conjugated polymers on conducting surfaces has been investigated by the UAB and HP groups. We report the formation and patterning of conjugated polymer films by novel electro-deposition of materials on specific sites of substrates and sequences. We have investigated a range of feature sizes using this method with features below micron size. We have also investigated the formation of unique blend film structures, with emphasis on light emitting materials. Previous attempts in using electrodeposition resulted in 'brittle' and defective (pinholes) film surfaces. Our results indicate that the overall optical, mechanical quality and physical integrity of the films are superior compared to previously reported systems.

Organic Electronic Materials Topical Conference
Room 4C - Session OE-MoP

Poster Session

OE-MoP1 STM/Photo-Assisted EFM Investigation of Morphology-Photoconductivity Relationships in Photogenerating Dye Molecule Thin Films*, **M.E. Stawasz**, N. Takeda, B.A. Parkinson,* Colorado State University

STM and photo-assisted EFM (Electric Force Microscopy) were used to study the relationship between morphology and photoconductivity for a photogenerating dye molecule used commercially in photoreceptor devices. Bis(4-dimethylamino-2-hydroxyphenyl) squaraine was adsorbed from solution onto the basal plane of HOPG. Several polymorphs of adsorbate structure were determined with STM. EFM coupled with a 0.5W 690nm diode laser to illuminate the sample surface was used to spatially resolve areas of differing polymorph in terms of their differing photoconductivity. By identifying regions of differing polymorph, then measuring the relative photoconductivities of each phase a polymorph structure-photoconductivity relationship was identified.

OE-MoP2 Ordered Thin Film and Organic Heterojunction Formation from Luminescent Organic Dyes*, **D.M. Alloway**, N.R. Armstrong,* University of Arizona*; A. Back,* Physical Electronics*; B. Schilling,* VG Micromass

Perylenes, phthalocyanines, certain quinacridones, and related dyes can be vacuum deposited to form ordered monolayers and multilayers. The ordering in these monolayers can be monitored with electron diffraction techniques, and scanning probe microscopies (STM/AFM), but we have recently also found that luminescence spectroscopies can be used to follow the nucleation and growth of the first monolayer, and subsequent multilayer formation. This paper will focus on recent studies of the growth of perylenetetracarboxylicdianhydridebisimide (PTCDI) dyes (both C4 and C5 tails on the bisimide), and substituted quinacridones on both single crystal metal and nonmetal surfaces. Layered growth is seen in all multilayer films, with flat-lying monolayers apparently formed in most cases, and where the structure of the 2nd and subsequent layers is strongly dependent upon the stable bulk structures for these materials. Luminescence spectroscopies indicate the degree of cofacial interaction between these dyes, during monolayer nucleation, and as layer-by-layer growth is achieved. For certain quinacridone dyes the substituent side chains control the approach distance of adjacent molecules, significantly altering the luminescence spectra relative to the parent molecule. In addition, luminescence spectra are useful in characterizing the degree of interaction between two dissimilar dyes, at the organic/organic' interface in a heterojunction assembly, and the degree of luminescence quenching appears to correlated with interface dipole formation as indicated by XPS/UPS studies.

OE-MoP3 Contact Resistance Measurements on Individual Grains of @alpha@-Sexithiophene*, **A.B. Chwang**, C.D. Frisbie,* University of Minnesota

We describe four point probe measurements on individual grains of the molecular semiconductor sexithiophene (6T). These measurements utilize thin 6T grains (2-14 nm in thickness and 1-2 µm in length and width) deposited by vacuum sublimation onto SiO@sub 2@/Si substrates previously patterned with sets of four closely spaced (<400 nm) Au electrodes. The 6T grains grow between the four contacts and their electrical behavior is probed as a function of temperature and gate voltage applied to the substrate. From these data, we extract the Au-6T contact resistance and determine its sensitivity to both gate field and temperature.

OE-MoP4 Electronic Transport Properties of Self-assembled @pi@-conjugated Azomethine Oligomers*, **J.J.W.M. Rosink**, L.J. Geerligs, E. van der Drift,* Delft Institute of Microelectronics and Submicrontechnology, The Netherlands*; A.I. Onipko,* Bogolyubov Institute for Theoretical Physics, Ukraine*; Y. Klymenko,* Space Research Institute, Ukraine*; B.A.C. Rousseeuw,* Delft Institute of Microelectronics and Submicrontechnology, The Netherlands*; S. Radelaar,* Netherlands Institute for Metals Research, The Netherlands

