Organic Films and Devices
Room 131 - Session OF+NS+SS+BI-WeM
Self Assembled Monolayers/Ordered Films

Moderator: R. Maboudian, University of California, Berkeley

8:20am **OF+NS+SS+BI-WeM1 Preparation and Characterization of Nano-Scale Mixed Self-Assembled Monolayers***, S. Chen, L. Li, C. Boozer,* ***S. Jiang,*** University of Washington

Fabrication of nano-scale structures by mixed self-assembled monolayers (SAMs) has recently attracted much attention due to its scientific importance and potential applications to chemical and biological sensors, and biocompatible materials. However, it is still difficult to prepare nano-scale mixed SAMs since phase segregation occurs when two components are quite different. Recently, we proposed a new kinetically-trapped method to prepare nano-scale uniform mixed SAMs. In this work, we prepared various mixed SAMs, such as dodecanethiol(C12)/octanethiol(C8), tetradecanethiol (C14)/C8, 11-mercaptoundecanol(C11OH)/C8, and 11-mercaptoundecanoic acid(C10COOH)/C8 at a range of compositions using the kinetically-trapped method. Our results by low-current scanning tunneling microscopy (STM) revealed homogenous mixed SAMs with various terminal groups and a solution composition up to 25% of long chains formed at higher solution temperatures. Possible mechanism for forming uniform mixed SAMs will be discussed.

8:40am **OF+NS+SS+BI-WeM2 The Role of Linker Molecules in the Controlled Adsorption of Polystyrene (PS) Nano Particles***,* ***M. Himmelhaus,*** Universität Heidelberg, Germany*; H. Takei,* Hitachi Central Research Laboratory, Japan

Controlled adsorption of PS nano particles onto specific regions of flat surfaces has found increasing interest as potential applications for surface-adsorbed PS particles, such as fabrication of quantum dots, optical switches, mesoscopic lasers, biosensors, as well as dosing of biomolecules, require an easily applicable adsorption scheme capable of addressing macroscopic areas. Among the various techniques those utilizing linker molecules to promote particle-particle as well as particle-surface interaction have only recently been applied as to date the role of the linker molecules in the various physical and chemical adsorption mechanisms is only poorly understood. We have studied the effect of several water-soluble linker molecules on the adsorption behavior and packing density of surfactant-free polystyrene latex spheres from suspension. By variation of several parameters, such as molarity of the linker molecules, pH of the suspension, as well as choosing differently functionalized PS particles we can distinguish several adsorption mechanisms from each other, reaching from purely physical ones to covalent bonding. This basic study is a first step to the fabrication of 2D crystalline monolayers of macroscopic lateral extension by means of chemically driven self-assembly.

9:00am **OF+NS+SS+BI-WeM3 Characterization of Biphenyl-substituted Alkanethiol Self-assembled Monolayers by High-resolution X-ray Photoelectron Spectroscopy***, K. Heister, H.-T. Rong, M. Buck,* University Heidelberg, Germany*; L.S.O. Johansson,* University Karlstad, Sweden*;* ***M. Zharnikov,*** *M. Grunze,* University Heidelberg, Germany

Synchrotron-based high resolution X-ray photoelectron spectroscopy was applied to characterize self-assembled monolayers (SAM) of biphenyl-substituted alkanethiols CH@sub 3@(C@sub 6@H@sub 4@)@sub 2@(CH@sub 2@)@sub n@SH (BPn, n = 1-4) on Au and Ag substrates. Beyond previously identified odd-even changes in the packing density and the tilt angle of the biphenyl moieties, the high resolution spectra reveal a number of additional odd-even effects upon variation of the number of methylene groups in the aliphatic part in the BPn molecule. Their occurrence and mutual correlation suggests that a BPn SAM represents a strongly correlated, highly ordered molecular assembly. In particular, periodical changes of a shake-up feature in the C 1s region are observed, which are related to the differences in the arrangement of the aromatic matrix. The width and binding energy of the S 2p signals also exhibit odd-even changes. The width changes are associated with the occupation of either equivalent or non-equivalent adsorption sites on the polycrystalline (111) Au and Ag substrates. The comparison of the width values with those for conventional alkanethiols implies that the substrate bonding of alkanethiols on gold cannot be described by a single adsorption site. At the same time, the FWHM of the S 2p@sub 3/2,1/2@ peaks in the loosely packed BPn/Au (~0.50 eV) was found to be the smallest one among all thiol-derived SAMs investigated by HRXPS until present. Therefore, this value can be associated with the occupation of equivalent adsorption sites on the Au(111) surface. This work has been supported by the German BMBF (05 SF8VHA 1 and 05 SL8VHA 2), DAAD (313/S-PPP), and DFG (Bu820/11-2).

9:20am **OF+NS+SS+BI-WeM4 Separation via Self-assembly of Enantiomers of Chiral Aromatic Hydrocarbons Adsorbed on Metal Surfaces***,* ***K.-H. Ernst,*** *Y. Kuster, R. Fasel,* EMPA Duebendorf, Switzerland

We studied the interaction of heptahelicene ([7]H), a helically shaped, polyaromatic phenanthrene derivative, with well-defined single-crystal metal surfaces under ultra high vacuum (UHV) conditions. The molecules, racemate as well as the pure enantiomers, were deposited via molecular beam technique and subsequently characterized with surface sensitive techniques like temperature programmed desorption (TPD), Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), low-energy electron diffraction (LEED), scanning tunneling microscopy (STM), time-of flight secondary mass spectrometry (ToF-SIMS), X-ray absorption spectroscopy (NEXAFS), and X-ray photoelectron diffraction (XPD). On Ni(111), the [7]H-molecule is adsorbed intactly at room temperature. TPD, however, shows only desorption of molecular [7]H from the multilayers. The first layer undergoes decomposition into carbon and hydrogen at 650 K. From Cu(111), molecular desorption is also observed at low coverages. The closed packed monolayers of [7]H on Ni(111) and Cu(111) show two-dimensional lattice structures. Adsorption of racemic [7]H leads to self-alignment into domaines on the surface, which are mirror images of each other. This is not observed after exposure to pure enantiomers and can be explained with a lateral separation of the enantiomers into homochiral domaines on the surface. For the pure M-enantiomer on the stepped Cu(332) surface, an azimuthal alignment of the molecular spirals is observed. Models for the monolayer structures and the mechanism of the separation will be discussed. Support by the Swiss National Science Foundation (NFP 36) is gratefully acknowledged.

9:40am **OF+NS+SS+BI-WeM5 Mesoscopic Correlation of Supramolecular Chirality in One-Dimensional Hydrogen-Bonded Assemblies***,* ***J.V. Barth,*** Ecole Polytechnique Federale de Lausanne, Switzerland*; J. Weckesser,* Max-Planck-Institut fuer Festkoerperforschung, Germany*; A. De Vita,* Institut Romand de Recherche Numerique en Physique des Materiaux, Switzerland*; C. Cai,* University of Houston*; K. Kern,* Max-Planck-Institut fuer Festkoerperforschung, Germany

We studied enantioselective self-assembly in two dimensions employing the molecule 4-[trans-2-(pyrid-4-yl-vinyl)] benzoic acid. Scanning tunneling microscopy observations at noble metal surfaces reveal the formation of hydrogen-bonded supramolecular twin chains in two mirror-symmetric species, each containing only molecules of a given chirality. The twin chains are ordered in µmm-gratings, where a mesoscopic correlation of supramolecular chirality over the entire domain size without intimate molecular contact persists. This novel phenomenon reflects mesoscopic chiral segregation due to chiral recognition in the formation of the supramolecular assemblies. Theoretical modelling in conjunction with direct observations indicate that twin chains act as enantioselective templates for transient molecular attachment, which process mediates self-replication of supramolecular chirality and the enantiopure gratings' evolution.

10:00am **OF+NS+SS+BI-WeM6 Controlling Molecular Orientation in Solid Films Via Self-organization in the Liquid-crystalline Phase***, I.K. Iverson, S.-W. Tam-Chang,* ***S.M. Casey,*** University of Nevada, Reno*; B.A. Pindzola,* University of California, Berkeley

We report the control of molecular orientation in solid films through self-organization and induced-orientation processes. We synthesized water-soluble cationic 3,4,9,10-perylene diimide (1) and studied its self-organization in aqueous solution. By UV-vis spectroscopy, H-aggregates of 1 are observed forming in solutions with concentrations as low as 10@super -7@ M. At concentrations above approximately 0.1 M (7% w/w) these solutions are observed with polarized microscopy to form a chromonic N phase (a nematic lyotropic liquid crystalline phase) at room temperature. Upon induced alignment (by shearing) of the chromonic N phase on a glass substrate and removal of solvent, anisotropic solid films of the dichroic dye are produced. These films have dichroic ratio values that routinely exceed 25 and in some cases 30, making them excellent sheet polarizers over the blue and green region. Using a combination of polarized UV-vis and FT-IR spectroscopies, the orientation of the average molecular plane in these films is determined to be perpendicular to both the shearing direction and the substrate plane. X-ray diffraction studies indicate that the molecules in the solid film possess a high degree of order.

10:40am **OF+NS+SS+BI-WeM8 Effect of Lipid Vesicle Fusion on the Ordering and Redox Activity of 11-(ferrocenyl carbonyloxy) Undecanethiols Self-assembled Monolayers***, A.T.A. Jenkins,* University of Bath, U.K., Great Britain*; **J.F. Le Meur,*** University of Bath, U.K.

