Organic Films and Devices
Room Exhibit Hall B - Session OF-TuP
Poster Session

OF-TuP1 Fabrication of Micro-Pumps for Organic Micro-Fluidic Devises using Asymmetric Electrode Arrays, ***H.G. Jeong***, *M. Dhayal,* Dongshin University, South Korea*; H.J. Lee,* Chonnam National University, Korea*; J.S. Choi,* Dongshin University, South Korea

Recently micro-fluidics devises are of a great interest to use in fabrication of "lab-on-a-chip" and micro electromechanical systems (MEMS). A new types of microelectrodes structures have been developed for controlling fluid movement in micro-systems using AC electric fields. In our research we are developing a design tool of asymmetric electrode arrays to fabricate micro-fluidic devises to use in control of different biological fluids. An optimisation of performance of the bio-MEMS fabricated using conventional techniques such as photolithography and reactive ion etching in our study has been also investigated.

OF-TuP2 Investigation on the Interfacial Reaction of Metal/Fluorinated Polymide, ***C.-Y. Yang***, *S.L.-C. Hsu, J.-S. Chen,* National Cheng Kung University, Taiwan

In this work, the surface states of fluorinated polyimide synthesized from 6FDA-BisAAF-PPD, before and after plasma treatment, were characterized by X-ray photoelectron spectroscopy (XPS). The interfacial states of metal-fluorinated polyimide were examined by XPS after metal films of Cu, Cr and Au were deposited onto the fresh cured fluorinated polyimide with or without plasma treatment. The influence of plasma treatments on interfacial reaction was examined. XPS analysis results reveal that the surface of fluorinated polyimide will be oxidized and nitridated after O2 and N2 plasma treatment. In the metal/polyimide interface, chemical bonding of Cr-C is observed in the untreated polyimide system. However, no metal-carbon bonding is found in the Cu, Au and polyimide interface. Slight interface change is observed after the N2 plasma treatment. In addition to M(metal)-C bonding, M-C-O bonding is also observed at the metal-polyimide interface in those samples with O2 plasma applied to the polyimide surface. The relationship between adhesion and interfacial reaction of metal/fluorinated polyimide, and the role of fluorine in the interfacial reaction are also discussed.

OF-TuP3 XPS and FTIR Studies of Dye Molecule Doped Conducting Polymer Films, ***H. Kato***, *S. Takemura,* Kanto Gakuin University, Japan*; O. Nishikawa, M. Taniguchi,* Kanazawa Institute of Technology, Japan

Conducting polymer polythiophene(PT) films incorporated with dye molecule such as brilliant green(BG) were prepared by electrochemical doping and diffuse injection methods. Charge transfer and interaction between the doped dye molecule and PT polymer chains were investigated by analyzing the core-level energies and spectral profiles of the atomic components. Vibrational states of the doped dye molecule and the polymer backbone were also investigated by FTIR RAS and ATR in order to examine the dopant configuration into polymer chains in the hybrid films. In the case of brilliant green doping, XPS core-level analysis of S 2p split indicates simultaneous doping of BG cation and HSO4- in the hybrid films prepared by electrochemically reduced and dye diffuse injection methods. Synthesized film samples were categorized into two types by the difference of S 2p core-level energy shift. In the cation-like doped sample, the energy shift of the lower peak of S 2p suggests the charge transfer between BG molecule and polymer chains creating a n-type conducting polymer state. The polymeric state and the dopant configuration were also investigated by FTIR. CH in plane modes of the PT backbone which appeared around 750 cm-1 and ring stretching modes which appeared around 1050 cm-1 indicate the polymeric structure based on a thiophene ring. The profile of the vibrational spectra reflected the detailed polymeric structure. The orientation of the dopant BG molecule in the hybrid films was discussed by analyzing the benzene out-of-plane mode of a BG molecule which appeared at 2000 cm-1.Three possible BG configuration models were closely discussed.

OF-TuP4 Effects of High Electric Fields on Charge Transport and Morphology in Solution Processed Conducting Polymer Films, ***P.S. Chung***, *P.H. Holloway,* University of Florida

One of the attractive qualities for using organic materials for electronic applications is their ability to be processed in solution, which ultimately leads to lower processing costs. A major obstacle preventing organic electronics from obtaining a greater share in todayâ?Ts technological markets is their inferior performance characteristics when compared to traditional inorganic materials. Polymer and molecular orientation are key issues in governing the electrical and morphological properties of the film. In this study, spincoated films consisting of p-type polymers (i.e. polyvinyl carbazole) and n-type dye molecules (i.e. 3,9-perylenedicarboxylic acid dissobutyl ester) are subjected to high electric fields (200 V/cm to 15,000 V/cm) during solvent evaporation. The polar sidegroups and branches on the polymer and molecule adjust their orientation under the electric field, thereby improving the electrical and morphological properties of the film. Models to quantitate these effects will be presented and discussed.

OF-TuP5 Topology and Growth Behavior of Evaporated Organic Films on Crystalline Metal Layers: Perylene-3,4,9,10-Tetracarboxylic Dianhydride (PTCDA), ***K. Seo***, *M. Haythe, C. Bonner,* Norfolk State University

PTCDA films were prepared on metal films under four different deposition conditions employing all combinations of low and high substrate temperature with various deposition rates. The films were grown by organic molecular beam deposition (OMBD) in an ultrahigh vacuum chamber from a Knudsen cell, using sublimation temperatures of 430, 380 and 330 ºC, respectively. The grazing-incident-angle x-ray diffraction (GIXD) technique has been measured the anisotropy of the structure in the directions perpendicular and parallel to its surface. We have used the real-time in-situ spectroscopic ellipsometry to determine the optical functions of PTCDA films. The influence of the substrate temperature on the metal films is investigated using spectroscopic ellipsometry and atomic force microscopy. We have found that the grain size of the crystallites and surface roughness increase with increase substrate temperature.

OF-TuP6 Poly(3-hexylthiophene) Organic Thin Film Transistor on Polyimide using Electroplated Gold Electrodes, ***J.G. Lee***, *S.H. Cho, S.W. Na, N.-E. Lee,* Sungkyunkwan University, South Korea

Organic thin film transistors (OTFT) on flexible substrate using electroplated gold electrodes have potential advantages in the fabrication of low cost sensors, smart cards, and field-effect transistors. This method can be a competitive candidate for OTFT applications requiring large area coverage, structural flexibility, low temperature processing, and especially low cost. In particular, the application of electroplating enables one to obtain electrode with high aspect-ratio and good reliability in terms of mechanical flexibility and thermal stress. In this work, poly(3-hexylthiophene) (P3HT) OTFT device uses a top gate structure with electroplated Au source and drain electrodes. Organic thin film transistors (OTFTs) were fabricated using (P3HT) as a semiconducting layer and electroplated gold (Au) as source and drain electrodes. First, since the adhesion of electrodes on the flexible substrate is of great importance for the application in flexible devices, the adhesion improvement of electroplated electrode structures was investigated by plasma treatment of polyimide substrate by using Au/Cu/Cr/polyimide structures. Cu(seed)/Cr(adhesion) layers were sputter-deposited in sequence on the plasma-treated polyimide substrate. Then, a negative photoresist, SU-8, was spin-coated on the Cu/Cr/polyimide substrate and patterned by ultra-violet photolithography for source and drain electrodes. After photolithography, Au source and drain electrodes were electroplated into the patterned SU-8 mask. After P3HT film was spin-coated, SiO@sub 2@ gate dielectrics and Al electrode were evaporated with a shadow mask. The channel length ranged between 10 and 25 µm, and the channel width was 800 µm. Electrical properties of fabricated OTFT were characterized and the effect of various process conditions and structures on the performances of fabricated devices will be discussed. Keyword Organic thin film transistor, P3HT, Au electroplating, polyimide, flexible devices.

OF-TuP7 Influences of Ion Irradiation for Depositing Aluminum Cathode in Organic Light-emitting Diodes, ***S.M. Jeong***, *W.H. Koo, S.H. Choi, S.J. Jo, H.K. Baik,* Yonsei University, Korea*; S.J. Lee,* Kyungsung University, Korea*; K.M. Song,* Konkuk University, Korea

To demonstrate the effects of argon ion irradiation during cathode deposition, aluminum cathode prepared by ion beam assisted deposition process on spin-coated soluble phenyl-substituted poly-p-phenylene-vinylene (Ph-PPVs) thin films have been investigated and compared to those by thermal evaporation. Although energetic particles of Al assisted by Ar+ ion may damage the organic material, I-V-L characteristics are improved by applying thin Al buffer layer. It may be deduced from the smaller contact resistance between Al and Ph-PPV induced by large contact area, increase of density of state and lithium diffusion in ion beam assisted device. In addition, highly packed structure of Al cathode inhibits the permeation of H@sub 2@O and O@sub 2@ into Ph-PPV film through pinhole defects, and thus retards dark spot growth. In conclusion, the lifetime of organic light-emitting device (OLED) has been extended through ion beam assisted deposition process.