A novel technique for the controlled fabrication of @pi@-conjugated azomethine oligomers bonded to a substrate is presented. The resulting thin films can be used to study the intra-molecular electronic transport properties. Starting from a gold substrate, monolayers of small monomeric organic units are alternately deposited from solution. They order and connect to the previous layer by self-assembly. In each deposition step, chemisorption takes place at the interface between two monolayers through a condensation reaction. Oligomer chain growth has been analyzed by ellipsometry, gaschromatography, mass-spectrometry and x-ray photoelectron spectroscopy (XPS). Molecular mechanics calculations support the observation from ellipsometry and XPS that the azomethine molecules order roughly perpendicular to the gold surface. Based on scanning tunneling spectroscopy (STS) experiments an electronic model for these experiments is proposed. The Green function method is used to establish the relationship between the I-V curves registered in the STS measurements and the @pi@-electronic structure of the oligomers of type M@sub 1@-M@sub 2@-M@sub 1@... probed in the experiments. We have succesfully fitted I-V curves observed in STS of a single monomer film. Modelling of organic multilayers with a particular focus on the role of molecule-to-metal contact is in progress.

OE-MoP5 Perfluorinated Alkane Self-assembled Monolayers Studied with XPS and ISS*, **D.E. King**, A.W. Czanderna,* National Renewable Energy Laboratory*; L.S. Dake,* Susquehanna University

Perfluorinated Alkane Self-assembled Monolayers Studied with XPS and ISS D.E. King, A.W. Czanderna, and L.S. Dake* National Renewable Energy Laboratory, MS-3214 1617 Cole Blvd. Golden CO 80401-3393 The purpose of our past work has been to use self-assembled monolayers (SAMs) as a model organic surface for studying the interactions and penetration of deposited metals on or through specific organic functional groups of the SAMs.@footnote 1@ Our future goal will be to study the interactions, reactions, and stability of deposited metals and metal oxides on SAMs, but in a simulated solar environment, e.g., UV irradiance, T to about 333 K, and in the presence or absence of humidity. Because we expect UV degradation to complicate studies with the n-methylene groups (6<n<21) in alkanethiols in our past work,@footnote 1@ we are reporting our feasibility studies with perfluorinated alkane (PFA) SAMs. We will discuss our approach for the assembly of PFASAMs by using an acid attachment group instead of a thiol and demonstrate the presence of a single monolayer film. We have characterized the PFASAMs by contact angle, XPS, and ISS. The erosion rates in ISS for PFASAMs of different chain-length and with several different end groups will be discussed as they relate to macroscopic film properties such as the contact angle. The stability of the PFASAMs during X-ray exposures will also be compared with results of similar chain-length alkanethiols. @FootnoteText@@footnote 1@D.R. Jung, G.C. Herdt, and A.W. Czanderna, J. Vac. Sci. Technol., A14 (1996) 1779. This work was performed under DOE Contract No. DE-AC36-98GO10337.

OE-MoP6 Resonant Photoemission Study of Poly(p-PhenyleneVinylene)*, **Y. Park**,* Korea Research Institute of Standards and Science, KOREA*; Y. So,* Korea Research Institute of Standards and Science*; G.S. Lee,* Korea Research Institute of Standards and Science, Korea*; E. Cho,* Chonnam National University, Korea

We have employed synchrotron radiation resonant photoemission technique to investigate the electronic structures of one of the prototype organic electroluminescent polymer Poly(p-PhenyleneVinylene) (PPV). When the photon energy was near the binding energy of C 1s core level, at least three strong resonacnes at the approximate binding energies of 5, 6.5, and 9 eV could be observed We discuss the origin of the observed resonances and identify the symmetries of related valence energy levels. The results of resonance photoemission on Ca-induced gap states formed in near-surface region of PPV thin film were also discussed.

OE-MoP7 Investigation of the Influence of LiF-Coatings on the Electronic Structure of Organic Semiconductor/Electrode Interfaces by Photoemission Spectroscopy*, R. Schlaf,* State University of New York at Binghamton*; **P.A. Lee**, K.W. Nebesny, N.R. Armstrong,* University of Arizona

Recently, it was demonstrated that the performance of organic light emitting diodes (OLED) can be considerably improved by inserting thin (~1nm) LiF layers between charge injecting electrodes and organic semiconductor layers. We have determined the electronic structure of typical metal/LiF interfaces with photoemission spectroscopy (PES). In our experiments LiF thin films were grown in multiple steps on sputter-cleaned Al, Pt and ITO substrates. Before growth of the LiF films and after each LiF deposition step the samples were characterized in-situ by combined X-ray and UV photoemission spectroscopy (XPS, UPS) measurements. Our results suggest that the LiF coatings considerably lower the work function of the electrode surfaces, hence resulting in a much reduced electron injection barrier between low work function electrodes and organic electron transport materials. In the case of Al electrodes a surface dipole created by chemisorbed water emitted from the LiF evaporation source is partially responsible for the work function reduction observed after the LiF deposition. Our measurements also demonstrate that even in insulators such as LiF effects similar to band bending in semiconductors may occur.