Self-assembled Monolayers (SAMs) of 11-(ferrocenyl carbonyloxy) undecanethiol were made following a procedure given by Chidsey et @footnote 1@ The formation of the 11-(ferrocenyl carbonyloxy) undecanethiol SAM on gold was followed in-situ by Surface Plasmon Resonance (SPR)and showed a film of thickness 13 Å was formed. Impedance measurements indicated a high level of film coverage. Cyclic voltammetry was subsequently used to electrochemically characterise the SAM, and check its stabilty with respect to immersion in electrolyte. Egg-Phosphatidylcholine lipid vesicles were created by extrusion through a 50 nm membrane and were adsorbed on the SAM. SPR was used to follow the lipid adsorption on the SAM. Cyclic voltammetry measurements on the SAM-lipid system showed a large and reproducible increase in the peak anodic and cathodic currents after lipid adsorption, although the total quantity of charge transfered stayed the same. This is likely to be due to an increase in order of the ferrocene units in the SAM, allowing for a faster transfer of electrons on the lipid covered SAM than the SAM alone. The above experiments were repeated with binary mixtures of SAMs containing both 11-(ferrocenyl carbonyloxy) undecanethiol and mercaptoundecanol moities. It was found that the increase in anodic and cathodic current maximums measuresed by cylic voltammetery was disproportionately lower than the single component SAM (relative to the coverage). From this we propose a model for how the SAM structure changes upon lipid adsorption. @FootnoteText@ @footnote 1@ Chidsey, C.E.D.; Bertozzi, C.R.; Putvinski, T.M.; Mujsce, A.M. Journal American Chemical Society, 1990, 112, 4301-4306.

11:00am **OF+NS+SS+BI-WeM9 Temperature-dependent Morphology of Crystalline p-sexiphenyl Thin Films on KCl(001)***, **E.J. Kintzel, Jr.,*** Florida State University*; D.-M. Smilgies,* Cornell University*; J.G. Skofronick, S.A. Safron,* Florida State University

Investigations of the morphology of ultrathin films of p-sexiphenyl (p-6P) vapor deposited onto KCl(001) have been carried out using the complementary techniques of X-Ray Diffraction (XRD) and Atomic Force Microscopy (AFM). XRD studies have shown that the molecular orientation of the p-6P is dependent on the substrate temperature during deposition. For films prepared at low temperatures, the p-6P molecules take a lying orientation, with the long axis of the molecule aligned parallel to the substrate. As the substrate temperature was increased during deposition, XRD results indicate two coexisting molecular orientations, corresponding to lying and standing p-6P molecules. AFM images provide independent confirming evidence of the influence of substrate temperature on molecular orientation, consistent with the XRD results.

11:40am **OF+NS+SS+BI-WeM11 Characterization of Photoisomerization Reaction of Azobenzene-contanining SAMs: Reaction Kinetics and Thermal Stability***, **K. Tamada,*** National Institute of Advanced Industrial Science and Technology (AIST), and Frontier Research System, RIKEN, Japan*; H. Akiyama, T. Wei,* AIST, Japan

We studied the change of photoreactivity of azobenzene disulfide SAMs under thermal stress. Azobenzene-containing unsymmetrical disulfide (C6AzSSC12) SAM was annealed at each temperature (70, 85, 100, 120, 140°C) for 1 hr, then the photoreaction was monitored with surface plasmon resonance spectroscopy (SPR) in hexane. The photoreaction was stable under 100°C when no decomposition of adsorbed molecules was detected, while it was suddenly reduced at over 100°C when the decomposition was taking place. After annealing at 140°C, the reactivity of the unsymmetrical disulfide SAM reached to the level of the corresponding azobenzenethiol SAMs (single component), suggesting the phase segregation of the adsorbed molecules by annealing. We designed new azobenzene thiol/disulfides (C6Az(Me)thiol, C6Az(Me)SSC12) to achieve more thermally stable photoresponse. In these molecules, CH@sub 3@-group is introduced to the azobenzene ring directly to avoid dye aggregation sterically. The C6Az(Me)thiol SAM exhibited much higher photoreactivity than conventional azobenzenethiol, which suggests that dye functions are less aggregated even in the single component SAMs. The C6Az(Me)SSC12 exhibited much higher photoresponse compared with C6AzSSC12 after annealing, since these azo dyes can react even in phase segregated domains. We also discuss photoisomerization reaction kinetics (cis to trans, trans to cis) in correlation with dye alignment.

Organic Films and Devices
Room 131 - Session OF+TF+EL-WeA
Growth of Organic Thin Films

Moderator: T. Fritz, TU Dresden, Germany

2:20pm **OF+TF+EL-WeA2 Resonant Mid-Infrared Pulsed Laser Deposition of Polymer Films**, ***R.F. Haglund***, *M.R. Papantonakis,* Vanderbilt University; *D.M. Bubb, J.S. Horwitz, J.S. Callahan, R.A. McGill, E.J. Houser, D.B. Chrisey,* Naval Research Laboratory; *M. Galicia, A. Vertes,* George Washington University; *B. Toftmann,* Risoe National Laboratory, Denmark

Resonant, picosecond-pulse, mid-infrared laser irradiation has been shown to ablate glassy and crystalline solids with high efficiency and low collateral damage.@footnote 1@ We have extended this concept to show that resonant infrared (IR) pulsed-laser deposition (PLD) is an effective method for depositing polymer films with physical and chemical structure as well as optical properties virtually identical to those of the bulk starting material. This contrasts sharply with PLD at ultraviolet (UV) wavelengths, where deposited polymer material is sometimes significantly degraded. In our experiments, the organic starting material was ablated by a pulsed infrared, free electron laser tuned into resonance with various vibrational modes; the vapor was collected on a room-temperature substrate. For polyethylene glycol (PEG, MW 1450) the laser was tuned to either C-H or O-H stretching modes at 2.9 and 3.4 µm, respectively. The properties of the deposited film were determined using infrared absorption spectroscopy and mass spectrometry. When the infrared laser was detuned from resonance, the structure and optical properties of the deposited PEG film were significantly altered, showing that the off-resonance ablation process thermally damages the polymer. The potential for generalizing this technique can be seen in the successful deposition of poly(lactide co-glocolide) (PLCA, MW 67,000). PLCA films were deposited using 5.7 µm excitation (1754 cm@super-1@), where the laser excitation is localized by the C=O stretch. The mechanism of ablation appears to be explosive vaporization; in contrast to the photochemical mechanism typical of UV ablation, the ablated material seems to remain in the electronic ground state. The technique appears promising for biomedical and electronic applications of polymeric and organic thin films. @FootnoteText@ @footnote 1@ D. R. Ermer, M. R. Papantonakis, M. Baltz-Knorr, D. Nakazawa and R. F. Haglund, Jr., Appl. Phys. A 70, 633-635 (2000).

2:40pm **OF+TF+EL-WeA3 Synthesizing Thin and Ultrathin Polymer Films by a Two-step Deposition/Polymerization Process**, ***J. Bai***, *C.M. Snively, W.N. Delgass, J. Lauterbach,* Purdue University

The goal of this work is to understand and further develop an in-situ preparation method for producing high quality polymer thin films. In this two-step vacuum process, a monomer film is deposited onto a cooled substrate, and then the polymerization reaction is initiated; thus the polymerization is confined to the substrate. Compared to other preparation techniques, this process has the major advantages of allowing the fabrication of films from insoluble polymers and providing better control of film quality. This investigation focused on the molecular orientation and packing of the monomer, as well as polymerization kinetics and film quality characterization. In-situ adsorption and polymerization studies were done using Reflection-Absorption Infrared Spectroscopy (RAIRS) and Temperature-Programmed Desorption (TPD). Time resolved FTIR spectra were taken to study the factors controlling the rate of polymerization. GPC, ellipsometry and AFM provided information about molecular weight, film thickness, and morphology characterization of the films. The model systems investigated were styrene and methyl methacrylate (MMA) on platinum. For the styrene/Pt model system, kinetic studies reveal that the polymerization reaction is preferred in amorphous monomer layers. Ellipsometry measurements show that, in the range of 25-200nm, the polystyrene film thickness is a linear function of the monomer dosage. AFM data suggest that the resulting film morphology is influenced by the platinum substrate. Polarized RAIRS spectra of MMA show that, up to 0.2 micron, only p-polarized component of the beam contributes to the spectrum, indicating that RAIRS can be used to determine the molecular orientation of films with sub-micron thickness.

3:00pm **OF+TF+EL-WeA4 Surface Growth Study of Pentacene, Perylene and CuPc**, ***S. Zorba***, *N.J. Watkins, L. Yan, Y. Gao,* University of Rochester

Pentacene, Perylene and CuPc are widely used organic semiconductors in organic light emitting diode (OLED) and organic thin film transistor (OTFT) applications. It has been well established that the transport properties of these materials are strongly dependent upon the way they are grown as organic thin films. One of the reasons why these materials are so popular is the fact that their electronic properties, such as their mobilities and barrier to charge injection ratios, can be altered and improved by changing their morphologies. In this talk we will present our recent results on the different growth modes of these substances on different substrates and try to relate their observed electronic and transport properties to their morphologies and account for their favorable features.

