## Tuesday Afternoon, October 26, 1999

#### 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 surfacesensitive 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) 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 asreceived 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. Understandi ng t he 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 noctadecylsilanetriol 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

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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 reflectionabsorption 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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