The results suggest, that a redistribution of charged Schottky or Frenkel type defects in the LiF layers, caused by the thermodynamic equilibration between LiF and the contact metal, is possibly responsible for the observed phenomena.

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

Interfaces and Characterization of Organic Thin Films
Moderator: Y. Gao, University of Rochester

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

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

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

We have investigated the interface formation of Al on tris-(8-hydroxyquinoline) aluminium (Alq@sub 3@) and Al on LiF/Alq@sub 3@ using X-ray and ultraviolet photoemission spectrascopy (XPS and UPS). We observed significant modifications of O1s, N1s and Al2 p core level spectra as Al was directly deposited on the Alq@sub 3@ surface. The Alq@sub 3@ features in the UPS spectra were also quickly destroyed. In contrast, a dramatically different behavior was observed for Al on the LiF/Alq@sub 3@ interface. With o nly 5Å of LiF deposited on the Alq@sub 3@ surface as a buffer layer, the reaction between Al and Alq@sub 3@ is significantly suppressed. A well-defined gap state is formed. The Alq@sub 3@ features in UPS shift to higher binding energies but remain easily recognizable. Both the core level spectra and the gap state suggest that the Alq@sub 3@ anion is formed in the presence of Al and LiF.

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

The effect of the deposition sequence on the electrical behavior of metal-organic interfaces is an important issue in the context of multiple layer organic light emitting devices (OLED). Metals deposited on organics generally lead to more extensive interface chemistry, and have been reported to produce different electrical behavior, than organics deposited on metals. To address this issue, we investigate the interface chemistry, electronic structure and electrical transport in nominally symmetric Mg:Ag/8-hydroxyquinoline aluminum(Alq@sub 3@)/Mg:Ag structures fabricated and tested in ultra-high vacuum and under controlled atmosphere. We perform detailed X-ray photoemission spectroscopy measurements which confirm that the metal-organic chemical reaction and interdiffusion are different at the Mg-on-Alq@sub 3@ interface than at the of Alq@sub 3@-on-Mg interface. We also show, however, that the chemical state of the bottom electrode surface plays a major role in the device electrical behavior. The Mg:Ag/Alq@sub 3@/Mg:Ag structure built in ultra-high vacuum leads to symmetric top and bottom electron injection, whereas controlled oxidation of the bottom metal surface leads to a two-order-of-magnitude lower bottom contact injection. These results fully explain earlier results obtained for devices made under "standard" conditions, i.e. in moderate 10@super -5@ Torr vacuum. A similar study of the Al/Alq@sub 3@/Al structure is under way and will be reported as well at the conference.

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

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

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

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

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

We present independent measurements of metal/organic Schottky energy barriers and their charge injection characteristics in metal/organic/metal structures. The Schottky energy barriers were measured using internal photoemission and built-in potential techniques. The Schottky energy barriers to a poly (p-phenylene vinylene) based polymer (MEH-PPV) and to Alq were measured for a variety of metals with work functions ranging from 2.7 eV (Sm) to 5.6 eV (Pt). For MEH-PPV we find good agreement with the ideal Schottky model. In contrast, for Alq we find that the ideal Schottky picture is not applicable and that electron injecting contacts are pinned about 0.6 eV below the electron conducting states. The charge injection characteristics of these contacts were investigated by measuring the current-voltage characteristics of single carrier structures. The dependence of the current-voltage characteristics on the Schottky energy barrier is quantitatively described by a device model which includes charge injection, transport and space charge effects in the structure. For Schottky barriers less than about 0.3 eV the current in the structure is space charge limited and the contact is ohmic. Finally, we present results using organic self-assembled monolayers to manipulate the metal/organic Schottky energy barrier and to control charge injection into the organic material. The monolayers are used to insert a thin (1 nm) dipole layer between the metal contact and the organic material. Depending upon the orientation of the dipole layer the Schottky energy barrier may be increased or decreased and the corresponding charge injection properties degraded or enhanced.

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

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

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

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

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

We report on the effect of various treatments by base and acid solutions on the work function of indium tin oxide (ITO). Ultraviolet and x-ray photoelectron spectroscopy (UPS and XPS) were used to measured the work function and chemical composition, respe ctively, of the processed ITO surface. The results indicate that the magnitude of the work function shift is highly dependent on the nature of the solution. In contrast, for the same solution, the concentration of the solution appears to have little effe c t on the work function shift. In addition, the interface formation between processed ITO and N,N'-bis-(1-naphthyl)-N,N'-diphenyl-1,1'-biphenyl-4,4'-diamine (NPB) using XPS and UPS is presented. The reactivity of the treated ITO surfaces versus NPB is co mp ared with the case of plasma-treated sample. The low current onset obtained from the single-layer devices based on acid-treated ITO can be attributed to the low energy barrier for hole injection at the ITO/hole-transporting material interface. This work was supported in part by DARPA DAAL 0196K0086, NSF Grant DMR-9612370, and the Swiss National Science Foundation.