3:20pm **OF+TF+EL-WeA5 Substrate Controlled Crystallisation of Ultra-thin Films of Perylene**, ***Q. Chen***, *N.V. Richardson,* University of St Andrews, UK; *P.J. Unwin, T.S. Jones,* Imperial College of Science, Technology and Medicine, UK; *T. Rada, A.J. McDowall,* University of St Andrews, UK

There has been recent interest in the electronic and optoelectronic properties of polyaromatic hydrocarbons, such as tetracene, pentacene and perylene, because of their potential use as organic lasers, OLEDs and OFETs. Device performance is likely to be s trongly influenced by the structural quality of crystals or thin films. We have carried out a detailed investigation of the deposition and growth of ultra-thin films (0-30 monolayers) of perylene on a variety of substrates including Cu{110}, H/Si(111), InAs(111) and InSb(111), using STM, TPD, LEED and vibrational spectroscopies. The substrate has a profound influence on growth and subsequent crystallinity of the film. For example, films grown on a hydrogen terminated Si(111) surface show no evidence o f layer-by-layer growth and, from the earliest stages, small clusters of randomly oriented molecules are present which eventually cover the surface with a rough polycrystalline film. In contrast, vacuum deposition on a Cu{110} surface leads to large crysta l line domains upto one monolayer coverage. Electron energy loss spectroscopy confirms that the molecules are flat-lying and @pi@-bonded to the substrate. Multilayer growth takes place epitaxially layer-by-layer on this first monolayer into a structure whic h, although commensurate with the underlying copper surface along the direction is incommensurate along and is unrelated to the bulk crystal structure of perylene. The 2D unit cell at all layer thicknesses (to 30 monolayers) is rectangula r with dimensions 2nm x 1.9nm containing two, flat-lying molecules per layer at 90° to each other around an axis normal to the substrate surface. The molecular rows along are out-of-phase with each other in the direction from layer to layer, in an ABA packing sequence of rows along the growth direction. The implications for the modification of film properties implied by this control over film structure and crystallinity will be discussed.

3:40pm **OF+TF+EL-WeA6 Probing the Reactivity of Multifunctional Compounds on Semiconductor Surfaces: Pyrrole and its Derivatives on Si and Ge(100)-2x1**, ***G.T. Wang***, *C. Mui, C.B. Musgrave, S.F. Bent,* Stanford University

While the chemistry of amines has been extensively studied on the Si(100)-2x1 surface, relatively little is known about their reactivity with the Ge(100)-2x1 surface. In this study, the reactions of pyrrole and multiple pyrrole derivatives, including methylpyrrole, pyrrolidine, and methylpyrrolidine, with the Ge(100)-2x1 and Si(100)-2x1 surface were investigated via multiple internal reflection infrared spectroscopy and ab initio quantum chemistry calculations. This series of compounds comprises a model system for examining the competition of multiple functionalities on Ge(100) and Si(100) and the role kinetics and thermodynamics play on selectively controlling growth of organics on semiconductor surfaces. Although these compounds are structurally similar, they each follow different reaction mechanisms on the Si surface, including dative bonding, N-H dissociation, cycloaddition, and electrophilic aromatic substitution. We have also found that the adsorption of pyrrole and its derivatives on the Ge surface is surprisingly different from the Si surface. While the reaction of organics on Si is typically under kinetic control, the experimental and theoretical results show that thermodynamical considerations are also necessary to explain the reaction of organics on Ge. Additionally, aromaticity and charge transfer to the surface are found to have significant effects on the adsorption behavior of these compounds.

4:00pm **OF+TF+EL-WeA7 Chemisorption of Vinylacetic Acid on Si(001) and Its Subsequent Reaction with Iron Pentacarbonyl**, *K. An, S.S. Lee,* ***Y. Kim***, Korea Research Institute of Chemical Technology, South Korea

Chemisorption of vinylacetic acid (VAA) on clean Si(001) substrate at room temperature and the change of its adsorption with temperature have been investigated by x-ray and ultraviolet photoelectron spectroscopy. It was hoped that the C=C double bond of the chemisorbed VAA may be utilized in the subsequent reaction with the second adsorbate, iron pentacarbonyl, Fe(CO)@sub 5@, in this study. VAA first adsorbs on Si(001) molecularly, and as the substrate temperature is increased to 350°C, loses the acidic hydrogen resulting in the configuration that has two equivalent oxygen atoms according to the change in the O 1s XPS peak. The curve-fitted Si 2p peak indicates formation of the Si@super 2+@ state on the surface. UPS also showed that the photoemission peak due to the OH group of VAA loses its intensity significantly. This surface species is stable up to about 350°C. As the temperature is raised even more to ~450°C, the adspecies are decomposed leaving a mixture of oxidized silicon and silicon carbide. At about 700°C, only tenacious oxygens remain on the carbided substrate surface. Iron pentacarbonyl was introduced into the XPS analysis chamber to 35000 L with the monolayer of the anionic species of VAA at 350°C. The surface, after the introduction of Fe(CO)@sub 5@, was found to consist of the acid anion and an iron species that shows metallic behavior according to XPS and UPS data. The Fe(CO)@sub 5@ molecules must have been completely dissociated since no accumulation of C or O adspecies has been detected. Also the surface iron atoms do not seem to have been oxidized judging from the shape of the Fe 2p level and the appearance of the Fermi level crossing. However, it is not yet clear whether the iron species have formed microscopic structures or not, while the change in the C 1s peak suggests that they may each have a chemical bond with the surface C=C double bond. At the moment a scanning tunneling microscopy experiment is in preparation to examine the surface structure of the iron species.

4:20pm **OF+TF+EL-WeA8 Possibilities of Electron Beam Nanometer-scale Fabrication of Si(111) Using Alkyl Monolayers***, **T. Yamada,** N. Takano, K. Yamada, S. Yoshitomi, T. Inoue, T. Osaka,* Waseda University, Japan

Utilization of monolayer materials covering Si wafer surfaces is prospective in mass-production of nanometer-scale patterns generated by electron beam drawing, maintaining the spatial resolution. This paper presents application or monolayers of organic moieties bonded on Si(111) for electron-beam patterning and successive chemical metal deposition processes over the patterns. For the purpose of passivation and chemical alteration of Si(111) surface, alkyl groups were deposited by contacting H:Si(111)(1x1) with Grignard reagents (C@sub n@H@sub 2n+1@MgX, X=Cl, Br, I, as tetrahydrofuran solutions).@footnote 1@ Vibrational spectroscopy by FT-IR and HREELS indicated that the bonds in alkyl groups delivered as the Grignard reagent remained unbroken, and that most of the terminating H atoms were replaced by the alkyl groups. STM revealed the original step/terrace structure of Si(111) uniformly covered with a monolayer of organics. The alkyl groups were arranged in a rather disordered manner within the monolayer. Auger electron spectroscopy resulted that the number of alkyl groups per a unit area is constant with respect to the chain length n in the range of 1 ~ 18. All these facts indicate that the alkyl groups are covalently bonded to Si(111). Electron bombardment in vacuum did not introduce useful alteration of the adlayer, and patterning by electron beam (incident energy <3 kV) with ambient O@sub 2@ atmosphere (<10@super -6@ Torr) deposited SiOx on the irradiated portions. Metals such as Ni and Cu were deposited only over the patterns by immersion into aqueous solutions including metal ions. The electron beam patterns were even visualized as metal-deposited area limited by the passivation effect of alkyl monolayer. Application of this entire process to the patterns of <100 nm is now attempted to explore the spatial resolution limit on the nanometer scale. @FootnoteText@ @footnote 1@R. Boukherroub, S. Morin, F. Bensebaa and D. D. M. Wayner: Langmuir 15 (1999) 3831.

Organic Films and Devices
Room 131 - Session OF+TF-ThM

Characterization of Organic Thin Films

Moderator: N.V. Richardson, University of St Andrews

8:20am **OF+TF-ThM1 Characterization and Modification of ITO Surfaces: Use of Chemisorbed Probe Molecules as Indicators of Electron Transfer Rates and Their Use in Improving OLED Performance***, **C. Carter**, C.L. Donley, N.R. Armstrong,* University of Arizona

XPS characterization of ITO surfaces, following various pretreatments, shows that the surface coverage of hydroxyl groups, and oxygen defects, can be varied significantly. Probe molecules, such as ferrocene dicaroboxylic acid (Fc(COOH)2) can be chemisorbed to these surfaces through hydrogen bonding interactions, at coverages up to 40% of a compact monolayer. The coverage and electron transfer rates of these chemisorbed molecules vary by up to 100% depending upon pretreatments used. Organic light emitting diodes, prepared by spin coating single polymer layers (PVK), doped with Alq3, and its tri-sulfonamide analog, Al(qs)3, show signficant lowering of onset potentials for electroluminescence for ITO films modified with the Fc(COOH)2 probe, following air plasma cleaning. These differences in onset potential are most significant for devices where electron injection is not the chief limitation to electroluminescence.

8:40am **OF+TF-ThM2 XPS Characterization of Photo-Alignment of Liquid Crystals using Adsorbed Dichroic Materials***, **L. Su**, J.L. West,* Kent State University*; Y. Reznikov,* Ukraine Academy of Science*; K. Artyushkova, J.E. Fulghum,* Kent State University

The alignment layer is one of the most important parts of a twisted nematic (TN) display. Many methods exist for producing alignment, and the quality of the alignment layer directly influences the performance of the display. The most popular alignment method used by the Liquid crystal display (LCD) industry is mechanical rubbing of a polymer film. However, there are many disadvantages associated with this method, such as the introduction of dust particles, formation of electrostatic charges and other defects on the rubbed surface. Photo-alignment of liquid crystals is emerging as one of the most promising substitutes for mechanical rubbing. Photo-alignment generates surface anisotropy through the interaction between the irradiated substrate and the light source. Photo-alignment using adsorbed dichroic materials provides an efficient and versatile way to produce effective alignment of liquid crystals. Successful photo-alignment results from properly matching the adsorbed and substrate materials. In this study, poly(vinyl) alcohol (PVA) and adsorbed dichroic materials, including the dye Brilliant Yellow, are utilized as the alignment layer. We will demonstrate the use of polarized UV-Vis spectroscopy and angle-resolved x-ray photoelectron spectroscopy (XPS) for studying the interaction of the polymer, dye and liquid crystal. Using ARXPS, it is possible to study the distribution of all three organic layers. Both techniques indicate that intermolecular interaction between the adsorbed dichroic molecules and the substrate polymer is critical to the outcome of photoalignment. This work has been supported in part by NSF ALCOM (DMR 89-20147), and the Air Force (DAGSI SN-AFIT-9903).