**OF-TuP8 The Effect of Atmospheric Pressure Plasma Treatment on Indium Tin Oxide Anode for Organic Electroluminescent Devices*, S.H. Choi*, *S.M. Jeong, W.H. Koo, H.K. Baik,* Yonsei University, Korea*; S.J. Lee,* Kyung Sung University, Korea*; K.M. Song,* Kon Kuk University, Korea

The effect of atmospheric pressure plasma (APP) treated indium-tin-oxide (ITO) substrate on poly (9,9-dyoctilfluorene) (PFO)-based light-emitting diodes was studied. It was found that the chemical composition and surface roughness at the ITO surface were changed after APP treatment. Organic light-emitting diodes (OLEDs) fabricated on APP treated ITO surfaces showed three times better electroluminescence and current injection than OLEDs fabricated on as-received ITO surfaces, due to the increase of the smooth contact area between the ITO surface and the organic layer. The ITO substrate after APP treatment showed similar behavior of LPOP. Therefore, APP is an effective treatment for enhancing the performance of OLEDs.

OF-TuP9 Characterization of Porphyrin Monolayers Bearing (O, S, and Se) on Si and Au: Towards Hybrid Memory Storage in Electronic Devices*, A.A. Yasseri*, *F. Zaera,* University of California Riverside*; J.S. Lindsey,* North Carolina State University*; D.F. Bocian,* University of California Riverside

We report on the characterization of a novel group of redox-active porphyrin molecules synthesized with terminal chalcogen subunits for attachment on to electro-active surfaces. A series of porphyrins has been prepared and characterized as surface bound redox-active monolayers. The molecules designated as (ZnPBz-,ZnPCH2-) bear two linker types substituted on a meso-position of the porphyrin and are terminated with a diverse series of surface anchor groups in free and protected form (hydroxy, S-acetylthio, and Se-acetylseleno) for attachment to Si (100) and Au (111). Communication with the covalently bound adsorbates is achieved through activation of pre-patterned Si-hydride test-platforms to anchor the Si-O, Si-S, or Si-Se tethers to the surface. Similar monolayers were prepared as SAMs on Au yielding analogous Au-S and Au-Se tethers for comparison. Each porphyrin was investigated on Au and Si surfaces using X-ray photoelectron spectroscopy, Fourier transform infrared spectroscopy, and various electrochemical methods including (fast scan cyclic voltammetry, swept-waveform AC voltammetry, and open circuit amperometry). The objective of the study was to demonstrate the (1) the chemical robustness of monolayer binding through each anchor group to the surface, (2) measure the packing density of the molecular monolayers on each surface, (3) and to probe the influence that terminal surface anchor groups (O, S, Se) and linker type bear on the electron transfer (in presence of applied potential) and charge retention (in absence of applied potential) characteristics of the monolayers on each platform. XPS, FTIR, and voltammetric measurements confirm semi-quantitative displacement of surface di-hydride species with -O, -S, and -Se terminated porphyrins, respectively. The electron transfer kinetics of the Si-O, Si-S, and Si-Se indicate that the kinetics strongly depend on the linker type and surface concentration of the porphyrin monolayers, independent on the substrate used.

OF-TuP10 Assembly of Synthetic Molecular Motors on Surfaces*, T. Takami*, Visionarts Research, Japan*; T. Ye,* The Pennsylvania State University*; J.M. Tour,* Rice University*; K.-I. Sugiura,* Tokyo Metro. Univ., Japan*; P.S. Weiss,* The Pennsylvania State University

We attempt to assemble synthetic molecular motors mounted on Au{111} and graphite surfaces. Two kinds of molecular motors are proposed: (1) in-plane rotation of molecular rotors: the substrate-bound shaft of the rotor assembly, a metal porphyrin is attached to the shaft through axial ligation with a pyridine group, (2) perpendicular rotation of molecular rotors: sandwich porphyrins are used for the tables to stand on the surface and a perpendicular bifunctional shaft is attached between the porphyrins. The rotation of the molecular motors will be imaged with scanning tunneling microscope (STM) in air and in solution, and will be detected via single molecule resonance spectroscopy with alternating current STM (ACSTM).

OF-TuP11 Chemical Conversion Patterns of the 1,7-octadien Monolayer on Si(111) Surface*, S.H. Lee,* Nagoya University, Japan*; N. Saito,* Nagoya University, Japan, Japan*; T. Ishizaki, O. Takai,* Nagoya University, Japan

The organic monolayer covalently attached to silicon has been expected to have a better chemical resistivity compared to organosilane monolayer. The Si-C interface provides a good electronic property for molecular devices constructed on silicon substrate. Many researchers have reported the structural configurations and the chemical bonding states of such organic monolayers. However, scanning probe lithography on the organic monolayers has been reported scarcely. In particular, the electronic properties of nanopattern lithography have not yet been understood. In this study, we investigated the surface potential at the locally scanned area, i.e., nanopattern, onto an organic monolayer formed on a Si substrate. An oxide layer on a Si substrate was removed using chemical etching for 15min in NH4F solution. The substrate was immersed in 1,7-octadien (OD) solution heated at 120°C for 1hour. The OD molecules reacted with the hydrogen-terminated Si surface, resulting in the formation of an OD-monolayer on the substrate. Atomic force microscope (AFM) lithography on the OD-monolayers resist was performed using SPI-3800N AFM with a Si probe in contact mode by applying a positive or negative bias. The pattern on the OD-monolayers resist was fabricated by VUV irradiation thorough a mask. The chemical changes of the OD surfaces were traced by Kelvin probe force microscope (KFM), AFM and fluorescence-labeled spheres.

OF-TuP12 Site Specific Binding of Analyte Gases on Metallophthalocyanine Thin Films: Dft Calculations and Sticking Probability Measurements*, N.L. Tran,* University of California, San Diego, U.S.A*; G.C. Poon, S. Bishop, A.C. Kummel,* University of California, San Diego

Several groups report the use of metallophthalocyanines (MPcs) as thin film resistive sensors for analyte gases such as NO@sub x@, CO, O@sub 3@ and NH@sub 3@; however, the chemisorption energies and mechanisms for these gases reacting with various MPcs have not been studied. Density functional theory (DFT) calculations performed in this study show that chemisorption energies vary strongly with metal center and analyte. These calculations also investigate the mechanism of chemisorption. Four analyte binding sites on the MPcs were investigated computationally: (i) metal centers, (ii) inner ring nitrogen atoms, (iii) outer ring nitrogen atoms, and (iv) organic rings. For NO@sub 2@ on FePc and CoPc as well as NH@sub 3@ on FePc , the simulations show chemisorption onto the metal centers and physisorption onto the outer ring nitrogens and organic rings. These calculations also show a multi-step absorption mechanism in which NO@sub 2@ initially binds to the inner ring nitrogens and subsequently migrates to the deep chemisorption well on the metal centers for FePc and CoPc. In contrast, only physisorption was observed for any bonding sites of NO@sub 2@ on NiPc and NH@sub 3@ on CoPc and NiPc. Sticking experiments are being performed to investigate the chemisorption mechanism and selectivity.