Flat Panel Displays Topical Conference
Room 604 - Session FP+OE+EM-TuA
Thin Film Transistor Materials and Devices

Moderator: G.N. Parsons, North Carolina State University

2:00pm **FP+OE+EM-TuA1 Nanoprobing Electrical Transport in Organic Semiconductors*, C.D. Frisbie,*** University of Minnesota **INVITED**

Commercial interest in mechanically flexible plastic electronics is the key motivator behind efforts to fabricate transistors, light-emitting diodes, and lasers from organic thin films. Continued development depends on increasing comprehension of factors affecting charge carrier mobility. In particular, the importance of film microstructure on transport in organic films has been recognized, but is currently not well understood. In this talk, I will describe experiments designed to address microstructural effects on conductivity in polycrystalline organic films. Our approach is to probe transport in individual grains, or even small collections of grains, which we characterize by atomic force microscopy (AFM). Experiments have focussed on crystalline grains of the molecular semiconductor sexithiophene (6T). Isolated grains of 6T are grown by vacuum sublimation onto SiO2/Si substrates. The crystals range from 1-6 molecular layers (2-14 nm) in thickness with diameters on the order of a micron. In one approach, these thin crystals are contacted with source and drain electrodes fabricated by electron-beam lithography; heavily doped Si underneath the SiO2 serves as a gate electrode. The resulting transistor structures are used to probe field effect conductance and carrier mobility as a function of temperature (5-300K) and the number of discrete molecular layers in the crystals. The second experiment uses a conducting AFM probe as a positionable electrical contact to grains contacted by a fixed electrode at the other end. This configuration allows variation of the tip-electrode separation, yielding the single grain resistivity and an 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 both types of experiments, the conjunction of AFM imaging with transport measurements is critical to correlating transport properties with specific microstructures.

2:40pm **FP+OE+EM-TuA3 Photolithographically Defined Pentacene Thin Film Transistors on Flexible Plastic Substrates*, D.J. Gundlach,*** *C.D. Sheraw, H. Klauk, J.A. Nichols, J-R. Huang, T.N. Jackson,* The Pennsylvania State University

We report photolithographically-defined pentacene thin film transistors (TFTs) on flexible plastic substrates with performance similar to hydrogenated amorphous silicon (a-Si:H) devices. Organic TFTs fabricated on flexible plastic substrates are of interest for mechanically rugged, low-cost broad-area electronic applications. Pentacene TFTs with performance similar to a-Si:H TFTs have been reported,@footnote 1@ however, such devices are typically fabricated on oxidized silicon or glass substrates. Since photolithographic processing of organic semiconducting materials is problematic, such devices, including more recent devices on polymeric substrates,@footnote 2@ typically use source and drain contacts deposited through a shadow-mask after the organic active layer deposition. We have fabricated photolithographically-defined pentacene TFTs on polyethylene naphthalate (PEN) and polyimide (PI) films. For ease of processing, the films were mounted to silicon wafers using a pressure sensitive silicone adhesive and pre-shrunk by heating to 150°C for 1 hour in vacuum. A 30 nm thick Ni gate electrode, 160 nm thick SiO@sub 2@ gate dielectric, and 80 nm thick Pd source/drain contacts were deposited by ion-beam sputter deposition. The TFTs were completed by thermally evaporating pentacene onto substrates heated to 60°C. All deposited layers were photolithographically-defined using a two-layer resist lift-off process. Field-effect mobility larger than 0.3 cm@super 2@/V-s was extracted for TFTs on both PI and PEN film, current on/off ratio was greater than 10@super 5@, and subthreshold slope was less than 1.5 V/decade, all obtained using drain-to-source and gate-to-source biases of -30 volts or less. @FootnoteText@ @footnote 1@ Y-Y. Lin, D. J. Gundlach, S. F. Nelson, and T. N. Jackson, IEEE Electron Device Lett., vol. 18, pp. 606-608, 1997. @footnote 2@ C. D. Dimitrakopoulos, S. Purushothaman, J. Kymissis, A. Callegari, and J. M. Shaw, Science, vol. 283, pp. 822-824, 1999.