9:00am **OF+TF-ThM3 An STM , XPS and RAIRS Study of Cobalt(II) Hexadecafluorophthalocyanine (CoF16Pc) and Its Co-adsorption with Nickel(II) Tetraphenylporphyrin (NiTPP)on Au (111)***, **S.L Scudiero,*** Washington State University, US*; D.E. Barlow, K.W. Hipps,* Washington State University

Scanning tunneling microscopy (STM) images show that cobalt(II) hexadecafluorophthalocyanine (CoF16Pc) forms disordered structures when deposited on Au(111) under UHV conditions at 300K, while nickel(II) tetraphenylporphyrin (NiTPP) forms a tightly packed well organized structure under the same conditions. X-ray photoelectron (XPS) and reflection-absorption infrared spectroscopy (RAIRS) data obtained on thin films of the pure compounds confirm that the chemical composition of these films is the same as the starting bulk materials. When CoF16Pc and NiTPP are co-deposited with a monolayer coverage, the resulting surface structure is a well ordered 2D array having a 1:1 ratio and a nearly square unit cell as revealed by high resolution STM images. The composition of the mixture was confirmed by XPS. We believe that this new structure is due to the weak electrostatic interactions associated with the local partial charges and their images, along with differences in Van der Waals forces.

9:20am **OF+TF-ThM4 Solution-Assisted Tribological Modification of Surfaces Using an Atomic Force Microscope***, **F. Stevens**,* Washington State University, USAS*; R. Leach, J.T. Dickinson,* Washington State University

The response of thin polymer films to combined stress and solvent is important for applications such as protective barriers (e.g., various wrappings), in controlled drug release from polymer hemispheres, resists for lithography, and nanometer scale surface modification. Over a wide range of normal forces, when a polymer is scanned by SFM in contact mode in a solvent, material is not worn away, but rather the polymer surface expands forming a nanometer scale "bump" at and surrounding the scanned location. Furthermore, for sub-micron scan areas one often observes a series of parallel ridges (moguls) perpendicular to the fast scan direction. Previous reports of the formation of raised material have nearly all been in air, required long times or very high forces to form; little evidence has been presented for the mechanism of formation. We have engaged in a detailed study of protrusion formation and raised ridges using poly(methyl methacrylate) in alcohol based solvents. In addition to scanning in air, we have scanned the polymer surface in four solvents with dramatic differences in response. We have also observed the effects of varying contact force, and the effect of using cantilevers with different force constants. We present evidence that both plastic deformation and tip induced swelling play major roles in the observed polymer surface modification by SFM. The stresses applied by the tip generate tensile forces around the tip that likely increase the quantity of solvent that can enter the surface. We show that adding Rhodamine 6G dye to the solvent provides us with evidence that indeed solvent is going into the polymer. Using fluorescence microscopy we can monitor the uptake of dye as a function of scanning and solvent parameters. This study also shows the possibility of introducing small quantities of a chemical into the polymer surface in a highly localized (nanometer scale) fashion.

9:40am **OF+TF-ThM5 Viscoelastic Properties of Thin Liquid Crystal Films***, **I. Zori@aa c@**, P. Borchard, T. Carlsson, B. Kasemo,* Chalmers University of Technology, Sweden

Viscoelastic properties of thin liquid crystal (LC) films are strongly affected by the changes in orientational and/or translational order in the system. These changes may be induced via a temperature variation or by a presence of the two phase interface (e.g. a free surface or a LC-solid substrate interface). In this contribution we report the viscoelastic properties of thin (500-7000Å) 5CB films, spin coated on the Au electrode of the quartz crystal microbalance (QCM), with one free surface. The system (LC film) is exposed to a periodic shear force (at 5 MHz respectively 15MHz) and the changes in the QCM oscillator frequency, @DELTA@f, and dissipation factor, @DELTA@D, are measured as a function of temperature while the system undergoes a series of phase transitions (smectic-nematic-isotropic). Both @DELTA@f and @DELTA@D show unusual temperature dependence in the vicinity of the nematic-isotropic phase transition. Two approaches are used to deduce the temperature dependent viscoelastic coefficients from the measured frequency and dissipation factor changes. In both approaches the QCM is treated as a harmonic oscillator and the Navier Stokes equation is used to calculate the velocity profile in the viscous overlayer caused by the periodic shear. Once the velocity profile in the film is known, a frictional force causing a change in the oscillator frequency and dissipation, may be calculated. In the first case the overlayer is treated as a homogenous isotropic thin liquid film (Voight model) while in the second case a proper anisotropic structure of the LC film is taken into account in the hydrodynamic continuum approach (Leslie-Ericksen theory). We compare our results to generalized viscosities obtained using different methods.

10:00am **OF+TF-ThM6 Structure of Ultrathin Pentacene Films***, **S. Lukas**, G. Witte, C. Wöll,* Ruhr-Universität Bochum, Germany

The structure of ultrathin films (1-3ML) of pentacene grown by evaporation under UHV conditions on various copper surfaces has been studied by LEED, STM and NEXAFS. The enhanced binding energy of acene molecules at step edges which was measured systematically by TDS can be utilized to prepare ordered monolayer films on vicinal copper surfaces with close packed terraces while only disordered films grow on the flat Cu(111) surface.@footnote 1@ Highly ordered mono- and multilayer films were also obtained for the Cu(110) surface and their corresponding molecular orientation was determined by NEXAFS as a function of the film thickness. For comparison additional films were grown also on gold and sapphire surfaces. In addition to the geometrical structure the electronical properties of these pentacene films were investigated by UPS. @FootnoteText@ @footnote 1@ S. Lukas et al., J. Chem. Phys. 114 (2001) .

10:40am **OF+TF-ThM8 Photoelectron Spectroscopy of Exciton Dynamics and Interactions in Organic Thin Films: C@sub60@ and Photopolymerized C@sub60@*, J.P. Long*,** *S.J. Chase, M.N. Kabler,* Naval Research Laboratory

Of fundamental importance to the operation of many organic electronic devices are the controlling nonequilbrium populations of singlet (S@sub 1@) and triplet (T@sub 1@) excitons and charged carriers. For example, optoelectronic device efficiencies may be depressed if dark T@sub 1@ excitons compete with fluorescent S@sub 1@ states or if annihilation interactions limit excited state population densities. Because pump-probe photoelectron spectroscopy is uniquely capable, in principle, of resolving in energy and time the electrons of all nonequilibrium species, it promises to provide useful insights into the densities, lifetimes, and mutual interactions of the various nonequilibrium populations. Using both synchrotron and laser-harmonic photoemission sources, we have applied this technique to study the dynamics of excitons pumped by visible laser radiation in the model systems of C@sub 60@ and photopolymerized C@sub60@ films prepared in ultrahigh vacuum and studied in situ. We report the unambiguous identification of the transient photoelectron spectra of both S@sub 1@ and T@sub 1@ excitons. Studies on time scales from 100 ps to 10 µs and of exciton concentrations from below 10@super 18@ cm@super -3@ to more than 10@super 19@ cm@super -3@ reveal a rich dynamics. For exciton densities above ~10@super 19@ cm@super -3@, excited-state interactions lead to a surprising excess of T@sub 1@ excitons at the expense of S@sub 1@ excitons for times much less than the intersystem crossing time of ~2.5 ns. Such excess T@sub 1@ generation suggests that interactions among excited species may interfere with the operation of potential devices that would operate at high nonequilibrium densities. A rate-equation model that couples interacting S@sub 1@, T@sub 1@, and carrier populations reproduces the complex dynamics, including non-Markovian decays, and provides evidence for the annihilation of excitons by charged carriers.

11:00am **OF+TF-ThM9 Optical Properties of Highly Ordered Ultrathin Epitaxial Films of PTCDA on Au(111)***, R. Nitsche, S. Mannsfeld, H. Proehl,* ***T. Fritz,*** TU Dresden, Institut fuer Angewandte Photophysik, Germany

Highly ordered organic thin films on a gold single crystal have been prepared by means of organic molecular beam epitaxy and investigated by optical absorption spectroscopy. The organic dye molecule perylene-3,4,9,10- tetracarboxylic-3,4,9,10-dianhydride (PTCDA) has been deposited on Au(111) with submonolayer to multilayer coverage. All films were structurally characterized by combining Scanning Tunneling Microscopy (STM) with Low Energy Electron Diffraction (LEED), clearly indicating epitaxial growth in the point-on-line mode. In order to determine the optical constants of those films, Differential Reflection Spectroscopy (DRS) has been applied. Subsequently, the optical constants have been calculated based on a model dispersion formula, thereby deconvoluting the absorption index k into several molecular transitions. The thickness dependence of the parameters (position, width, strength) of those transitions is discussed. Contrary to a simple discussion of the peak position of the entire spectrum, which would indicate an energetic shift, our thorough analysis reveals that the dominant effect consists of a change in the relative contributions of the several transitions rather than an energetic shift. The results are compared to polycrystalline PTCDA layers of comparable thickness on polycrystalline gold films, exhibiting a larger inhomogeneous broadening.

