SYMPOSIUM I

Organic Thin-Film Electronics

March 28 - April 1, 2005

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* Invited paper
The binding of biotin by the small glycoprotein avidin is one of the strongest non-covalent interactions known, and is widely used in life sciences, for instance in isolation (affinity chromatography), localisation (affinity cytochemistry, cell cytometry, and blotting technology), diagnostics (immunoassay, histopathology, and gene profiling), and bioaffinity sensors. Regioregular polyalkylthiophenes have been widely studied as TFT materials because of their high field effect mobility, unusual for a polymer material, and they also have particularly marked solvato and thermochromism as a consequence of their regioregularity. We have synthesized regioregular polyalkylthiophene copolymers in which a small proportion (typically 1 to 5%) of the alkyl chains bears a covalently attached biotin group. These polymers undergo dramatic colour changes in solution upon interaction with avidin. When covalently attached to a solid surface, the oxidative electrochemistry of the polymers is greatly attenuated upon avidin binding. The conductivity of a 100 nm spin coated film on a glass substrate decreases by over three orders of magnitude on exposure to avidin. Work is ongoing to develop polymer modified microelectrodes to lower the electrochemical detection limit, to make more water-compatible polymers using oligo(oxyethylene) sidechains, and to investigate other biological receptors (e.g. oligonucleotides, sugar-protein interactions etc.).

Non-Volatile Memory Effect in Polymer Based Device for Data-Storage Applications. Yan Song1, Qidan Ling2, Shijin Ding2, Chunxiang Zhu1, Yihu Wang2, Siuhung Daniel Chan1, En-Tang Kung2 and Dim-Lee Kwong1.

SESSION II: Materials and Organic Devices

Chair: Nir Tessler

Tuesday Morning, March 29, 2005
Room 2001 (Moscone West)

8:30 AM II.1 Memory Elements based on Polymer Nanoparticles Blends.

Luigi Dominico Bozano1, Ryan Chiu2, Kenneth R. Carter2 and J. Campbell Scott3: IBM Almaden Research Center, San Jose, California; 2Polymer Science and Engineering, University of Massachusetts, Amherst, Massachusetts; 3Chemistry and Biochemistry and Exotic Materials Institute, University of California Los Angeles, Los Angeles, California.

Non-volatile solid-state memory devices can be fabricated by sandwiching a thin layer of semiconducting polymer blended with metal nanoparticles between two electrode contacts. The electrical response shows bistable behavior in which ON and OFF states can be easily set by proper choice of the applied voltages (L.Bozano et al APL 2004). However, the process is expensive in a wide variety of organic and inorganic composite materials. In this study, the role of the host semiconductor is explored in more detail by comparison of two polymers, differing primarily in their hole mobility: a conjugated triarylamine (HTFA) with hole mobility greater than 10-5 cm2/Vs and a vinyl polymer with pendant donor groups (polyvinylcarbazole - PVK), in which the hole mobility is of order 10-7 cm2/Vs. The selected polymer materials were then blended with a Au metal nanoparticles of variable concentration and size and fabricated into devices. Switching performance of the memory elements like ON/OFF current ratio, switching voltages and times, retention and cycling endurance, were determined by DC, pulse and AC electrical measurement. The resulting data are presented in the context of a model in which charge transport occurs both by conduction in the polymer host and tunneling between nanoparticles.

8:45 AM II.2 Progress in Organic Thin Films for Memory Storage Applications.

M. Lauter, B. McCarthy, D. Sarid and G. E. Ibbounge: Department of Chemical and Materials Engineering & Flexible Display Center, Arizona State University, Tempe, Arizona.

We will discuss the use of ultra thin films of organic materials as potential candidates for data storage applications. Various structures that might help shed some light on the mechanism behind the observed switching in the organic layers will be presented.

9:15 AM II.3 Functionalized Regioregular Polyalkylthiophenes for Biosensing Applications.