3:00pm **FP+OE+EM-TuA4 Reduced Process Complexity Organic Thin Film Transistors*, H. Klauk,*** *D.J. Gundlach, M. Bonse, T.N. Jackson,* The Pennsylvania State University

The performance of organic thin film transistors (TFTs) has improved dramatically over the past few years and recently, pentacene TFTs with carrier mobility of 0.6 cm@super 2@/V-s were demonstrated on glass substrates.@footnote 1@ The TFT device structure used in this earlier work required 4 material depositions and 4 lithography steps: one each for the gate, the gate dielectric, the source/drain contacts, and the pentacene active layer. Patterning of the pentacene layer is important to avoid leakage since pentacene TFTs often have large positive threshold voltage. We report here a simplified device structure for depletion-mode pentacene TFTs. Only 3 material depositions and 3 lithography steps are required and the same metal deposition is used for the gate electrode and the source/drain contacts. Gate-to-source and gate-to-drain overlap are not required, since the pentacene layer is normally conducting, thus allowing a drain current to flow at zero gate bias; devices are turned off by applying a positive gate bias. Palladium was used for the gate and source/drain metal, and low-temperature (80°C) ion-beam sputtered SiO@sub 2@ was used as the gate dielectric; both layers were patterned by lift-off. To pattern the pentacene active layer, a double-layer photoresist technique was used to create a reentrant profile over which the pentacene was deposited by evaporation. Upon deposition, the pentacene layer breaks over the resist profile, leaving isolated TFT areas. At a relatively low drain-source voltage of -20 V, devices have carrier mobility as large as 0.3 cm@super 2@/V-s, on/off current ratio near 10@super 5@, subthreshold slope as low as 0.9 V/decade, and threshold voltage between +10 V and +17 V. @FootnoteText@ @footnote 1@ Hagen Klauk, David J. Gundlach, Jonathan A. Nichols, and Thomas N. Jackson, "Pentacene Organic Thin-Film Transistors for Circuit and Display Applications," IEEE Transactions on Electron Devices, vol. 46, no. 6, June 1999.

3:20pm **FP+OE+EM-TuA5 Soft Lithographic Patterning and Low Temperature Film Deposition: Methods to Fabricate Amorphous Silicon Thin Film Transistors at Low Temperature*, H.-C. Jin,*** *J.R. Abelson, M.K. Erhardt, R.G. Nuzzo,* University of Illinois, Urbana

We fabricate amorphous silicon thin film transistors on glass substrates at low temperature (125@super o@C) using "soft" lithographic patterning in place of traditional photolithography. In soft lithography, polymer templates are formed on the film by holding an elastomer block containing the desired pattern in contact with the substrate, flowing an uncured precursor into the micro-channels of the pattern, then curing the polymer. Such templates replace photoresist for all etch and deposition steps, and have been successfully used for the fabrication of multilayer device architectures with micron-scale feature resolution. It appears possible to pattern sub-micron features, as well as large area and curved substrates. In this talk, we show the patterning methodology, preliminary results for TFT devices on planar and curved substrates, and discuss future prospects.

3:40pm **FP+OE+EM-TuA6 Low Damage Etching Utilizing Activated Hydrogen Beam for ITO Transparent Electrode in Flat Panel Display*, T. Miyata,*** *T. Minami, M. Ishii,* Kanazawa Institute of Technology, Japan

Recently, low damage dry etching has become necessary for transparent electrode patterning in flat panel display fabrication. This paper introduces a newly developed low damage and high rate etching technique utilizing an activated hydrogen beam to etch Sn-doped indium oxide (ITO) transparent conducting films. The etching was carried out using an apparatus consisting of an etching chamber and an activating chamber interconnected with a 0.9 mm-diameter orifice; the pressure in the activating chamber was higher than that in the etching chamber. The hydrogen gas introduced into the activating chamber was first activated by applying microwave power and then introduced through the orifice into the etching chamber. The etching was accomplished by the activated hydrogen beam acting on patterned photoresist coated ITO films placed on a sample holder. The etching rate was strongly dependent on conditions such as sample temperature, orifice-sample separation and pressure in the etching chamber. It should be noted that the ITO film was only etched at sample temperatures above 160@super o@C and the etching rate increased as the sample temperature was increased. A maximum etching rate above 50 nm/min was obtained at a sample temperature of 220@super o@C. These results suggest that ITO films are mainly etched by chemical reactions.

4:20pm **FP+OE+EM-TuA8 Excimer Laser Processing for a-Si and poly-Si Thin Film Transistors for Imager Applications*, J.P. Lu,*** *P. Mei, R.T. Fulks, J. Rahn, J. Ho, Y. Wang, J.B. Boyce, R.A. Street,* Xerox Palo Alto Research Center **INVITED**