11:20am **OF+TF-ThM10 Importance of Structural Order for the Low Surface Energy of Perfluoroalkyl Substituted Polymethacrylates***,* ***J. Luning,*** Stanford University*; D.Y. Yoon,* Seoul National University, Korea*; J. Stohr,* Stanford University

Perfluoroalkyl substituted PolyMethacrylate (PFPM) polymers are today widely used as low surface-energy coatings playing an essential role in microelectronics, anti-fogging, and anti-fouling applications, and even have promising medical applications. It is generally believed that the anti-wetting properties -solely determined by the structures present in the surface region- of these and related polymers arise from the segregation of CF@sub 3@ groups to the surface. However, proof of a direct correlation between surface structure and surface energy, and the importance of order in the underlying bulk, is still lacking as most experimental techniques do not have the required surface sensitivity. For preferentially oriented polymers the asymmetry in chain orientation translates to an asymmetry in the electron charge density as the electron orbitals are oriented along the molecular bonds. Such a charge asymmetry can give rise to a dependence of the Near Edge X-ray Absorption Fine Structure (NEXAFS) on the orientation of the electric field vector of the linearly polarized x-rays relative to the sample. Consequently, such a linear dichroism can be used to study orientation phenomena quantitatively. The required surface sensitivity is obtained by recording simultaneously the more bulk sensitive total (TEY) and the more surface sensitive Auger (AEY) electron yield. Our studies of three PFPM's with different bulk order phases reveal a greater order at the surface than in the bulk, and the surface order parameter is found to correlate with the surface energy. Most importantly, temperature dependent NEXAFS measurements covering several bulk phase transitions show that the achievable surface order, and hence the surface properties, is ultimately limited by the bulk order (phase).

Organic Films and Devices
Room 131 - Session OF+EL+TF-ThA

Electronic Properties of Organic Thin Films

Moderator: M. Himmelhaus, Universität Heidelberg, Germany

2:00pm **OF+EL+TF-ThA1 Interface Formation in Organic Thin Film Transistors: A Photoemission Spectroscopy Study***, **N.J. Watkins**, L. Yan, Y. Gao,* University of Rochester

Pentacene, perylene, and sexithiophene are all materials being used in organic thin film transistors due to their relatively large mobilities. It has been suggested that the functional behavior in organic thin film transistors occurs within the first few molecular layers of the device at the interfaces between the organic and the metals and dielectrics used in fabrication of the thin film transistors. This makes understanding the electronic behavior of the interfaces involved in these devices critical. In order to better understand these interfaces we investigated the interface formation of pentacene, perylene, and sexithiophene on conductors and dielectrics using photoemission spectroscopy to examine layer by layer organic growth onto these materials. We observed indications of dipole formation at the interfaces between the metals and organics for organic on metal deposition, ranging from a 1eV dipole at the interface between sexithiophene and gold to a -0.46eV dipole at the interface between pentacene and calcium. There appears to be a linear relation between the interface dipole and metal workfunction. On the other hand, for metal on organic deposition, more complex material intermixing takes place and as a result, the electronic structure of the interface differs from that of organic on metal deposition. Possible charge transfer, dipole formation and energy level bending at these interfaces will be discussed.

2:20pm **OF+EL+TF-ThA2 Controlling Metallic Contacts to Self-Assembled Monolayers and Molecular Electronic Devices***, **A.V. Walker**, B.C. Haynie, T. Tighe, D.L. Allara, N. Winograd,* Pennsylvania State University

An understanding of the nature of the metal â€“ atom organic monolayer interaction is vital in the development and design of molecular electronic devices. To fully characterize these interactions, we employ a multi technique approach using time-of-flight secondary ion mass spectrometry (ToF SIMS), infrared spectroscopy (IRS), x-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). Using a methoxy terminated alkanethiol monolayer on Au{111}, we demonstrate that the metal organic monolayer contact can be varied from complete destruction of the monolayer to contact formation at the terminal group to complete penetration through the layer. For metals of intermediate reactivity, e.g. Cu, we observe that the metal atoms interact with the terminal group and penetrate through the layer to the monolayer / Au{111} interface. We have also studied the interaction between promising molecular wire and electronic and device candidates and metal atoms. By using a variety of metals, the formation of the metal molecule contact can also be controlled. This leads us to suggest new metallic contact materials for molecular electronic devices.

2:40pm **OF+EL+TF-ThA3 Dependence of Electrical Properties of Metal/Organic/Metal Systems on Interface Electronic Structure, Morphology and Chemistry***, C. Shen, **A. Kahn**,* Princeton University **INVITED**

Interactions between metals and organic molecules are varied, and depend sensitively on the nature of the metal, of the organic molecule, and on the mode of the formation of the interface. In general, an interface formed by deposition of a metal on an organic film is broader than the interface formed by reverse deposition sequence. Metal atoms diffuse and/or react in the organic layer, acting as electrically active dopant and altering the electronic properties and the structure of the molecular film. These interactions have a profound impact on the injection of charge carriers across these organic interfaces. We present here a comprehensive investigation of these effects performed on a series of metal/organic/metal structures. All experiments are performed in ultra-high vacuum to eliminate extrinsic effects. The organic materials are Alq@sub 3@ (tris-(8-hydroxy quinoline) aluminum), amorphous emissive material extensively used in molecular OLEDs; and F@sub 16@-CuPc (hexadecafluoro copper phthalocyanine), a good electron-transport material that forms molecular stacks. The metals are Al and Au. Combinations of structures including permutations of Al and Au as top and bottom contacts, and even ultra-thin metal layers inserted into the bulk of the organic film, are used to investigate the effects. Key results are: 1. The predominant role of chemistry-induced electronic gap states in leading to identical metal/organic barriers for systems like Al-on-Alq@sub 3@ and Alq@sub 3@-on-Al; 2. the "p-like" doping induced by Au atoms deposited on, and diffused deep into, organic films like Alq@sub 3@ and F@sub 16@-CuPc; and the structural disruption in the F@sub 16@-CuPc stacks resulting from Al-F@sub 16@-CuPc chemical reaction, leading to considerable decrease in electron mobility through the material. General conclusions concerning metal/organic contacts will be discussed. Work supported by the MRSEC program of the National Science Foundation (DMR-9809483) and the NJCOE.

3:20pm **OF+EL+TF-ThA5 Organic Modified Schottky Contacts: Barrier Height Engineering and Chemical Stability***, **D.R.T. Zahn**, T.U. Kampen, S. Park,* TU Chemnitz, Germany*; A. Bushell,* University of Wales Aberystwyth*; M. Rus,* TU Chemnitz, Germany

The electronic properties of metal-GaAs(100)-contacts have been modified using 3,4,9,10-perylene-tetracarboxylic dianhydride (PTCDA) and dimethyl-3,4,9,10-perylen-tetracarboxylicdianhydride (DiMe-PTCDI). Silver is used as a top electrode. The influence of the organic films on the electronic transport properties was investigated using in situ current-voltage (IV) and capacitance-voltage (CV) measurements. The IV curves show a strong dependence on the modification of the Schottky contacts with PTCDA. The effective barrier height varies between 0.81 ~ 0.64 eV by changing the thicknesses of the PTCDA interlayer between 0 ~ 60 nm. For layer thickness above 60 nm space-charge limited currents in the organic layer determine the carrier transport in the diodes. The CV characteristics do not vary upon introducing an organic interlayer, indicating that the overall capacitance is dominated by the depletion layer within the GaAs substrates and that the width of the depletion region is hardly affected by the PTCDA modification. Therefore, the change in the effective barrier height can be explained by an increasing image-force lowering in the presence of the organic interlayer. The decrease in barrier height as a function of the organic layer thickness is not observed after an exposure of the samples to air. Here, barrier heights are independent of the organic layer thickness and have a value similar to the one of a bare Ag/GaAs(100) Schottky contact. This sensitivity to air is attributed to a reaction of the anhydride groups of the PTCDA with oxygen and/or water leading to carrier type conversion in the organic layer. Similar experiments are currently being performed using DiMe-PTCDI. First results also reveal a comparable decrease in barrier height. In addition, the DiMe-PTCDI modified Schottky contacts are found to be less sensitive to exposure to air because the imide groups are chemically more stable compared to the anhydride groups of the PTCDA.

3:40pm **OF+EL+TF-ThA6 Characterization of Organic/organic' Heterojunctions using UV and X-ray Photoemission Spectroscopies and Luminescence Quenching***, **D. Alloway**,* University of Arizona*; D. Schlettwein,* University of Bremen and University of Oldenburg, Germany*; N.R. Armstrong,* University of Arizona

Heterojunctions based on ultrathin films of perylenedicarboxylicbisimide (PTCDI) dyes, and various phthalocyanine (Pc) overlayers, have been explored using combinations of UPS and XPS, to define the band-edge offset of these systems, and quenching of the luminescence response of the PTCDI layers as a function of coverage of the Pc layer. Depending upon initial PTCDI coverage, the quenching of its luminescence response is extremely efficient using less than 1-2 monolayer coverages of Pc, and can be seen to be due to a combination of energy transfer, and exciton dissociation events. UPS measurements suggest small interface dipoles are formed for some of the PTCDI/Pc heterojunctions, especially those which are based on perfluorinated Pcs, which have high electron affinities. These interface dipoles have the potential to accelerate exciton dissociation, and may be of importance in the application of these systems to organic photovoltaic applications.

4:00pm **OF+EL+TF-ThA7 The Influence of Substrate Interactions on the Metallicity of Polyaniline Films****, **B. Xu**,* University of Nebraska, Lincoln*; J. Choi,* Louisiana State University*; P.A. Dowben,* University of Nebraska-Lincoln

Both Na doped and undoped short chain vapor deposited polyaniline (PANI) thin films were studied using angular-resolved photoemission spectrascopy (ARPES) and X-ray photoemission spectrascopy (XPS). Films, grown on two different substrates, Si and Au, using vapor deposition method show distinctly different properties. Some indication of preferential molecular orientation was observed for ultrathin film deposited on Au substrate, but not on the Si substrates. Clear indication of metallic character was observed for the undoped polyaniline films consistent with recent theory suggesting that for alignment of chain parallel with a metal substrate enhances metallicity. The polyaniline films became more insulating with sodium doping, suggesting that Na doping leads to an increase in insulating behavior that may due to the completion of band filling. @FootnoteText@ *Supported by the Office of Naval Research and the Nebraska Research Initiative.