Simon J. Higgins1, Fouzi Mouffok1, Stewart J. Brown1, Bill Eccleston2, Andrew Cosma3, Daryl Williams1, Stuart Reeman1, and Naser Sedghi2: Department of Chemistry, University of Liverpool, Liverpool, United Kingdom; 2Electrical Engineering and Electronics, University of Liverpool, Liverpool, United Kingdom; 3Biosciences, University of Liverpool, Liverpool, United Kingdom; 4Chemical and Biological Sciences, Dent Porton Down, Salisbury, United Kingdom.

Organic thin film transistors (OTFTs) have been proposed for a wide range of applications. Among other possibilities, OTFTs offer a promising route towards dramatically lowering the cost of electronic sensors, ultimately enabling low-cost applications such as food packaging with integrated gas detection. The ability to tailor the chemical sensitivity of organic semiconductors through organic chemistry makes these materials well-suited for sensor array applications such as electronic noses. Moreover, the potential for solution deposition allows for low-cost integration of multiple sensing materials onto a single substrate and compatibility with cheap substrates such as plastics or foils. One of the greatest concerns in the field of organic electronics, however, is the long-term stability of devices under continuous operation. Here, we present an OTFT
opalional lifetime study for short-term sensing applications such as disposable food spoilage detection, where continuous operation is expected to last for hours to days. Gate insulators fabricated with an array of different active materials are monitored for shifts in performance characteristics during continuous operation over many days in both inert and ambient environments. We explore the effects of organic and inorganic materials on device stability, processing parameters on device stability, and discuss the trade-offs in optimizing for stability versus sensitivity. Because many of the mechanisms responsible for an OTFT’s sensor response are the same as or very similar to the causes of bias stress degradation, we also find that stressing a device can modify its sensor response. We discuss approaches to decoupling a device’s sensor response from its stress response and propose a method for quantifying the stability and useful lifetime of OTFT sensors.

11:00 AM II.8
Large Magnetoresistance at Room Temperature in Semiconductor Polymeric Sandwich Devices.
GMotranavaran VG, Omer Mermer2, Thomas Lee Fradis3, Yungg Sheng2, Tho Duc Nguyen4 and Markus Weihgelenm5.
1Department of Electrical & Computer Engineering, University of Iowa, Iowa City, Iowa; 2Department of Physics and Astronomy, University of Iowa, Iowa City, Iowa.

Organic conjugated materials have been used to manufacture promising devices such as organic light-emitting diodes (OLEDs), photovoltaic cells and field-effect transistors. In particular, polyaniline has emerged as a bright source of high efficiency p-channel organic transistors (OTFTs). Recently, we have observed that OTFTs with an active layer of a polyaniline-based semiconducting polymer exhibit a large room-temperature magnetotransport effect. This work was supported by the National Science Foundation grant number EEC-0123572. We explore the fundamental properties of these organic semiconducting polymers and the mechanisms responsible for the observed magnetotransport effects at room temperature. We will present results on the discovery of a large, room-temperature magnetoresistance effect in these materials and discuss the implications for the development of organic spintronic devices.

11:15 AM II.9
High-Temperature Operation of Pentacene Field-Effect Transistors with Polyimide Gate Insulators.
Takahiro Seki, Yusuke Kato1, Shingo Iida1, Yasuyuki Takayanagi1, Takasawa Suzuki2, Takao Someya1,2.
1OPSEC, Univ. of Tokyo, Bunkyo-ku, Tokyo, Japan; 2CCR, Univ. of Tokyo, Meguro-ku, Tokyo, Japan.