Pulsed Excimer-Laser Annealing (ELA) has become an important technology to produce high performance Thin Film Transistors (TFTs) for large area electronics. The application of these advanced TFTs in flat pannel displays@footnote 1@ and flat panel imagers for two-dimensional X-ray imaging have attracted much interest. TFTs made from laser crystallized poly-Si thin films with mobility higher than 100 cm@super 2@/Vs can be consistently achieved and are well suited for the integrated driver circuits. Recently, leakage currents as low as 2fA/µm at 5V for these poly-Si TFTs have been achieved and enable one to consider making flat panel imagers using a full poly-Si process. Laser doping@footnote 2@ or dopant activation is another important application of the ELA process. Using a laser doping process, we have fabricated a-Si TFTs with self-aligned poly-Si source/drain contacts. These new devices have reduced source/drain parasitic capacitance and their channel length can be easily scaled down without stringent lithography requirements. Excellent DC performance, such as low leakage current (0.02fA/µm), sharp turn on (0.44V/decade) and high mobility of a-Si TFTs are preserved. In addition, good AC performance of these self-aligned a-Si TFTs has been demonstrated in four phase dynamic shift registers operating at 250kHz. In this talk, these two areas will be reviewed along with a report on the current status in developing poly-Si TFTs and self-aligned a-Si TFTs using ELA process for flat panel imager applications. @FootnoteText@ @footnote 1@ J. G. Blake, M. C. King, J. D. Stevens III, and R. Young, Solid State Technology, p151, May 1997. @footnote 2@ P. Mei, G. B. Anderson, J. B. Boyce, D. K. Fork, and R. Lujan, Thin Film Transistor Technologies III, Electrochemical Soc. Proc., PV 96-23, p51 (1997).

5:00pm **FP+OE+EM-TuA10 Solid-phase Crystallization of Hydrogenated Amorphous Silicon-Germanium Alloy Films*, O.H. Roh,*** *I.H. Yun, J.-K. Lee,* Chonbuk National University, Korea

We have investigated the solid-phase crystallization of hydrogenated amorphous silicon-germanium alloy (a-Si@sub 1-x@Ge@sub x@:H) films by using electron spin resonance (ESR) and x-ray diffraction measurements. The films were deposited on Corning 1737 glass in a plasma-enhanced chemical vapor deposition system using SiH@sub 4@ and GeH@sub 4@ gases. The substrate temperature was 200°C and the r.f. power was 3W. The films were then annealed to be crystallized at 600°C in a N@sub 2@ atmosphere. The total spin density first increased with annealing time due to hydrogen evolution, and then rapidly decreased as the film was crystallized. The Ge dangling bond spin density increased faster with annealing time than the Si dangling bond spin density. However, it was observed that the H evolution from Si-H bond and Ge-H bond was strongly affected by the Ge composition of the films.

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

Organic Thin Film Growth

Moderator: H. Baessler, Philipps Universität, Germany

2:00pm **OE+EM+AS-TuA1 Tailoring of Properties of Organic Thin Films by Interface Control*, E. Umbach,*** *M. Sokolowski, R. Fink,* Universität Würzburg, Germany **INVITED**

The properties of ultrathin organic films in organic/inorganic hybrid systems are largely determined by their interfaces. This is particularly true for the electronic and structural properties which depend on chemical bonding and ordering processes. In favourable cases weak chemisorption on smooth single-crystal surfaces leads to long-range lateral order, and even true epitaxial growth of organic overlayers can be achieved. For such structurally well-defined films significantly improved transport and optical properties can be expected. It will be shown how high-quality organic thin films can be prepared by vapour-deposition on suited substrates and how the observed superstructures depend on the molecular shape and the functional groups, on the substrate material and orientation, and on the preparation parameters. Moreover, based on a few examples it is demonstrated that epitaxial growth with huge domains and even with new, substrate-induced structural parameters can be achieved. In view of their optical properties, for instance, such films show very few defects, considerably improved quantum efficiency, and reduced substrate-induced quenching. The knowledge about the various properties and their interdependences has been achieved by combining a number of surface-sensitive methods for studying the geometric (STM, (SPA)LEED), chemical (XPS, TDS, HREELS), orientational (NEXAFS), and electronic (UPS, NEXAFS) properties with in-situ measurements of the optical and electric properties. As substrates different metal (e.g., Ag, Ni, Cu) and semiconductor surfaces (Si, Ge, ZnSe, HOPG) have been investigated, and the properties of more than 20 different large organic molecules have been compared. On the basis of the present results one can now start to tailor the properties of ultrathin organic films by selecting a proper combination of molecules, substrates and preparation conditions.

2:40pm **OE+EM+AS-TuA3 Ordering in Two Dimensions - Phthalocyanines, Perylenes, and Related Molecular Thin Films*, N.R. Armstrong,*** University of Arizona **INVITED**

Well-ordered two-dimensional thin films can now be routinely produced by either vacuum deposition and/or self-assembly deposition technologies, and rules for epitaxial growth of such materials on a variety of single crystal substrates are becoming well understood. This talk will review recent work on the growth of both phthalocyanine and perylene dye thin films, on both single crystal metal and nonmetal surfaces. Many of the crystalline organic dyes tend to form flat-lying ordered monolayers, with coincident epitaxial relationships with the substrate. Several interesting cases have recently emerged, however, where such flat-lying monolayers are not formed, and/or where neither coincident nor commensurate epitaxial structures are formed, but ordered films result nevertheless. In all events organic heterojunction formation is of interest for these materials, and characterization of such heterojunctions by combinations of XPS/UPS will be discussed. In addtion, we will discuss recent self-assembly approaches to ordered phthalocyanine thin films, by non-vacuum deposition approaches, which produce coherence in thin film structures rivaling the best vacuum deposited materials.