OF-TuP14 Organic Polymer Thin Films Deposited on Silicon and Copper by PECVD Method and Characterization of Their Electrochemical and Optical Properties*, I.-S. Bae,* *S.-H. Cho, Z.T. Park, J.G. Kim, J.-H. Boo,* SungKyunKwan University, South Korea

Polymer-like thin films have been deposited on glass, silicon and copper substrates at temperature range of room temperature and 100 °C by plasma enhanced chemical vapor deposition (PECVD) method using Cyclohexane as a precursor for analysis their electrochemical and optical characteristics. Cyclohexane was utilized as organic precursor, and hydrogen and Ar were used as a bubbler and carrier gases, respectively. In order to compare the difference of the corrosion resistant and the optical properties of the plasma polymerized organic thin films with conditions of various RF (radio frequency using 13.56 MHz) power in the range of 20~50 W and deposition temperature. The optical and electrical properties of the as-grown plasma polymerized thin films were analyzed by FT-IR, UV-Visible spectroscopy, I-V and C-V curves. The corrosion protective abilities of Cyclohexane were also examined by AC impedance measurements in 3.5 wt.% NaCl solution. We found that the corrosion protection efficiency (P@sub K@), which is one of the important factors for corrosion protection in the interlayer dielectrics of microelectronic devices application, was increased with increasing RF power. The highest P@sub K@) value of plasma polymerized Cyclohexane film was (85.26% at 50 W), AFM and SEM showed that the polymer films with smooth surface and sharp interface could be grown under various deposition conditions.

OF-TuP15 Damage Mechanism of Emitting Polymer Treated by Low Pressure Plasma*, D.Y. Lee,* *H.K. Baik,* Yonsei University, Korea*; K.M. Song,* Konkuk University, Korea*; S.J. Lee,* Kyungsung University, Korea

In this study, we investigated the damage mechanism of emitting polymer (poly(9,9-dioctylfluorene)(PFO)) films for organic light emitting diode (OLED). For top emission organic light emitting diode (TOLED), indium tin oxide (ITO) films are used as a cathode material due to its high transparency in visible light. In conventional, ITO is deposited by RF/DC magnetron sputtering. But there have been many reports that sputtering process including high energy ions and neutrals degrades emitting polymer. Therefore, metal buffer layer must be inserted between emitting polymer and ITO films, not only to improve electron injection but also to prevent polymer damage. It is very important to reduce a thickness of buffer layer as thin as possible so that low driving voltage and high transparency are achieved. However, low thickness of buffer layer is not effective in prevention of polymer damage from magnetron sputtering. So, this problem is pending unsolvable. We used plasma treatment on emitting polymer (PFO) to eluciate damage mechanism so as to find effective solution for polymer degradation. Low pressure glow discharge was perform with He and O2 gas at 2ï‚´10-1 torr. Anode electrode is patterned ITO films and hole transport layer is PEDOT. Al/LiF films were deposited on blue Emitting polymer (PFO) as a electron injection layer and cathode buffer. ITO films was fabricated by RF magnetron sputtering at room temperature. ITO target (SnO2: In2O3 = 1: 9) was sputtered by mixture gas of argon and oxygen. Oxygen partial pressure, working pressure and other deposition parameters were optimized. RF coupled DC was used as a power source and its voltage was changed from 45 V(only RF) to 350 V(only DC). The temperature of cesium reservoir was varied from 80 to 200 Â°C. Negative sputtered particles including In, Sn, O and electron were generated from the target surface and accelerated to the substrate by target voltage.

Organic Films and Devices

Room 304C - Session OF+EM-WeM

Molecular and Organic Films and Devices - Electronics

Moderator: A. Kahn, Princeton University

8:20am **OF+EM-WeM1 Self-assembled Monolayers in Organic Electronic Devices***, **G. Horowitz**, P. Lang,* ITODYS, University Denis Diderot, France*; W. Kalb,* RWTH Aachen, Germany*; M. Mottaghi, A. Roumiantseva, A. Yassar,* ITODYS, University Denis Diderot, France **INVITED**

The use of molecular materials as active component in electronic devices has recently experience considerable interest. Organic electronic devices are fabricated by piling up several layers on top of each other. Because of that structure, the role of interfaces is crucial in the performance of the devices. An elegant way of controlling the quality of interfaces is the use of self-assembled monolayers (SAMs), which consists of a single layer of molecules chemisorbed on a surface. The molecules are most often based on long alkyl chains that tend to self-assemble to form highly ordered single layers. One end of the chains is substituted with a group capable of inducing chemisorption on the surface, while the other end can be used to control the quality of the modified surface. This technique will be exemplified by two approaches. The first one is a transistor made of a thin film of pentacene deposited on an alumina layer that serves as the gate dielectric. We show that the performance of the transistor is strongly influenced by the modification of the alumina surface by a SAM of a fatty acid. Correlation is made between the structure of the pentacene film and the properties of the transistor. In the second example, the SAM is made of hybrid molecules comprising an alkyl chain connected to a conjugated part (e.g., thiophene or acene). In that case, the SAM constitues the very heart of the device, which may open the way to electronics at the molecular level.

9:00am **OF+EM-WeM3 AFM Study of @beta@-7T Oligothiophene Films on Mica: Humidity-Dependent Mechanical Properties and Structure***, **J.Y. Chen**, I. Ratera, D.F. Ogletree, M. Salmeron,* Lawrence Berkeley National Laboratory*; AR Murphy, JMJ Frèchet,* University of California, Berkeley

Langmuir-Blodgett films of @beta@-7T@footnote1@ oligothiophene, a molecule with potential molecular electronic applications, were transferred to mica and studied with contact AFM. Mono and multilayer films exhibited structural and mechanical properties that depend on humidity, temperature and applied force as well as the LB transfer pressure. We found that monolayers were adsorbed through the carboxylic acid group, exposing the alkyl chains to the air interface. Two structural phases of the molecular film were observed. In the "A" phase the molecules were fully stretched and the film had a height of 2 nm. This phase was stable at high humidity and under low loads. The "B" phase had a height of 1.2 nm and was stable under dry conditions and high loads. Domains of both A and B phases were observed in the same larger islands. Changing humidity reversibly modified the A:B ratio and the sizes of the domains. Heating the samples resulted in an irreversible decomposition of the continuous film islands into small aggregates. @FootnoteText@ @footnote1@ @beta@-7T: a 7 thiophene oligomer with two alkyl side chains and an acetic acid group, 3'',4''''-didecyl-5,2';5',2'';5'',2''';5''',2''''; 5'''',2''''';5''''',2''''''-heptathiophene-4'''-acetic acid.

9:20am **OF+EM-WeM4 Fabrication of High Performance O-TFT Devices with Long Term Stability by using Atmospheric Plasma Treament and Passivation Layer***, **W.J. Kim**, H.K. Baik,* Yonsei University, Korea

We report the effect of a surface treament of the various dielectric layers by using atmospheric plasma on the device performance. We also employ the SiO based passivation layer to the top of fabricated devices with plastic-based substrates for the long term stability. With cost-effective atmospheric glide arc plasma treatment, the surface of dielectric layers was modified to fit more well to the organic active layer resulting in the high value of saturation current and field effect mobility. The O-TFT device with our SiO based passivation layer shows good device performance even after it has been exposed to Air in long period of time. Both high performace and long term stablity of the O-TFT devices could be achieved by our cost-effective method.

9:40am **OF+EM-WeM5 Pentacene Thin Film Transistors***, **G.G. Malliaras**,* Cornell University **INVITED**

The growth of pentacene films on oxide surfaces plays a major role in determining the device performance. A combination of synchrotron x-ray diffraction and atomic force microscopy was used to probe this interface. In-plane diffraction from films down to one monolayer thick was observed, which allowed to probe the early stages of film growth. Depositions at various substrate temperatures and deposition rates were found to yield films with crystallite sizes from hundreds of nanometers to tens of microns. The performance of these films in thin film transistors was investigated. The scaling of the transistor characteristics down to nanometer size channel lengths is discussed. Finally, applications in sensors are demonstrated.

10:20am **OF+EM-WeM7 OMBD of Organic Semiconductors on Metal Surfaces: Structural and Electronic Properties***, **G. Witte**, C. Wöll,* Ruhr-Universität Bochum, Germany

The promising potential of using organic semiconductor materials as active layers for organic electronic applications and the increasing interest in molecular electronics have expressed an urgent necessity of understanding the molecular microstructure and growth properties of ordered organic films. Of particular interest for the fabrication of thin films organic field effect transistors are polycyclic aromatic hydrocarbons which reveal a large variety of structures upon growth on inorganic substrates.@footnote 1@ Here we report results of a comprehensive growth study of pentacene and perylene films on various metal surfaces. By combining LEED, HAS, XPS, NEXAFS, TDS and AFM we were able to characterize the molecular microstructure developing upon film growth. In all cases a characteristic molecular reorientation from a substrate controlled interface phase towards a bulk-like thick film phase was obtained. On particular surfaces such as Cu(110) even epitaxial film growth was achieved.@footnote 2@@footnote 3@ The studied organic films revealed further a pronounced dewetting which favours the formation of crystalline islands upon deposition. Moreover, the electronic properties of thin pentacene films on various metal surfaces were characterized by UPS. It was found that the magnitude of the interface dipole moment is not directly related to the adsorption energy of the molecules at the metal surface but is caused to some extend by an exchange like coupling mechanism. @FootnoteText@ @footnote 1@ G. Witte and Ch. Wöll, J. Mat. Res. (focuss issue Organic Electronics, 2004).@footnote 2@ S. Lukas et. al., ChemPhysChem 5, 266 (2004).@footnote 3@ S. Söhnchen et al., J.Chem. Phys. in print (2004).