4:20pm **OF+EL+TF-ThA8 The Electronic Structure Studies of Fluoride Layer Insertion between Al and Organic EL Material@footnote 1@***, Y. Park,* Korea Research Institute of Standards and Science, Korea*; J. Lee,* Korea Research Institute of Standards and Science*; D.Y. Kim,* Hallym University, Korea*; S.K. Lee,* Chonnam 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 X-ray and UV photoelectron spectroscopy (XPS and UPS) to probe the electronic structures of Al/fluorides/Alq@sub 3@ interfaces. While the presence of LiF layer exhibited enhanced gap states and concomitant formation of shoulder peak in N 1s core level peaks, insertion of other fluorides showed distinctively different behaviors. For example, the presence of MgF@sub 2@ does not form N 1s shoulder peak although weak gap states were observed. Other fluorides including CsF and CaF@sub 2@ are also studied. In addition, the mixture of Al, LiF, and AlF@sub 3@ sequentially deposited on Alq@sub 3@ were investigated. The various core level peaks in this system revealed that this combination does not distinguish LiF and AlF@sub 3@, rather it is more like a homogeneous mixture of LiF, AlF@sub 3@ and Al, which is in contrast to the view that the deposition of Al on LiF/Alq@sub 3@ forms AlF@sub 3@ and liberated Li. We discuss the implications of these results in the electrical properties of the interface and eventually the organic ELD performance that employs this type of electrodes. @FootnoteText@ @footnote 1@ This work was supported in part by MOST of Korea through NRL Program and ASSRC.

4:40pm **OF+EL+TF-ThA9 Direct Observation of Fermi Level Pinning at LUMO in Alkali Metal Doped Organic Films***, **L. Yan**, N.J. Watkins,* University of Rochester*; C.W. Tang,* Eastman Kodak Company*; Y. Gao,* University of Rochester

The electronic structures of pristine and alkali metal doped organic films are investigated using the combination of photoemission spectroscopy (PES) and inverse photoemission spectroscopy (IPES). The lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) can be directly observed by IPES and UPS simultaneously. We found that the Fermi level position in the organic film can be modified by alkali metal doping. For example, in CuPc films, the observed LUMO of the CuPc film is shifted by the Cs doping to less than 0.2eV above the Fermi level. This pinning may be explained by the charge transfer process from Cs to CuPc. Our observation is the direct confirmation of widely used assumption that the LUMO can be inferred from HOMO position in organic films when a valance band shift is observed. The result indicates that energy alignment and charge injection properties of the organic materials can be modified by a simple doping process. Our findings could lead to various interface-engineering methods useful in organic optoelectronic devices. Possible interface dipoles, energy level shifts, charge transfer, metal diffusion and chemical reactions at the interface will be discussed.

Organic Films and Devices
Room 134/135 - Session OF+SS-ThP
Molecular Aspects of Organic Films Poster Session

OF+SS-ThP1 In-situ Characterization of Photoisomerization Process and Thermal Stability of Highly Photoreactive SAMs on Gold with PM-IRRAS*, **T. Wei,*** National Institute of Advanced Industrial Science and Technology (AIST), Japan*; K. Tamada,* AIST and Frontier Research System, RIKEN, Japan*; H. Akiyama, K. Yase,* AIST, Japan*; S. Kim,* Hanyang University, Korea

In this paper, we discuss conformational change of photoreactive azobenzene SAMs composed of unsymmetrical disulfides on Au(111)/mica under UV/Vis photoirradiation, by use of polarization modulation infrared reflection absorption spectroscopy (PM-IRRAS). Two different azobenzene dyes are utilized in this study; One is a conventional azobenzene unit, and another is a "CH3-attached azobenzene" unit, in which methyl group is introduced to the azobenzene ring to avoid dye aggregation sterically. The "CH3-attached azobenzene" SAM exhibited the stronger nas-CH2 peak at higher frequency position compared with the conventional azobenzene SAM, sugesting more disordered film structures due to the methyl group. For in situ observation of photoisomerization reaction, we performed PM-IRRAS measurements under irradiation of 365nm UV light for cis, and 440nm Vis light for trans. For both unsymmetrical disulfide SAMs, with conventional azobenzene unit (C6AzSSC12) and with "CH3-attached azobenzene" unit (C6Az(Me)SSC12), the intensities of n(benzene ring) and nas (c-o-ph) vibration modes clearly decreased after UV irradiation, as a evidence of photo-isomerization reaction taking place. These IR spectrum changes by photoirradiation were not detected for azobenzene thiol SAMs. After annealing in oven at 100°C for three hours, the IR spectra of both disulfides (C6AzSSC12, C6Az(Me)SSC12) changed to the direction of more disordered or tilted chains, however, the change of C6Az(Me)SSC12 is rather larger than that of C6AzSSC12. These results were compared with our SPR and AFM data for thermal stability.

OF+SS-ThP3 Scanning Tunneling Microscopy Investigation of the Self-Assembly of Photochromic Molecules on Au(111)*, T. Fritz, **S. Mannsfeld**, T.W. Canzler,* TU Dresden, Institut fuer Angewandte Photophysik, Germany*; S. Stumpf, K. Gloe,* TU Dresden, Institut fuer Anorganische Chemie, Germany*; K. Leo,* TU Dresden, Institut fuer Angewandte Photophysik, Germany

The self-organization of photochromic molecules on Au(111) surfaces has been investigated by Scanning Tunneling Microscopy (STM). Self-assembly films of the organic molecule 6-[4-(phenylazo)phenoxy]hexane-1-thiol (AzoC@sub 6@) have been prepared by immersion of epitaxial gold films on mica in ethanolic solutions (1mmol) for 24 h up to 72 h. High-resolution STM images, using a NanoScope III in air, reveal the ordered growth of AzoC@sub 6@ in several domains, typically 20 nm in size. A detailed structural analysis was performed on drift-corrected images. In contrast to literature results where a so-called bundle model was suggested which can hardly explain the growth of rather extended domains, we will show evidence that a molecular lattice is formed which is commensurate with the Au(111) surface lattice. The two-dimensional unit cell contains two AzoC@sub 6@ molecules. All experimental findings are compared to theoretical calculations, based on a geometric lattice match algorithm.

OF+SS-ThP4 On the Relation between Experimental Vibrational Spectra and Spectra Determined from Ab Initio Calculations: Small Organic Molecules on Single Crystal Metal Surfaces*, **P. Uvdal**, M.P. Andersson,* Lund University, Sweden*; A.D. MacKerell, Jr.,* University of Maryland

Using small organic molecules, alkoxies and pyridine, adsorbed on single crystal metal surfaces we show that a detailed understanding of the vibrational spectra is possible with the aide of ab initio electronic structure calculations. Specifically we investigate on an ab initio level the surface induced alteration of (a) isotopic shifts (b) intramolecular coupling and (c) Fermi resonance coupling between binary modes and fundamentals. The experimental data is obtained in UHV using a FTIR spectrometer.

OF+SS-ThP5 Surface Plasmon Resonance Techniques for In Situ Detection of LCST Behavior on Surface-Grafted Polymer Films*, **S. Mendez**, S. Balamurugan, L.K. Ista, G.P. Lopez,* University of New Mexico

Thin films of the temperature responsive polymer, poly(N-isopropylacrylamide) (PNIPAAM), were polymerized in situ on azo-initiator derivatized self-assembled monolayers (SAMs). Carboxylic acid and methyl-terminated alkanethiols were used to form mixed component SAMs on gold substrates. Reaction of the COOH moieties with Woodwards reagent K and an amine containing azo-initiator resulted in immobilization of the initiator on the surface. PNIPAAM was then grown from the surface upon exposure of the surfaces to heat and monomer solution. Varying the concentration of COOH-thiolate within the original SAM allowed us to control the surface coverage of the polymer. Surface plasmon resonance (SPR) was used to detect the lower critical solubility temperature (LCST) transition of these surface-grafted polymers by taking advantage of a difference in both thickness and refractive index of the polymers in their relaxed (low temperature) and collapsed (high temperature) states. Realtime, in situ reflectance measurements of the PNIPAAM films immersed in water were taken as the temperature of the samples was raised. The effect of surface coverage on the position and degree of the transition was also examined.

Organic Films and Devices
Room 134/135 - Session OF+TF-ThP
Aspects of Organic Films Poster Session

OF+TF-ThP2 Tuning Supramolecular Self-assembly of Trimesic Acid Molecules on Cu(100) by Copper Adatoms*, A. Dmitriev, **N. Lin**, J. Weckesser,* Max-Planck-Institut for Solid State Physics, Germany*; J.V. Barth,* EPFL, Switzerland*; K. Kern,* Max-Planck-Institut for Solid State Physics, Germany and EPFL, Switzerland

Recently, it was reported that one-dimensional supramolecular nanostructures can be realized via intermolecular hydrogen bonding.@footnote 1@ Here we demonstrate that, for the system trimesic acid (TMA) on Cu(100), one can tune the intermolecular hydrogen bonding by adjusting the density and mobility of Cu adatoms and hence fabricate various supramolecular nanostructures. In our experiments submonolayers of TMA on Cu(100) have been prepared by organic molecular beam epitaxy (OMBE) under ultrahigh vacuum and in situ characterized by scanning tunneling microscopy (STM). The TMA molecules are parallel to the surface (flat-lying) as deposited and form hydrogen-bonded chicken-wire networks via dimerization of their carboxylic acid groups.@footnote 2@ These networks are only stable at low-temperatures (< 250 K) and at room-temperature rapidly transform into a stripe-like structure, where the TMA molecules are perpendicular to the surface (up-standing). By means of CO predosing, Cu coevaporation or adjustment of the substrate temperature the Cu adatom density and mobility have been controlled, which allows to convert the hydrogen bonded carboxylic acid dimers into copper-carboxylate complexes.@footnote 3@ Sequences of STM images directly demonstrate the real time formation and dissociation of single chemical bonds in copper-coordinated supermolecules. Cu adatoms of high density and mobility finally leads to well-ordered two-dimensional supramolecular nanostructures of large domain size on the surface. @FootnoteText@ @footnote 1@ J.V. Barth, J. Weckesser, C. Cai, P. Gunter, L. Bargi, O. Jeandupeux and K. Kern (2000) Angew. Chem. Int. Ed. 39, 1230-1234 (Angew. Chem. 112, 1285-1288). @footnote 2@ S.V. Kolotuchin, P.A. Thiessen, E.E. Fenlon, S.R. Wilson, C.J. Loweth and S.C. Zimmerman (1999) Chem. Eur. J. 5 No. 9, 2537-2547. @footnote 3@ C.C. Perry, S. Haq, B.G. Frederick and N.V. Richardson (1998) Surf. Sci. 409, 512-520. .