We have investigated the high-temperature performance and the heat-resistant characteristics of high-quality pentacene field-effect transistors (OFETs) manufactured on a plastic base film with polyimide gate dielectric layers. It was found that mobility was enhanced from 0.27 to 0.71 cm2/Vs when the devices were heated from room temperature to 160 °C under light-shielding nitrogen environment. Furthermore, to investigate postannealing effects, the transfer characteristic was also measured at 30 °C after many heat cycles. We found that it had not changed after heating up to 150 °C. Therefore we have performed the excellent stability of the present pentacene FETs at high temperatures. High-performance OFETs with a mobility of 0.3 cm2/Vs at RT and an on/off current ratio of above 106 have been fabricated by using polyimide layer. First, the gate electrode was formed by thermal evaporation of 5-nm-Cr and 100-nm-Au through a shadow mask on a 75-μm-thick flexible polyimide-sheet plastic film. Then, a 900-μm-thick polyimide gate dielectric layer was prepared by spin coating and a 50-μm-thick
pentacene was deposited through a thermal evaporation. Finally the 60-nm Au drain and source electrodes were formed using a shadow mask. The channel length and width of OFETs are normally 100 μm and 1 mm, respectively. The electrical properties of the OFETs were measured using a three-lead probe with a precision semiconductor-parameter analyzer while the OFETs were heated using a thermal stage apparatus at temperatures between 150°C to 200°C. High-precision measurements have been performed in a light shielding glove box with less than 1 ppm oxygen and moisture. In the current-voltage characteristics with increasing measurement temperatures, the on current was enhanced up to 0.71 cm²/Vs when heating the device up to 150°C compared with 0.27 cm²/Vs at RT, which can be analyzed in terms of a transport model with carrier-lumping. Furthermore, it should be noted that no damage has been observed in the mobility by the removal of SiNx. On the other hand, annealing at the temperatures from 150 to 160°C results in the enhancement of mobility by 20% at RT. Excessive heating above 180°C causes the reduction of mobility, which was ascribed to the decrease with the partial separation of pentacene molecules. In high-temperature regions above 100°C, a lot of organic-based devices have been deteriorated. This is because thermal stress due to the different coefficient of thermal expansion at each layer results in the deformation and/or cracks of the devices. We demonstrated that our OFETs were fairly stable against the heat application because of the utilization of heat-resistant polyimide not only for a hose film but also for a gate dielectric layer, leading to a reduction of thermal-stress. The authors thank MEXT IT program and COE program for financial supports.

11:30 AM 11.10

Organic-Inorganic Hybrid Encapsulation for P3HT Field-Effect Transistors. Noriyuki Kawanishi, Kazumasa Nomoto, Masaru Wada and Jiro Kasahara; Fusion Domain Laboratory, Materials Laboratories, Sony Corporation, Ota-ku, Tokyo, Japan.

In recent years, there have been a lot of studies on poly(3-hexylthiophene) (P3HT) as a semiconductor material for field-effect transistors (FETs). P3HT FETs show relatively high mobility among available organic semiconductor FETs. However, it is difficult to maintain a high on/off current ratio under ambient conditions due to the effect of p-type dopants such as oxygen. We investigated the effects of thermal annealing in a dry N₂ atmosphere with different SiNx film thickness in bottom gate FETs, and improved their on/off current ratio up to 10^6. The on/off current ratio degrades to 10 within several hours in ambient conditions due to the increase in the off current of the FETs. These results suggest that the oxygen doped in P3HT film can be de-doped by thermal annealing under optimized conditions. We found that the 1510 cm⁻¹ absorption peak in the FT-IR spectrum observed in oxidized P3HT film, disappeared after thermal annealing, which implied that the peak is related to the oxidation of P3HT. In order to avoid this oxygen doping effect, we evaluated three types of encapsulation layers; SiNx, organic insulators, and organic-inorganic hybrid insulators. When we employed a SiNx layer, the damage caused by the deposition of SiNx resulted in a leakage current at the SiNₓ/P3HT interface, and the encapsulation itself reduced the on/off current ratio. Encapsulation of the organic insulator caused no leakage current and maintained a high on/off current ratio after coating. FETs encapsulated with an organic insulator maintained high on/off current ratios for up to 100 hours. However, a gradual increase in off current started to appear with extended exposure to air. A single organic insulator was insufficient in suppressing the penetration of oxygen into the active area of the FETs. Therefore, we adopted an organic-inorganic hybrid encapsulation and confirmed that the encapsulated FET maintained a high on/off current ratio for several hundred hours. The effect of encapsulation was quantitatively investigated for some insulators by a dopant concentration derived from the formula [1] by Brown et al. [1] A. Brown, C. Jarrett, D. Leeuw, M. Matters, Synth. Met. 88, p.37, 1997