10:40am **OF+EM-WeM8 A Soluble Photopatternable Pentacene Precursor for Use in Thin Film Transistors***, **K.P. Weidkamp**,* University of Wisconsin-Madison*; A. Afzali, R.M. Tromp*[1]*,* IBM T.J. Watson Research Center*; R.J. Hamers,* University of Wisconsin-Madison

The practical application of pentacene as an organic semiconductor has been hampered by its lack of solubility in common solvents. Here we report the synthesis and characterization of a photopatternable, soluble pentacene precursor. This precursor, based on an N-sulfinylcarbamate adduct of pentacene, is converted back to pentacene at relatively low temperatures in the presence of acid catalyst and can be patterned by way of chemical amplification in the presence of photoacid generator. After UV illumination, a short, low-temperature post-exposure bake is used to convert the precursor to pentacene and the unexposed area is then washed away with solvent. A very short higher temperature anneal helps to form a crystalline film of pentacene that has mobilities in the range of 10@super -2@ cm@super 2@ V@super -1@ s@super -1@. Features can be patterned as small as 10 µm, small enough for use in many applications such as active matrix displays.

11:00am **OF+EM-WeM9 Electronic Polarization at the Pentacene - Gold Interface***, **F. Amy**, A. Kahn,* Princeton University

Pentacene has been successfully used as a high-mobility hole transport material. One of the reasons is that the energy of relaxation of the molecular ion is smaller by at least a factor of two than in other commonly used hole transport materials@footnote 1@. However, the full benefit of this relatively high mobility can be realized only if charge carrier injection is not a significant bottleneck in the device. The pentacene/metal interface energetics are therefore of prime importance. We focus here on the specific issue of polarization and narrowing of the transport gap at the pentacene/Au interface. Tsiper et al.@footnote 2@ have shown both experimentally and theoretically for PTCDA/Au that the polarization induced by an electron (P@sub -@) or a hole (P@sub +@) resident on a molecule at the interface increases by ~0.2 eV with respect to the polarization in the bulk of the film. This increase is due to the large polarizability of the metal substrate and results in a narrowing of the transport gap at the interface. This, in turns, affects the modeling of charge

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[1] **Medard W. Welch Award Winner**

injection at interfaces. In this work, we use ultra-violet and inverse photoemission spectroscopy (UPS, IPES) to measure highest occupied and lowest unoccupied molecular orbitals (HOMO, LUMO) of pentacene as a function of film thickness, from one to ten molecular layers. HOMO and LUMO levels represent the hole and electron transport levels, respectively. We find the increase in polarization at the interface to be in line with that measured on PTCDA. @FootnoteText@ @footnote 1@ N.E. Gruhn, et al. J. Am. Chem. Soc., 124, 7918 (2002)@footnote 2@ E.V. Tsiper, Z. Soos, W. Gao and A. Kahn, Chem. Phys. Lett. 360, 47 (2002) .

11:20am **OF+EM-WeM10 Planar Molecular Networks Built by 1D and 2D Polymerization***, **M. Stöhr**, M. Wahl, M. De Wild,* University of Basel, Switzerland*; C.H. Galka, L.H. Gade,* University of Heidelberg, Germany*; T.A. Jung,* University of Basel and Paul Scherrer Institute, Switzerland*; H.-J. Güntherodt,* University of Basel, Switzerland

Self-assembly of molecules on surfaces directed by different supramolecular interactions has been widely explored. There are striking examples of molecular surface structures, whose formation is driven by metal co-ordination, dipolar coupling or hydrogen bonding. In contrast to these examples, our aim is the formation of covalently linked planar structures by means of polymerization confined in one or two dimensions. The perylene derivative (DPDI) we investigated belongs to a class of compounds which serve as precursors for the production of photovoltaic devices. Recent investigations using differential thermoanalysis and gravimetry demonstrated that bulk DPDI can polymerize releasing ammonia. Inspired by this observation, we tried to exploit the formation of covalent networks on metallic surfaces and to check the feasibility of such an approach for the formation of stable polymer-nanostructures. For this purpose, thin films of DPDI were prepared on Ag(111) and Cu(111) by evaporation in a UHV setup. In a first step, the supramolecular arrangements were analyzed with a home-built STM. A condensed phase with a rectangular unit cell was found on both substrates if the coverage was in the range of 1ML. After annealing to 580K, a rearrangement of the DPDI molecules into a rhombic unit cell structure was observed. This symmetry change was accompanied by the appearance of a link between individual perylene groups which we identify as covalent bonds. Further evidence, in favor of a covalent bond formation is provided by the shortening of the intermolecular distance of the ad-molecular patterns after the thermal activation. We identify these structures as arrays of 1D polymer rows. For lower coverage in the range of 0.3ML only a mobile phase was detected before annealing. However, upon annealing to 580K a stable 2D network with a honeycomb-like structure was observed which conveniently matches the angles and distances expected for the chemically feasible polymer structure.

11:40am **OF+EM-WeM11 UHV-STM/XPS Studies of ACA Molecular Assemblies on Ag(111)***, **B. Xu**, D. Evans, B. Varughese, J. Reutt-Robey,* University of Maryland

The structures of acridine carboxylic acid (ACA) molecular films grown on Ag (111) by physical vapor deposition were characterized using UHV-STM and XPS. On large terraces (with terrace-spanning diameters exceeding 100 nm), ACA molecules form well ordered 2-d islands. The driving force for island formation is attributed to hydrogen-bond formation between ACA molecules (attractive along [1-10]) and substrate mediated attraction along [11-2]. XPS experiments reveal that H-bond interaction involves the ring nitrogen acting as the H-bond acceptor(O-H...N). On narrow terraces (~3 nm in width) completely different ACA structures are observed. In these confined regions, ACA molecules assemble into dimers, which are further organized into coverage-dependent adlayer structures. Finally, we report the observation of bi-layer and tri-layer structures.

Surface Science
Room 213B - Session SS+OF-WeA
Contacts to Molecules and Molecular Films

Moderator: G.G. Malliaras, Cornell University

2:00pm **SS+OF-WeA1 Electron Transport at Interfaces and Junctions: Understanding Molecular Electronics***, **X.-Y. Zhu**,* University of Minnesota **INVITED**

Charge transport at or across molecule-electrode interfaces is central to the operation of a wide variety of molecule-based electroic devices. The critical charge transporting interfaces in most systems are buried interfaces which are not readily accessible to conventional structural or spectroscopic probes. For any given device, two critical questions are: (1) What is the structural and chemical nature of the molecules at the buried interface before or during operation? (2) How is the electrical conductance across an interface related to physical properties such as electronic energy level alignment and charge redistribution? This talk will attempt to address both questions from spectroscopic measurements and to demonstrate that such a spectroscopic view is of critical importance in achieving a quantitative understanding of moleular electronics.

2:40pm **SS+OF-WeA3 The Influence of Chemical Coupling Groups on the Electronic Structure of Conjugated Self-Assembled Molecular Monolayers***, **S.W. Robey**,* NIST*; C.D. Zangmeister,* NIST, US*; R.D. Van Zee,* NIST

The performance of conjugated molecular systems in electronic applications, either for organic light emitting diodes (OLED's) and field effect transistors, or in more speculative applications proposed for molecular electronics, depends critically on coupling at the molecule-electrode interface. Interactions at this interface determine the alignment of the contact Fermi level with the transport levels in the molecular system, which in turn controls charge injection into the molecular @pi@ levels. Using one-and two-photon photoemission to access occupied and unoccupied levels, we have examined the influence of the metal-molecule coupling chemistry on the Fermi level alignment and electronic structure in the prototypical "molecular wire", 4,4'-(ethynylphenyl)-1-benzenethiol system on Au. Photoelectron spectroscopies reveal an increase in the binding energies (relative to the Fermi level of Au) for the C @sigma@ and @pi@ derived valence levels and the C (1s) core level upon substitution of the isocyanide coupling for thiol. No spectral changes are observed, however, in the region of the molecular @pi@ levels important for transport. Optical absorption measurements also reveal no change in optical band gap. These results indicate that substitution of the isocyanide linking chemistry for thiol based chemistry leads to a large shift, by ~ .5 eV, of E@sub f@ away from the highest occupied level in the molecule, but little modification of the extended @pi@ molecular electronic structure. The interaction at the Au-thiol-OPE interface will be compared and contrasted with the Au-isocyanide-OPE interface in terms of bonding and charge transfer effects and contact made to RAIRS and transport data for related systems.