OF+TF-ThP3 Current Response of Nickel Phthalocyanine Ozone Sensing Films Formed by Plasma-activated Evaporation*, **S. Takeda,*** Takushoku University, Japan

Nickel phthalocyanine(NiPc) sensing films for O@sub 3@ gas have been fabricated by r.f.- plasma-activated evaporation and common vacuum deposition techniques. Sensor structure as a detecting element has a inter digital type Au or Pt electrode deposited on a glass substrate. Sensing NiPc films formed on the electrode are about 400 and 800 Å in thickness. Original value of electric resistance of the NiPc films between the electrodes is about 10@super -10@-10@super -11@ @ohm@ , but exposing the sensing film to O@sub 3@ gas it immediately changes down to 5-6 order of magnitude under the applied voltage d.c.1.5 V. Response time of the current corresponding to 63% of the saturated value (time constant 1 @tau@) is about 3.5 min. Due to more thinner NiPc films response time can be shorten and saturate more quickly. In this report we showed the data of only with 150 ppm but this kind of sensors can be detectable it more lower than 5 ppm. From the results of response characteristics, it suggests that absorbed O@sub 3@ gases on the NiPc film diffuse inside the film, so that the response time of cause, depends on the film thickness and structure. Comparing the response times with 400 and 800 Å, thinner one is shorter several times than the other, and also the films prepared by plasma-activated evaporation respond quickly than that the films without plasma-activation. To clarify the reason of different responses, morphologic images of the NiPc films were observed by Atomic Force Microscope. Surface of the films formed by common vacuum deposition is likely needle crystals but the other films show very flatness.

OF+TF-ThP4 Mobility, Binding Transition and Ordering of C@sub 60@ on Pd(110): Investigations at the Local and Mesoscopic Scale*, **J. Weckesser**,* Max-Planck-Institut fuer Festkoerperforschung, Germany*; C. Cepek,* Laboratorio Nazionale TASC-INFM, Italy*; R. Fasel,* Swiss Federal Laboratories for Materials Testing and Research, Switzerland*; J.V. Barth,* Ecole Polytechnique Federale de Lausanne, Switzerland*; T. Greber, J. Osterwalder,* Universitaet Zuerich, Switzerland*; K. Kern,* Max-Planck-Institut fuer Festkoerperforschung, Germany

We present a comprehensive study of C@sub 60@ on a Pd(110) surface using scanning tunneling microscopy (STM), low-eneregy electron diffraction (LEED), x-ray photoelectron spectroscopy and diffraction (XPS and XPD). The mobility and interactions of C@sub 60@ on a Pd(110) surface have been characterized by variable temperature scanning tunneling microscopy. The motion of isolated C@sub 60@ molecules was directly monitored and the corresponding tracer diffusion barrier was determined to (1.4±0.2) eV. Upon annealing to 700 K the C@sub 60@ molecules undergoe an irreversible bonding transition resulting in a second, more strongly bound C@sub 60@ species. This is associated with a local substrate reconstruction whereupon C@sub 60@ molecules sink into the formed microscopic pits. The rearrangement of Pd substrate atoms turns out to play a crucial role similarly in the formation of C@sub 60@ thin films. In STM three well-ordered structures consisting of alternating dark and bright molecular rows are found, in combination with LEED and XPS their real space structures are determined. The height difference in STM is attributed to a local reconstruction of the Pd substrate. Whereas the C@sub 60@ molecules of the bright molecular rows are adsorbed in one layer deep microscopic pits, C@sub 60@ accommodated in two layer deep pits account for the dark molecular rows. XPD results complete the understanding of the film structure and reveal the orientation of the C@sub 60@ cages.

OF+TF-ThP7 In-situ Synthesis of Self-assembled Polyaniline/ Poly(styrene sulfonic acid) Composite Ultra Thin Films*, **T. Koga**, H. Otsuka, A. Takahara,* Kyushu University, Japan

In-situ preparation method of self-assembled polyaniline (PANI)/ poly(styrene sulfonic acid) (PSS) composite ultra thin films on aminosilane grafted surfaces was proposed. PSS was adsorbed onto the aminosilane grafted Si-wafers, then PANI/ PSS composite ultra thin films were prepared in-situ by template polymerization utilizing ionic interaction between PSS and aniline. PANI/ PSS composite ultra thin films were characterized by time of flight secondary ion mass spectroscopy (TOF-SIMS), atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), and ultraviolet-visible-near infrared (UV-Vis-near IR) spectroscopy. Composition of PANI/ PSS composite ultra thin films estimated by XPS gave good agreement with the calculated value based on the chemical structures. AFM images and UV-Vis-near IR spectra revealed that the progress of conjugation of PANI/ PSS composite ultra thin films. From these results, it can be inferred that the formation of ultra thin films is closely related to the electrostatic character of functionalized substrate surfaces. In this method, PSS plays an important role as a template for polymerization of aniline. Therefore, the positively charged surfaces facilitated the formation.

OF+TF-ThP8 Growth and Nucleation of 2-methyl-4-nitroaniline (MNA)*, **K. Nam**, K.I. Seo, L. Wang, C.E. Bonner,* Norfolk State University*; E.S. Gillman,* Jefferson Lab

Despite the intense interest in the microstructure of MNA over the last decade, a detailed understanding of its structure with respect to growth conditions is still not clear. A relationship between structure and growth of thin films is often sought, however in many instances these relations are vague and complex. One reason is that thin film properties generally vary by orders of magnitudes depending upon preparation conditions. Thin films are, in general, not ideal materials systems in terms of bond distortion, coordination, point defects, dislocations, compositional inhomogeneities and impurities, grain boundaries and disordered low-density void regions. These defects are created by a complex array of parameters that are directly related to the surface interface. Thus, it is expected that any quantitative description of preparation-property relations must first start with a quantitative description of its internal and external morphology. Here we present results for MNA thin films that are grown using an organic molecular beam deposition (OMBD) technique.

OF+TF-ThP9 The Dielectric Properties of P(VDF-TrFE) Copolymer Thin Films by Physical Vapor Deposition*, **G.B. Park**,* Yuhan College, Korea*; M.Y. Chung, J.H. Yoon,* Inha University, Korea*; S.H. Park,* Unix Electric Co. Ltd, Korea*; S.H. Lee,* Korea Institute of Industrial Technology, Korea*; D.C. Lee,* Inha University, Korea

The copolymer thin films of poly(vinylidene fluoride-trifluoroethylene), which shows excellent piezoelectricity and pyroelectricity, were fabricated by physical vapor deposition method in the compositions 70/30 and 80/20 mol%. The effect of the substrate temperature and the mol% rates on the molecular structure, the dielectric and piezoelectric properties was investigated. In deposition process, the substrate temperature(Ts) was varied from 30°C to the Curie transition temperature(Tc). From the results of deposition rate, molecular and crystal structure of the films, it was found that 300°C was the optimal evaporation temperature in the process. The @beta@-form characteristic peaks increased with increasing the substrate temperature on account of the increase of the crystallinity, but over 90°C the peaks decreased according to the phase transition from the ferroelectric crystal phase to the paraelectric crystal phase. From this results, the copolymer films were fabricated from 30°C to 90°C substrate temperature. The relative dielectric constant decreased as a form of anomalous dispersion with increasing measurement frequency. With increasing Ts, the relative dielectric constant increased from 3.643 to 5.29 on the 70/30mol% films, and from 4.367 to 10.77 on the 80/20mol% films, respectively. The @alpha@ relaxation by interfacial polarization and the @beta@ relaxation by dipole orientation polarization were observed in low and high frequency region, respectively. The @alpha@ relaxation decreased and the @beta@ relaxation increased with increasing Ts. From the results, it is suggested that the crystallinity of the films increased with increasing Ts. The effect of increasing Ts on the piezoelectric properties will also be discussed in detail.