3:20pm **OE+EM+AS-TuA5 Influence of Steps on the Orientation of Monolayer Films of Copper Phthalocyanine (CuPc) on Au(111)*, I. Chizhov,*** *A. Kahn, G. Scoles,* Princeton University

The structure of monolayer films of copper phthalocyanine (CuPc) deposited on Au(111) surface in ultrahigh vacuum is studied via scanning tunneling microscopy (STM) and low-energy electron diffraction (LEED). CuPc molecules adsorb with the molecular planes parallel to the surface and form a highly ordered overlayer with a square unit cell. The structure of the CuPc molecular layer is analyzed via correlation of STM and LEED data. The azimuthal orientation of the monolayer is found to be distinctly different on wide and narrow terraces of the Au(111) substrate. On wide terraces the azimuthal orientation of the monolayer is determined by the underlying substrate with the sides of CuPc square unit cells aligned within a few degrees off the [11(bar)0] and [112(bar)] directions of the Au(111) surface. On the other hand, on narrow terraces and in the vicinity of the Au substrate steps the sides of CuPc unit cells are aligned along the step edges. Thus, CuPc/Au(111) represents a good model system for which a balance between the energy of interaction of a molecule with the metal surface and that of interaction with the step edges can be studied in detail. For CuPc films with coverages below and above 1 monolayer no molecular structure can be reproducibly resolved by the STM.

3:40pm **OE+EM+AS-TuA6 Growth Modes of N,N'-bis-(1-naphthyl)-N,N'-diphenyl1-1,1-biphenyl1-4,4'-Diamine on Standard and Ultra-flat Indium Tin Oxide*, E.W. Forsythe,*** *Q.T. Le, Y. Gao, L.J. Rothberg, M. Abkowitz,* University of Rochester

The ITO substrate morphology influences the growth conditions of N,N'-bis-(1-naphthyl)-N,N'-diphenyl1-1,1-biphenyl1-4,4'-diamine (NPB) for organic light emitting diodes. We have studied the growth modes of NPB on as-received indium tin oxide (ITO) and ult ra-flat ITO using atomic force microscopy (AFM). The ITO surface morphology has been reduced from an average area roughness of 1.8nm to less than 0.2nm with clearly distinguishable atomic terraces corresponding to the ITO lattice spacing. The room temper a ture NPB growth mode is initially islands with complete ITO coverage at 15nm for both ITO surfaces. With a substrate temperature less than 15C above room temperature, the growth modes are laminar with full ITO coverage at 7.5nm. The final NPB film on t h e ultra-flat ITO has an average roughness equivalent to the size of the NPB molecule, more than an order of magnitude less than NPB on standard ITO. Because NPB is trap free, a direct and self-consistent measure of the injection efficiency as a function IT O surface morphology and growth temperature can be determined at a given applied field from the ratio of the measured dark current to the calculated trap free space charge limited current. The trap free space charge limited current is calculated from t h e t ime of flight drift mobility measured in the same specimen at the same applied field.@footnote 1@ The OLED device performance shows an approximately 15% increase in the cd/A efficiency on the ultra-flat ITO as compared to standard ITO. Understanding the role of the ITO surface morphology on OLED device characteristics may contribute to improved large area device performance. This work was supported by DARPA DAAL01-96-K-0086, NSF DMR-9612370, AFOSR 96NL245, and the NSF Center for Photoinduced Charge Transfer. 0. @FootnoteText@ @footnote 1@ M.Abkowitz,J.S.Facci and J.Rehm. J. Appl. Phys. 83, 2670 (1998).

4:00pm **OE+EM+AS-TuA7 Self-Assembled Monolayers on Indium Tin Oxide***, C. Yan, M. Zharnikov,* ***A. Gölzhäuser****, M. Grunze,* Universität Heidelberg, Germany

Self-Assembled Monolayers (SAMs) of functionalized alkanethiols X(CH@sub 2@)@sub n@SH (X=CH@sub 3@, COOH) and carboxylic acid CH@sub 3@(CH@sub 2@)@sub n@COOH were prepared on indium tin oxide (ITO) surfaces and have been characterized by X-ray photoelectron (XPS) and Near Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopies as well as by Atomic Force Microscopy (AFM). Thiols as well as carboxylic acids form homogeneous, ordered films on ITO. NEXAFS data suggest that the films are molecularly oriented with average alkyl chain tilt angles between ~34° for thiolate and ~31° for bifunctional SH(CH@sub 2@)@sub 15@COOH. From coadsorption experiments we find that on ITO the COOH group adsorbs preferentially over the SH group. AFM and LFM images indicate a smoothing of the relatively rough ITO surface by the adsorbed films. These results suggest that ITO surfaces can be passivated with Self-assembled monolayers and that SAMs can be utilized to covalently attach specific chemical functionalities to ITO electrodes.