3:00pm **SS+OF-WeA4 Mechanical and Charge Transport Properties of Self Assembled Organic Monolayers***, **I. Ratera**, J.Y. Park, J. Chen, A. Liddle, D.F. Ogletree, M. Salmeron,* Lawrence Berkeley National Laboratory

We are interested in measuring and correlating electronic and mechanical properties of molecules. We will report our progress in the fabrication of insulating test substrates with embedded coplanar metallic nanoelectrodes. In this manner a monolayer of molecules can bridge two electrodes and be accessible to an AFM or STM tip. This approach may lead to a better understanding the nature of the molecule - electrode contact. The use of AFM with conducting tips provides the ability to vary the load on the nano-contact and also opens the way for exploring electron transfer as a function of molecular deformation. Initial results will be presented on the influence of mechanical stress on the structural and electrical properties of self-assembled alkylthiols on gold surfaces as a function of the chain length and tip pressure.

3:20pm **SS+OF-WeA5 Electronic Properties of Interfaces between Organic Semiconductors and Metals***, **M. Knupfer**,* Leibniz Institute for Solid State and Materials Research Dresden, Germany **INVITED**

The electronic properties and the energy level alignment of interfaces between organic semiconductors and metals have been studied using photoemission spectroscopy in the valence as well the core level region. Different contrubutions to the frequently observed interface dipoles are discussed. In particular, the role of a reduction of the metal workfunction in comparison to clean, uncovered surfaces and image charge screening will be addressed. Furthermore, there are several examples where a charge transfer is observed at the interface, in particular for technologically relevant cases, which is essential for the understanding of charge transport acroos the corresponding interface.

4:00pm **SS+OF-WeA7 Energy Level Alignment at Organic Interfaces: Interface Induced Gap States and Charge Neutrality Levels***, **T.U. Kampen**,* Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany

The energy level alignment at organic interfaces determines the efficiency of charge injection into organic films. Quite often the vacuum level alignment rule has been used to determine the energy level alignment at organic interfaces. Here, barrier heights can simply be calculated using the ionisation potentials or electron affinities of semiconductors materials and work functions of metals. For organic interfaces a conclusion has been reached that in general the vacuum levels do not align. At intimate, abrupt, and defect free interfaces of inorganic semiconductors interface induced gap states are the primary mechanism determining the energy level alignment. These interface states derive from the bulk states and their character changes across the band gap from more acceptor-like closer to the conduction band to predominantly donor-like nearer to the valence band. The branch point where the character changes has the significance of a charge neutrality level. This work shows that the concept of interface induced gap states may also be applied to organic interfaces. The charge neutrality levels of PTCDA, DiMe-PTCDI, and CuPc are found to be 1.96 eV, 1.93 eV, and 0.51 eV above the HOMO, respectively.

4:20pm **SS+OF-WeA8 Work Function and Charge Distribution XPS Study of Molecular Layers Self-Assembled on Gold***, H. Cohen, **S. Ray**, R. Naaman,* The Weizmann Institute of Science, Israel

Substrate-overlayer charge transfer frequently imposes considerable changes on the properties of self-assembled (SA) monolayers. The study of space charge distribution across molecular layers is targeted here, using XPS in a slightly modified setup, capable of in-situ work-function evaluation. Fine differentiation between chemical and electrical information across dipolar layers is demonstrated. Intra-molecular charge transfer is found to take place in part of the systems, giving rise to a directional flip of the dipole moment on the nanometer scale.

4:40pm **SS+OF-WeA9 Influence of Electrode Contamination on @alpha@-NPD/Au Hole-injection Barriers***, **A.S. Wan**, J.H. Hwang, A. Kahn,* Princeton University

Processing for OLEDs and other organic devices often involves exposure of surfaces and interfaces to nominally controlled atmosphere (e.g. N@sub 2@) or even ambient conditions. A model system for studying barriers built under such "practical" conditions, as opposed to barriers built on ultra-clean substrates prepared under ultra-high vacuum (UHV) conditions, is the interface between Au and @alpha@-NPD, a standard hole- transport material for OLEDs. In this work, we investigate the effect of ambient exposure of polycrystalline Au surfaces on the hole-injection barrier using ultraviolet photoemission spectroscopy (UPS) and I-V measurements. We compare @alpha@-NPD layers grown in UHV on: i. Au as-loaded, exposed to air; ii. Au cleaned by Ar@super +@ sputtering; iii. fresh Au deposited in UHV. Conventional wisdom is that the higher the work function of the contact metal, the lower the hole-injection barrier. However, our UPS studies unambiguously show that the injection barrier is 0.5-0.6 eV lower for Au exposed to air, which has a work function of 4.7-4.9 eV, than for clean Au (sputtered or UHV deposited), which has a work function of 5.3-5.4 eV. The vacuum level shift, or dipole barrier, (down from Au to organic) is 0.3 eV for the former and 1.3 eV for the latter. I-V measurements on Au/@alpha@-NPD/Au devices made on clean vs. "dirty" Au show several orders of magnitude increase in injection from "dirty" Au, entirely consistent with the changes in barriers measured in UPS. The large differences in dipole and injection barriers are attributed to the layer of contamination (consisting primarily of carbon) on the air- exposed Au, which lowers the work function of the metal and decouples the interface molecules from the Au atoms. Mechanisms based on disruption of interface bonding and/or metal-induced states will be discussed.

5:00pm **SS+OF-WeA10 Time-Evolution and Stability of Metal-Molecule Contacts***, G. Nagy, **A.V. Walker**,* Washington University in St. Louis

Understanding the nature of metal-molecule interactions is important for many technologies, including organic and molecular electronics. It has already been demonstrated using vapor-deposited metals on self-assembled monolayers (SAMs) that many interactions are possible, ranging from destruction of the SAM to organometallic formation to penetration through the SAM to the Au/S interface. We apply time-of-flight secondary ion mass spectrometry (TOF SIMS) experiments and density functional theory (DFT) calculations to investigate the time-evolution and the energetics of vapor-deposited metallic contacts. As model systems we are employing vapor-deposition of copper on alkanethiolate SAMs with -CH3, -OCH@sub 3@, -COOH, -OH and -COOCH@sub 3@ terminal groups. We observe at room temperature that vapor-deposited Cu on -COOH and -OCH@sub 3@ SAMs initially both penetrates to the Au/S interface and forms a weak complex with the terminal group. However, Cu at the vacuum interface is not stable in the long term and slowly penetrates through the monolayer. We demonstrate that the stability of metal-molecule contacts is dependent on a number of factors including the strengths of the metal-metal and the metal-molecule interactions and the rate of penetration through the monolayer, which itself is dependent on the diffusion of the SAM molecules on the Au substrate.