OF+TF-ThP11 Optical Characterization of ZnO-CdO Thin Films Grown by Sol-Gel Method*, **T. Hata**, H. Komaki,* Miyazaki University, Japan

Wide bandgap oxide-semiconductors have attracted much attention for liquid crystal displays and solar cells. Recently, ZnO based materials are much respected for UV light-emitting devices. ZnO is a semiconductor with a large bandgap of 3.4 eV and a large excitonic binding energy of 60 meV. CdO is an also semiconductor with a direct bandgap of 2.3 eV and small indirect bandgap of 0.8 - 1.1 eV. The bandgap energy can be changed from 2.3 to 3.4 eV on ZnO and CdO mixed crystal. Moreover, although CdO is known to have a poor optical transmittance in the visible spectral region in comparison with those of ZnO films, CdO thin films are enough to be used for the window material for solar cells. Pure ZnO and CdO films have been studied many research groups. However, ZnCdO films have been few studied previously.In this work, ZnO-CdO thin films were grown by sol-gel dip coat method on glass and Silicon (Si) substrates at 100 ~ 600 °C under air atmosphere. The sol-gel technique is known to have the distinct advantages of process simplicity, lower cost and ease of composition control. Precursor solutions of ZnO-CdO are prepared by dissolving both 5 wt.% zinc acetate dihydrate and 5 wt.% cadmium acetate dihydrate into anhydrous ethanol for the solutions to have the desired Cd/Zn at.%. Poly-ZnO and -CdO thin films are obtained on the glass substrate more than 500 ¡C and 200 °C, respectively. A value of full width at half maximum of (100) peak at the XRD spectra become small with the increasing the growth temperature. By using the Si substrate (100) instead of the glass substrate, poly-ZnO and -CdO thin films have (100) orientation. Moreover, an optical transmittance and bandgap energy of the Zn@sub X@Cd@sub 1-X@O thin films decrease nonlinearly with the decreasing X values.

OF+TF-ThP12 XPS Study of Conducting Polymer Film Growth on Si(111) by Electrochemical Deposition Method*, H. Kato, **S. Takemura**,* Kanto Gakuin University, Japan

Electochemically deposited conducting polymer polythiophene (PT) films on Si(111) were investigated by XPS. PT/Si(111) interface at the initial stage of electrochemical polymer growth was closely investigated by analyzing the core-level energies and spect ral profiles of the atomic components. Spectral profiles of Si core-level spectra showed that both Si 2s and 2p spectra were basically composed of different three Gaussian components correspond to different valence states of Si in contrast to the core-lev el spectra of non-deposited Si(111). The lower peaks (LS1 and LS2) observed in Si 2p spectra of PT/Si correspond to the Si states with strong interaction between Si and PT. The peak height of LS1 slightly increases and LS2 drastically grows in the case of PT polymer growth on Si substrate. The C 1s core-level spectrum was composed of a higher energy component and a lower energy component originated from the polymer backbone and oxidized Si layers, respectively. Affinity between a deposited polymer PT film and Si substrate was strong compared with the case of a PT film deposited on ITO substrate expecting bondings between polymer chains and Si substrate layers.

OF+TF-ThP13 XPS Studies of Conducting Polymer Hybrid Films Incorporated with Dye Molecules*, **H. Kato**, S. Takemura, N. Aragaki,* Kanto Gakuin University, Japan

Conducting polymer polythiophene (PT) films incorporated with dye molecule safranine T (ST) prepared by electrochemical doping and diffuse injection methods were investigated by XPS. Polymeric structure, charge transfer and interaction between dye molecul e and PT backbone in the hybrid films were closely investigated by analyzing the core-level energies and spectral profiles of the atomic components. XPS core-level analysis of N 1s showed that dye molecules were injected into polymer matrix in hybrid fil ms. In the case of PT film incorporated with ST, drastic change of C 1s, S 2p, and Cl 2p core-level spectra between electrochemically as-grown and reduced films was observed. In the case of electrochemically reduced sample core-level energies of C1s and S 2p were shifted to the lower energy side indicating the creation of n-type polymer chain while in the case of electrochemically as-grown sample the polymer chain is p-type. The splitting of S 2p reflects the strong interaction betwen ST molecule and PT backbone. The C 1s core-level spectrum varied with the degree of electrochemical reduction. The C 1s spectrum is basically composed of two different Gaussian components. In the highly reduced case lower energy component grows while in the low reduced case higher energy component becomes dominant. The spectral change reflects the existence of different charged states in polymer backbone.

OF+TF-ThP14 Surface Freezing and Self-ordering Phenomena of Long Chain n-Alkanes Studied by Newly Developed High Vacuum DTA Apparatus*, **Y. Ouchi,* Nagoya University, Japan*; Y. Yamamoto,* Nagoya Institute of Technology, Japan*; M. Kuroi, N. Yamaguchi, H. Ishii, K. Seki,* Nagoya University, Japan

We developed a new apparatus of differential thermal analysis (DTA) capable of simultaneous measurement of UPS, XPS, NEXAFS etc to investigate phase transitions of ultra-thin films of organic molecular systems. The apparatus is installed in a high vacuum chamber for thermal isolation and measurements of photoelectron emission. The performance of the apparatus was examined using a 650 Å-thick pentacontane (n-C@sub 50@H@sub 102@) film, which may exhibit a unique monolayer phase transition at air (vacuum)/liquid interface, known as a surface freezing self-organization effect. We observed two anomalies of DTA curve around the bulk melting temperature, one of which is apparently due to thebulk melting. Since the temperature dependence of the surface specific UV photoemission measurements showed corresponding changes in photoemission current, we could conclude that the other phase transition peak originates from the formation of frozen (crystallized) single molecular layer located at the top alkane liquid surface. We will report the detailed analysis on the transition entropy and the chain length dependence of the temperature region of the existence of this unique surface freezing layer up to n=72. Though it was believed from grazing X-ray reflection measurements that the effect will disappear around n=60, our DTA system could confirm their existence over n=60. This demonstrates that our DTA apparatus is sufficiently sensitive to examine the 2D phase transitions of monolayers. Simultaneous measurement with other photoelectron emission measurement will be beneficial for the investigation of temperature dependence of organic thin films and its self-organization process.

OF+TF-ThP15 Comparison of Alkyl-phosphonic Acid (APA) and Alkyl-carboxylic Acid (ACA) Self Assembled Monolayers on the Hydrated Alumina Surface of Aluminium*, **T.A. Lewington,*** UMIST, UK, U.K*; G.E. Thompson, M.R. Alexander,* UMIST, UK*; E. McAlpine,* Alcan International, UK

The interaction of organics with metal oxide surfaces is important in many areas including corrosion protection and adhesion promotion. Good corrosion protection has been obtained using APA SAMs deposited on Al prior to painting.@footnote 1@ The phosphonic acid head-group interacts with the surface of alumina to form a phosphonate bond.@footnote 2@ It is presumed that resin components react with the phosphonic acid tail-group when di-functional molecules are used. Detailed characterisation of ACAs on Al has been reported but not of APAs.@footnote 3@ The formation of alkyl-thiol SAMs on Au has been extensively studied.@footnote 4@ In contrast to the stable Au metal surface Al forms an oxide, the outer region of which is readily hydrated on exposure to ambient conditions. Two approaches have been employed to obtain reproducible Al surface chemistry for self-assembly: solution pre-treatment or atmospheric exposure. Here, SAMs have been formed on sputtered Al by immersion in 5 mM ACA and APA solutions in n-hexadecane and ethanol respectively. Surface pre-treatment with acetic or methyl-phosphonic acid was compared with 24 h atmospheric exposure. Both XPS and contact angle measurement of SAMs on Al indicate relationships between assembly, time and alkyl chain length similar to alkyl-thiols on Au. Notable differences include changes in the oxide surface, found by XPS to occur in ethanoic solutions, and the importance of pre-treatment. FTIR provides information on the orientation of the SAM and the bonding to the surface. This enables a model of the APA-Al system to be proposed, which may be compared with existing models of ACA-Al. The electrochemical properties of uncoated SAMs are investigated using cyclic voltammetry and rationalised in terms of the models. @FootnoteText@ @footnote 1@I Meage et al. Prog Org Coat 34(1998)1 @footnote 2@RD Ramsier et al. Surf Sci 203(1998)72 @footnote 3@DL Allara, RG Nuzzo Langmuir 1(1985)52 @footnote 4@GM Whitesides, PE Laibinis Langmuir 6(1990)87.

OF+TF-ThP17 Giant Polarization in Organic Heterostructures*, **T.U. Kampen**, I. Thurzo, D.R.T. Zahn,* TU Chemnitz, Germany

Deep levels or polarization effects can influence the charge transport through organic layers. Both effects can be identified by charge deep-level transient spectroscopy (Q-DLTS). Here, deep levels or polarization effects cause the charge transient signal Q(t) to be dependent or independent on the bias voltage, respectively. Q-DLTS, accompanied by feedback charge capacitance (FCM) measurements, has been used in the present work to investigate an organic heterostructure grown on an inorganic semiconductor. GaAs(100) substrates (n = 0.3 4x10@super 18@ cm@super -3@) were sulfur passivated by wet chemical etching and additional annealing under ultra-high vacuum (UHV) conditions. Organic molecular beam deposition was used for the growth of 20 nm of 3,4,9,10-Perylenetetracarboxylic dianhydride (PTCDA, Lancaster) and 27 nm of tris-(8-hydroxyquinoline) aluminum (Alq3, Syntec). Silver was evaporated on the Alq3 film through a shadow mask resulting in an array of circular contacts with an area of A = 2.1x10@super -7@ m@super 2@. The back contact to the GaAs(100) was achieved by an In-Ga-alloy resulting in a series resistance of less than 20@OMEGA@. The electrical characterisations were done at room temperature and in situ in the UHV system. The Q-DLTS measurements show a well resolved maximum in Q(t). The amplitude remains almost constant as a function of the bias voltage, which is a clear indication of a polarization in the organic heterostructure. From the experimental results the permittivity dispersion is determined to 2.37. The permittivity dispersion is independently obtained from FCM measurements. With the experimentally determined excess capacitance @DELTA@C of 90 pF and the thickness of the organic heterostructure the permittivity dispersion is determined to 2.42. The FCM scans show no hysteresis due to the absence of deep levels. The @DELTA@C/C = 1 presented here clearly indicates the presence of a giant polarization.

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