4:20pm **OE+EM+AS-TuA8 Mechanism of Formation of Self-Assembled n-Octadecylsilane Monolayers on Indium-Tin-Oxide***,* ***K.-W. Lee****, A.M. Raphel, S.L. Buchwalter,* IBM T.J. Watson Research Center*; M.M. Poliks,* IBM Microelectronics

Mechanism of formation of self-assembled n-octadecylsilane monolayers on indium-tin-oxide (ITO) has been studied. n-Octadecyltrimethoxysilane (OTMS) was hydrolyzed to n-octadecylmethoxysilanediol or n-octadecylsilanetriol in isopropanol/water (95/5). The 0.5 % hydrolyzed solution was spin-coated onto ITO substrate and then baked at 85 deg.C for 30 min. The subsequently formed organic layers were analyzed with dynamic contact angles, X-ray photoelectron spectroscopy (XPS) and reflection-absorption infrared spectroscopy (RAIR) and determined to have densely packed SAMs. Its RAIR and XPS spectra indicate that lots of silanol groups are left unreacted at the foot of SAMs and a small amount of unhydrolyzed Si-OCH3 groups may also be present. Silanol groups are expected to interact with each other and ITO surface through hydrogen bonding. The distance between Si atoms can be long enough to have a normal tilt angle (app. 30 deg.) of typical SAMs. Si-OH and Si-OCH3 groups were fully condensed to polysiloxane by further thermal treatment at 230 deg.C for 30 min, as evidenced by the disappearance of the O-H band in RAIR as well as by the decrease of the O1s band corresponding to silanol. The possible structural changes in the SAM driven by this condensation are discussed. In contrast to the fully hydrolyzed OTMS solution, a partially hydrolyzed OTMS solution provided loosely packed monolayers, apparently in islands of densely packed alkyl chains rather than as monotonically diminishing coverage.

4:40pm **OE+EM+AS-TuA9 Growth and Characterization of Poly(arylamine) Thin Films Prepared by Vapor Deposition***,* ***G.J. Szulczewski****, T. Selby, S. Blackstock,* The University of Alabama

We have synthesized a novel series of redox-gradient poly(arylamines) dendrimers for potential applications in organic-based electronic devices. The thermal properties of these materials have been measured by gravimetric analysis and differential scanning calorimetry. In general, these materials exhibit a glass transition temperature near 100 C and show negligible weight loss below 400 C. Thin films (1-100 nm) of these materials were grown under high vacuum conditions by vapor deposition onto a variety of substrates, including: gold, Si(100), and indium-tin oxide coated glass. Ex situ surface characterization was performed with reflection-absorption infrared spectroscopy, x-ray photoelectron spectroscopy, spectroscopic ellipsometry, and atomic force microscopy. These analyses show the formation of high quality films from the organic precursors with molecular weights exceeding 1300 amu without molecular decomposition. Thus, a new class of functional organic films for potential use in charge storage and transport have been prepared. The efficacy of these films as hole transport materials in electroluminescent devices and charge storage media is under current investigation.

5:00pm **OE+EM+AS-TuA10 HREELS Study of Ultra-thin Polyaniline Films Grown on Cu(110) by Vapor Deposition of Aniline Tetramers***,* ***K.K. Lee****, J.M. Vohs,* University of Pennsylvania*; N.J. DiNardo,* Drexel University

Substrate-dependent reactivity, thin film polymerization, and metallic conductivity upon doping have been demonstrated in previous HREELS studies of vapor-deposited emeraldine thin films on metal surfaces.@footnote 1@ In those studies, the chemical vapor was composed of a distribution of oligomeric sizes. In this HREELS study, the effect of the size of vapor-deposited oligomers on the growth of polyaniline at a metal surface is addressed through deposition of aniline tetramers on Cu(110). Analysis of vibrational and electronic spectra for growth up to ~70 Angstroms shows polymerization reactions with shorter chain lengths of the resulting polyaniline ultra-thin films than for deposition from emeraldine vapor. Upon doping, the far-infrared region exhibits intense tailing and a plasmon loss indicating that local conductivity is similar to ultra-thin films composed of longer chains. @FootnoteText@ @footnote 1@K. K. Lee - Surf Sci. 420 (1999) L115 and references therein.

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