Organic Films and Devices
Room 304C - Session OF+NS-ThM

Molecular Electronics

Moderator: X.-Y. Zhu, University of Minnesota

8:20am **OF+NS-ThM1 Molecular Engineering to Test the Mechanism of Conductance Switching for a Variety of Conjugated Molecules**, ***A.M. Moore***, *B.A. Mantooth, A.A. Dameron, Z.J. Donhauser,* The Pennsylvania State University*; J.W. Ciszek, F. Maya, Y. Yao, J.M. Tour,* Rice University*; P.S. Weiss,* The Pennsylvania State University

Phenylene ethynylene oligomers have been studied as candidates for molecular electronic devices using scanning tunneling microscopy.@footnote 1-6@ These molecules were inserted into host alkanethiolate self-assembled monolayers for isolation and individual addressability. Many different hypotheses and theoretical predictions have been put forth to describe conductance switching.3-4 We have tested several of these through variations in the molecular design of our molecular switches and have concluded that the only mechanism consistent with all the switching data are that changes in the molecule-substrate bond hybridization leads to the observed conductance changes. @FootnoteText@ @footnote 1@Donhauser, Z. J.; Mantooth, B. A.; Kelly, K. F.; Bumm, L. A.; Monnell, J. D.; Stapleton, J. J.; Price, D. W.; Rawlett, A. M.; Allara, D. L.; Tour, J. M.; Weiss, P. S. 2001, Science 292, 2303.@footnote 2@Donhauser, Z. J.; Mantooth, B. A.; Pearl, T. P.; Kelly, K. F.; Nanayakkara, S. U.; Weiss, P. S. 2002, Jpn. J. Appl. Phys. 41, 4871.@footnote 3@Mantooth, B. A.; Weiss, P. S. 2003, Proc. IEEE 91, 1785.@footnote 4@Moore, A. M.; Dameron, A. A.; Mantooth, B. A.; Yao, Y.; Ciszek, J. W.; Maya, F.; Tour, J. M.; Weiss, P. S. 2004, Nanotechnology In press.@footnote 5@Lewis, P. A.; Inman, C. E.; Yao, Y. X.; Hutchison, J. E.; Tour, J. M.; Weiss, P. S. In Preparation.@footnote 6@Dameron, A. A.; Ciszek, J. W.; Tour, J. M.; Weiss, P. S. In Preparation.

8:40am **OF+NS-ThM2 Room Temperature Molecular Memory Observed from a Nanowell Device**, *N. Gergel,* ***N. Majumdar,*** University of Virginia*; K. Keyvanfar, N. Swami,* University of Virgina*; L.R. Harriott, J.C. Bean,* University of Virginia

Researchers are debating whether the electrical switching behavior observed from some molecular devices can be attributed exclusively to the molecules@footnote 1@. We tested an OPE molecule with a nitro side group. This molecule showed electrical switching behavior when tested in a nanowell device at room temperature. This behavior was not seen when testing a simple conjugated molecule that lacked the nitro group. The test was performed in a nanowell device that consisted of a monolayer of molecules self-assembled on an area of gold 10-40 nm in diameter and capped with titanium and gold@footnote 2@. The I-V characteristics of the nitro molecule clearly showed two distinct conductivity states with a current ratio of 5 to 1 at room temperature. The experimental data showed that at a particular threshold voltage, the output current changed from a high current state to a low current state. This change in state was reversed with the opposite applied voltage. Hysteresis was not observed when testing a similar conjugated molecule without the nitro group at room temperature. Thus, the switching behavior could be attributed to changes in the conductivity of the nitro molecules due to the applied voltage. Other groups have reported seeing negative differential resistance behavior (NDR) in the I-V characteristics of the nitro molecule@footnote 3@. We saw similar peaks to those reported. However, our investigations indicate that this behavior is not reversible without the application of a negative threshold voltage. For this reason, these molecules may not be suitable for classic NDR circuits (e.g. Goto pairs@footnote 4@). This hysteretic behavior may nevertheless have device potential. @FootnoteText@ @footnote 1@ R.F. Forrest, Science 302, 556 (2003).@footnote 2@N. Majumdar, et al, submitted to J. Vac. Sci. Tech.@footnote 3@ M.A. Reed, et al, Applied Physics Letters 78, 3735 (2001).@footnote 4@ G. Rose, and M. Stan, IEEE NANO, San Fransisco, Aug (2003).

9:00am **OF+NS-ThM3 Metal/Molecule/Metal and Metal/Molecule/Semiconductor Device Structures**, ***D. Janes,*** Purdue University **INVITED**

This talk will describe the development and electrical characterization of two classes of molecular electronic components. The first class of structures involves metal-molecule-metal systems with pre-formed metal contacts, primarily lateral break junctions formed either by electromigration or by shadow evaporation. A number of molecular species have been studied using these structures, including short aromatic thiols and short DNA double strands with thiol bonding groups at each end. The electrical characteristics of these devices indicate that strong coupling between the contacts and the molecular species can be realized. The second class of devices involves metal/molecule/semiconductor device structures, which are lithographically defined and fabricated using an indirect evaporation technique for the metal (top) contact and p+ GaAs for the bottom contact. In these structures, the electronic conduction between the metal and semiconductor can be modulated by choice of molecular species. Several alkyl thiol and aromatic thiol molecules have been employed in order to determine the effects of molecular length, conjugation and intrinsic dipole moment. The current-voltage characteristics and conductance versus temperature both indicate that the molecular layers change the transport mechanism, generally involving a lower effective barrier height than that of a metal/semiconductor Schottky barrier. These results reflect previous studies in which nanoscale metal/molecule/semiconductor structures exhibited low resistance contacts, implying that effective coupling and control of the surface electrical properties can be achieved using a molecular layer.@footnote 1@ A simple model for the conduction has been developed, utilizing our prior studies on surface Fermi level unpinning in GaAs structures.@footnote 2@ @FootnoteText@ @footnote 1@ T. Lee, et al., APL 76, 212 (2000). @footnote 2@ S. Lodha, et al., Appl. Phys. Lett. 80, 4452 (2002).

9:40am **OF+NS-ThM5 Room Temperature Negative Differential Resistance Measured through Molecular Monolayers Adsorbed to Silicon Surfaces with Ultra-high Vacuum Scanning Tunneling Microscopy**, ***N.P. Guisinger,*** *R. Basu, M.E. Greene, A.S. Baluch, M.C. Hersam,* Northwestern University

In recent years, substantial progress has been made in the emerging field of molecular electronics. In particular, metal-molecule-metal junctions have been widely studied. In this paper, a continued study of charge transport through molecule-semiconductor junctions is considered. The presence of the energy band gap in semiconductors provides opportunities for resonant tunneling through individual molecules, leading to interesting effects such as room temperature negative differential resistance (NDR).@footnote 1@ In this study, the ultra-high vacuum scanning tunneling microscope was used to probe charge transport through two different molecular monolayers adsorbed to the Si(100) substrate. I-V measurements were taken on monolayers of TEMPO and cyclopentene for both degenerately doped n-type and p-type Si(100) substrates. Initial I-V measurements through the TEMPO monolayer exhibited a suppression of NDR behavior relative to previously reported transport through isolated molecules.@footnote 1@ I-V measurements were also taken on isolated cyclopentene molecules, as well as on cyclopentene monolayers. The cyclopentene monolayers similarly exhibited a suppression of the observed NDR behavior relative to transport through isolated molecules. For both molecular monolayers, the suppression of the peak-to-valley ratio (PVR) has been measured to exceed a 47 percent reduction compared to observed PVRs of isolated molecules. The resulting NDR suppression in both monolayers indicate that the local environment surrounding the molecules strongly influences charge transport. In addition to molecular monolayers, initial studies of transport through isolated TEMPO molecules adsorbed to both degenerate and non-degenerate Si(111) will be discussed. @FootnoteText@ @footnote 1@N. P. Guisinger, M. E. Greene, R. Basu, A. S. Baluch, and M. C. Hersam, "Room temperature negative differential resistance through individual molecules on silicon surfaces," Nano Letters, 4, 55 (2004).

10:00am **OF+NS-ThM6 Two Distinct Types of Switching Behavior in a Single Molecule**, ***A.S. Blum,*** *J.G. Kushmerick, C.H. Patterson,* Naval Research Laboratory*; J.C. Yang,* Duke University*; J.C. Henderson, Y. Yao, J.M. Tour,* Rice University*; R. Shashidhar,* Geo-Centers, Inc.*; B.R. Ratna,* Naval Research Laboratory

There is recent controversy surrounding the ability of molecules to function as switches in molecular electronic devices. We report the observation of two distinct types of switching in matrix isolated and complete monolayers of bipyridyl-dinitro-oligophenylene-ethynylene (BPDN). Extensive measurements in a scanning tunneling microscope (STM) demonstrate both stochastic and voltage driven switching in this molecule, representing the first description of two distinct types of switching in a single molecule. While stochastic switching has been reported for several molecular systems, we argue that the observed voltage controlled switching is a distinct physical event specific to BPDN. Furthermore, consistent switching behavior measured with both a scanning tunneling microscope and a crossed-wire tunnel junction demonstrates that the switching is intrinsic to the molecule and is not an artifact of the measurement system.

10:20am **OF+NS-ThM7 Electrical and Mechanical Contacts at the Atomic Scale: a Combined UHV STM/AFM Study**, ***Y. Sun***, *M. Henrik, S. Schaer, Y. Miyahara, A.-S. Lucier, M.E. Ouali, P. Grutter,* McGill University, Canada; *W. Hofer,* University of Liverpool, United Kingdom

Understanding electrical contacts is widely considered as one of the central issues in molecular electronics. As a first step, we have measured simultaneously at the atomic scale the interaction forces and the currents between a sharp tungsten tip and a Au(111) sample using a combined ultra-high vacuum scanning tunnelling and atomic force microscope (UHV STM/AFM). Close correlation between conductance and interaction forces were observed in the regimes from weak coupling to strong interaction. In particular, the electrical and mechanical points of contact are defined as a result of the observed barrier collapse and adhesive bond formation, respectively. The points of contact as defined by force and current measurements coincide within measurement error. We find experimentally that at contact the very front atoms of the tip apex experience repulsive forces, while the total interaction force remains attractive as a consequence of competing interaction decay lengths. Ab-initio calculations of the current as a function of distance were performed for our experimental tip-sample system. We find that in the weak coupling regime the calculated electrical current as a function of distance is in quantitative agreement with experimental results only if tip and sample relaxation effects are taken into account. The calculated relaxation of the tip apex atoms is 50-100 pm. We conclude that force effects of different decay lengths cannot be excluded if a detailed understanding of atomic scale contacts is to be achieved.

10:40am **OF+NS-ThM8 Structure of Self-Assembled Monolayers on Platinum**, ***D.Y. Petrovykh,*** University of Maryland, Naval Research Laboratory; *H. Kimura-Suda, A. Opdahl, L.J. Richter, R.D. Van Zee, M.J. Tarlov,* National Institute of Standards and Technology; *L.J. Whitman,* Naval Research Laboratory

We studied formation of self-assembled monolayers (SAMs) on polycrystalline platinum thin films using X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR), spectroscopic ellipsometry, and contact angle measurements. In particular we are interested in properties of SAMs on Pt with respect to their possible use as a substrate for Si-compatible molecular electronics. We find that SAMs formed on piranha-cleaned Pt from ethanoic solutions of n-alkanethiols have initial quality comparable to or better than that achieved under other conditions. The FTIR and XPS data indicate that films are formed with nearly normal orientation of alkane chains, have higher packing density than comparable SAMs/Au, and remain stable in ambient air for 3-5 days. XPS spectra of the S 2p region also show that SAMs/Pt are distinctly multicomponent. The main component, with the lowest binding energy, unambiguously corresponds to alkanethiol molecules adsorbed on Pt in a configuration similar to that for SAMs/Au. The minority higher binding energy components are not affected by exposure to good solvents and thus appear to correspond to different binding configurations related to surface roughness and oxidation (rather than to physisorbed molecules). Our results suggest that the use of oxide-free and atomically smooth Pt substrates may be necessary to attain a single-component, high-quality SAM on Pt.

11:00am **OF+NS-ThM9 Oligomer Length Dependent Study of Metal-Molecule Interactions in Model Molecular Wire Systems**, ***C.D. Zangmeister,*** NIST, US; *S.W. Robey, R.D. Van Zee,* NIST

Interactions at the molecule-contact interface perturb the molecular orbitals important for electron transport in conjugated systems. These perturbations are particularly important for the nanometer size junctions applicable in molecular-scale electronics. This study looks at the variation of the occupied electronic structure of fully conjugated model molecular wire compounds as a function of molecular length. Specifically, the number of phenyl rings was varied from a single ring to three rings in unsubstituted phenylene ethynylene monolayers chemisorbed on Au using ultraviolet photoemission spectroscopy. This provides a qualitative picture of the extent of perturbation of the electronic structure due to thiol coupling and the variation of the molecular @pi@ levels important for electron transport as a function of the degree of conjugation. These data show a shift towards the Au Fermi levels in the @pi@ levels by more than an eV as the conjugation length is increased. These observations will be discussed in terms of previous electron transport investigations of these compounds adsorbed on Au.

11:40am **OF+NS-ThM11 Electrical Properties of DNA Characterized by Conducting-Atomic Force Microscopy**, *C. Nogues,* ***S.R. Cohen****, S. Daube, R. Naaman,* Weizmann Institute of Science, Israel

DNA has been widely promoted as the key component of future molecular devices, due to its unique assembly and recognition properties. Specifically, the strong interaction between complementary base-pair sequences on interacting DNA strands can be utilized to self-assemble a desired structure in a molecular circuit. The most basic building blocks of such circuits can be formed through the hybridization of two single strands into a double one, and the specific binding of functionalized DNA strands to gold electrodes using the chemical thiol-gold linkage. Such manipulations can exploit the ease in which DNA strands can be synthesized, and modified chemically. Despite these advantages, the electrical properties of individual strands of DNA have yet to be reproducibly characterized, due to the inherent difficulties in reliably accessing and measuring single molecules. We have attacked this problem by developing protocols for reproducible formation and characterization of DNA monolayers, and then probing their electrical functioning using conducting atomic force microscopy (cAFM). The electrical contact to the DNA was made by chemical binding to a gold electrode on one end, and to a gold nanoparticle on the other. Thus, repeatable measurements of the conductivity of individual DNA strands have been performed. Meaningful differences could be detected between conductivity in single- and double-strand DNA. The single strand DNA was found to be insulating over the range of -2 to +2 V, while the double strand DNA passes significant current outside a 3 eV gap.

Organic Films and Devices
Room 304C - Session OF+EM-ThA
Molecular and Organic Films and Devices - Optoelectronic

Moderator: T.U. Kampen, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany

2:40pm **OF+EM-ThA3 Plasma Damage-Free Deposition of Metal and ITO Electrodes on Organic Light Emitting Diodes by Using Mirror Shape Target Sputtering(MSTS)***, **H.-K. Kim**, D.-G. Kim, K.A. Lee, M.-S. Huh, S.H. Jeong, K.I. Kim,* Samsung SDI, Korea

We report a successful fabrication of plasma damage-free organic light-emitting diodes (OLED) by using a mirror shape target sputter (MSTS) technique. Compared to leakage current (1*10@super-1@ ~10@super-2@mA/cm@super2@ at -6V) of the OLED consisted of Al cathode grown by conventional DC magnetron sputtering, that of the OLED with an Al cathode grown by MSTS shows much lower leakage current at reverse bias (1*10@super-5@ mA/cm@super2@ at -6V), indicative of no plasma damages. Therefore, the MSTS technique is expected to be useful in plasma damage-free and low temperature deposition technique for top and bottom-emitting OLEDs and flexible OLED. Possible mechanism is given to explain plasma damage free deposition of the metal and ITO electrodes by using current-voltage characteristics, SEM, AFM, XRD, and TEM examinations.

3:00pm **OF+EM-ThA4 Magnetic Field Effects in Transient Electroluminescence (EL) from Alq@sub 3@/NPB Bi-layer Organic Light Emitting Diodes***, **J. Wilkinson**, A.H. Davis, K. Bussmann, J.P. Long,* Naval Research Laboratory

The long electron spin lifetimes commonly found in organic materials make organic light emitting diodes (OLEDs) potential candidates for spin-injection controlled light sources. However, direct-current measurements of electroluminescence (EL) in OLEDs with non-magnetic electrodes (i.e. with no spin injection) show a variation in EL with applied magnetic field that must be understood. For example, EL can increase by as much as 6% around 0.1 Tesla (T) before decreasing by up to 20%, at 2 T.@footnote 1@ This shows that magnetic field effects are not due to spin injection, but are an intrinsic property of the light emission process. To probe the causes of these processes, we have performed sensitive transient EL experiments in the low-field regime (H = 80 mT) where the magnetic field enhances EL. The OLED is driven with rectangular voltage pulses producing a temporal response in EL with features down to the system resolution of 70 ns. The time-dependent magnetic field effect, defined as @DELTA@EL/EL = [EL(H) - EL(0)]/EL(0) increases EL by 6% for a 3.6 V drive at room temperature, as in direct-current measurements. But in addition @DELTA@EL/EL has interesting transient behavior when the device is first turned on, and again after the drive pulse is turned off during a long-lived delayed EL signal. As the device turns on, @DELTA@EL/EL doubles relative to its steady state value, which it attains on the microsecond timescale. Immediately after device turn-off, a long-lived increase in @DELTA@EL/EL is detected as well. The measured tendency for the magnetic field enhancement of EL to decrease as the transient EL increases is consistent with drive-dependent measurements. Together, these experiments indicate that high concentrations of non-equilibrium carriers or excitons interfere with the magnetic enhancement process. @FootnoteText@ @footnote 1@ A.H. Davis and K. Bussmann, Organic Light-Emitting Materials and Devices VII, eds. Z.H. Kafafi and P.A. Lane, 5214, 57-63 (2004).

3:20pm **OF+EM-ThA5 Molecular N-Type Doping of NTCDA by Pyronin B***, **C.K. Chan**, A. Kahn,* Princeton University

Molecular n-type doping of 1,4,5,8-naphthalene tetracarboxylic dianhydride (NTCDA) by pyronin B (PyB) is observed using ultraviolet photoemission spectroscopy (UPS) and inverse photoemission spectroscopy (IPES). The leuco form of the dopant molecule is prepared in situ by heating the stable PyB chloride salt until sublimation@footnote 1@. UPS of the neat PyB film shows that the highest occupied molecular orbital (HOMO) of the material is 5.69eV below the vacuum level (E@sub vac@), whereas the lowest unoccupied molecular orbital (LUMO) of NTCDA is at 4.08eV below E@sub vac@, as determined by IPES. Despite this relatively large energy difference between donor and electron transport states, the deposition of small amounts (<2Å) of PyB on pristine NTCDA films leads to a shift of the HOMO away from the Fermi-level by nearly 0.20eV, indicative of n-type doping of NTCDA by PyB and in agreement with the results of Werner et al.@footnote 1@. Interface and bulk energy levels of co-evaporated films show similarly efficient doping. Current-voltage measurements on doped NTCDA diode devices will also be presented. @FootnoteText@ @footnote 1@ A. G. Werner, F. Li, K. Harada, M. Pfeiffer, T. Fritz, and K. Leo, Appl. Phys. Lett. 82, 4495 (2003).

3:40pm **OF+EM-ThA6 Electrical Doping of Poly(9,9-dioctylfluorenyl-2,7-diyl) with Tetrafluoro-Tetracyanoquinodimethane by Solution Method***, **J.H. Hwang**, A. Kahn,* Princeton University

Electrical doping of organic materials has received attention for enhancing carrier injection and lowering drive voltages. We investigate here p-type doping of poly(9,9-dioctylfluorenyl-2,7-diyl) (PFO) with tetrafluorotetracyanoquinodimethane (F4-TCNQ) using a solution method. Doped and undoped films were compared using ultraviolet photoelectron spectroscopy (UPS) and current-voltage (I-V) measurement. Undoped PFO was prepared from 0.1wt% of tetrahydrofuran (THF) and p-xylene. For doped PFO, 5% of F4-TCNQ relative to each repeat unit of PFO was added to each solution. Undoped and doped films (~100Å thick) were spun on ITO or Au substrates in nitrogen, annealed in nitrogen at 50°C to remove residual solvent, and loaded without ambient exposure in an ultra-high vacuum chamber. UPS spectra were recorded for each film. The energy of the highest occupied molecular orbital (HOMO) was measured with respect to the Fermi level (E@sub F@). The ionization energy of PFO, determined as the difference between vacuum level (measured from the onset of photoemission) and HOMO, was found to be 5.75 eV, which is ~0.5 eV larger than the electron affinity of F4-TCNQ (5.24eV)@footnote 1@.In spite of the fact that this difference is significantly larger than for ZnPc (0.04 eV)@footnote 1@ and a-NPD (0.28 eV)@footnote 2@, F4-TCNQ p-dopes the polymer. EF-HOMO is 1.1 eV and 1.4 eV for undoped PFO on Au and ITO, respectively, and drops by 0.2 eV for PFO:F4-TCNQ, showing a shift in the expected direction for p-doping. We also performed I-V measurements on Au/1200Å PFO/ITO, which show an order of magnitude increase in current in doped PFO, consistent with higher conductivity and/or lowering of the hole-injection barrier. These measurements show that electron transfer from host to dopant occurs and produces p-type doping. @FootnoteText@ @footnote 1@ W. Gao, A. Kahn, Appl. Phy. Lett., 79, 4040 (2001)@footnote 2@ W. Gao and A. Kahn, J. Appl. Phys. 94, 359 (2003).

4:00pm **OF+EM-ThA7 Negative Capacitance in Hetero-Layered Organic Light Emitting Diodes***, **L.S.C. Pingree**, B.J. Scott, T.J. Marks, M.C. Hersam,* Northwestern University

Negative capacitance (NC) has been measured by impedance spectroscopy and correlated with time domain waveforms in ITO/NBP/Alq@sub 3@/Al OLED macroscopic devices. In addition, this behavior has been measured by Nanoscale Impedance Microscopy@footnote 1@ on 8 µm x 8 µm microscopic OLED devices. Beyond providing evidence of the scaling of NC, this AFM based technique provides spatially resolved capacitance variations in these structures. Due to the field dependent mobility of the charge carriers, and their subsequent dependence upon both bias and space charge, a slow rise time (t@sub R@) in the current response is detected when a step voltage is applied to the OLED. Such behavior is typical of a NC impedance response@footnote 2@. The typical t@sub R@ varies from 100 ms at 1 volt to 15 ms at 10 volts for electrons, and 100 ms at 1 volt to 1 ms at 10 volts for holes. The onset of NC in the frequency domain correlates strongly with the hole t@sub R@, and the corresponding frequencies are exponentially dependent upon the applied bias. These results agree with the exponential dependence of mobility upon applied field given by Poole-Frenkel theory. Also, the variation between the carrier rise times suggests that Richardson-Schottky injection dominates electron flow. Correlation of the data with device physics implies that NC behavior is hole dominated since the flow of electrons is modulated solely by holes trapped at the Alq@sub 3@/NPB interface, whereas holes respond to both bias and space charge. Additionally, temporal variations in the behavior of light emission as a function of frequency were acquired though the use of a dual lock-in technique. @FootnoteText@ @footnote 1@R. Shao et. al. Appl. Phys. Lett. 82 1869 (2003).@footnote 2@M. Ershov et. al. IEEE Trans. Elect. Dev. 45 2196 (1998).

4:20pm **OF+EM-ThA8 Electronic Structure and Molecular Orientation of Conducting Polymer Films Produced via Surface Polymerization by Ion Assisted Deposition***, **S. Tepavcevic**, Y. Choi,* University of Illinois at Chicago*; M. Bissen, D. Wallace,* University of Wisconsin-Madison*; L. Hanley,* University of Illinois at Chicago

Conducting polymer films are grown by mass-selected, hyperthermal organic cations coincident on a surface with a thermal beam of organic monomers, in a process termed surface polymerization by ion assisted deposition (SPIAD).@footnote 1,2@ SPIAD is applied here to create polymer films from thiophene ions and either @alpha@-terthiophene neutrals (3T SPIAD) or p-terphenyl neutrals (3P SPIAD). Mass spectrometry and x-ray photoelectron spectroscopy (XPS) verify the polymerization of both 3T and 3P SPIAD films. The electronic structure and molecular orientation of these films are probed by valence band XPS, ultraviolet photoelectron spectroscopy (UPS) and polarized near-edge x-ray absorption fine structure spectroscopy (NEXAFS). Valence band XPS and UPS of the 3T SPIAD films produced with 200 eV ions and an ion/neutral ratio 1/150 display similar spectral features as polythiophene films prepared electrochemically. A new state is observed 1 - 3 eV below the Fermi level in the 3T SPIAD film spectra which is not observed in films prepared by evaporation of 3T. This new state is attributed to an extended @pi@* bonding band along the conjugated aromatic chain of the polymerized 3T. Carbon K-edge NEXAFS probes the unoccupied @pi@* and @sigma@* bands of 3T SPIAD films which appear similar to those of the evaporated 3T film. Polarized NEXAFS show that the 3T SPIAD film is at least partially oriented with their molecular axes close to the normal of the substrate surface. The 3P SPIAD film prepared at 200 eV with an ion/neutral ratio 1/100 display more electron delocalization over the @pi@* bonding band compared with the 3P evaporated film. Polarized NEXAFS shows that as little or no orientation in the 3P SPIAD film, in contrast to the highly oriented 3P film. @FootnoteText@ @footnote 1@S. Tepavcevic, Y. Choi, and L. Hanley, J. Amer. Chem. Soc. 125 (2003) 2396. @footnote 2@Y. Choi, S. Tepavcevic, Z. Xu, and L. Hanley, Chem. Mater. (2004) in press.

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