11:45 AM 11.11

General Observation of n-Type Field-Effect Behaviour in Organic Semiconductors. Lay-Lay Chua1,2, Peter K.-H. Ho1,2, Jana Zaussnell1,2, Ji-Fen Chang3, Eric Ou2, Henning Stirnlinghaus1 and Richard H. Friend1,4; 1Physics, University of Cambridge, Cambridge, United Kingdom; 2Physics, National University of Singapore, Singapore, Singapore; 3Institute of Materials Research and Engineering, Singapore, Singapore; Functional π-Electron Materials for Nanoelectronics. Lay-Lay Chua1,2, Peter K.-H. Ho 2,1, Richard H. Friend l ; lphysics, University of Cambridge, Cambridge, California.

Organic semiconductors are attracting increasing attention owing to their emerging applications in light-emitting displays and printable electronic circuits. One long-standing mystery of their device physics has been the unusual field-effect behavior of negatively-charged electrons but not positively-charged holes. Most organic field-effect transistors (FETs) readily show p- but not n-type conduction. Electron conduction has only been found in a few special high electron-affinity (EA) or low band-gap organic semiconductors. The origin of this large difference in electron and hole behaviour is currently not well understood. Here we demonstrate the critical role of the gate dielectric to support electron field effect and that with the appropriate hydroxy-free gate dielectrics, such as benzocyclobutene derivative (BCB), n-channel FET operation is in fact a generic feature of most conjugated polymers. At these high-quality interfaces, electron and hole mobility values are amongst the highest values reported without alignment. We further show here the reason why n-type behaviour has previously been so elusive is the trapping of electrons by electrochemically active groups, such as silanols in the case of the commonly-used SiO₂ dielectric. Our research opens new opportunities for organic complementary metal-oxide semiconductor (CMOS) circuits.
received much attention, despite their critical roles in low-cost OTFTs. We present here our design of metal nanoparticles and their low-temperature annealing treatments to high temperatures suitable for application in low-cost electronics. As an illustration, we have utilized these metal nanoparticles for printing electrodes for OTFTs. Thin-film electrode features were printed from a dispersion of stable nanoparticle ink. This ink is stable for one week at room temperature. The created at 120-160 degree C to yield metallic electrodes with thin-film conductivities resembling those from vacuum deposition. OTFTs using these electrodes provided phototransistors which are essentially the same as those using vacuum deposited metal electrodes.

2:30 PM 12.4 Structure/Property Relations in Electrorheactive Polymers. Mary Q. C. Calvin1, Materials Science and Engineering, University of Delaware, Newark, Delaware; 2University of Delaware, Newark, Delaware; 3University of Delaware, Newark, Delaware.

While electroactive organics and polymers are beginning to be used commercially in light-emitting diodes (LEDs) and are being considered for use in thin film transistors (TFTs) and photovoltaic cells (PVs), a significant amount remains to be discovered with regards to the structure/property relationships that govern the performance of these materials. This talk will discuss two specific structure/property relationships in electroactive polymers. First, we will report on research that investigates the effect that sequence distribution in copolymers has on LED and PV performance. Specifically, alternating, random and block copolymers of oxadiazole containing phenylenevinylene (oxa-PV) and phenylenevinylene (PV) have been synthesized and characterized with regards to device efficiency. The random copolymers demonstrated significantly better than the alternating or block in OLEDs fabricated on flexible substrates with an Al cathode, having an external quantum efficiency of 1%. Secondly, we are investigating the role of architecture, synthesizing some novel molecules that contain a central tetra substituted phenyl ring. These molecules have a tendency to form stacks, further delocalizing the structure. These molecules have a trend to form stacks, further delocalizing the structure. These results obtained with these materials will be described.

3:30 PM 12.5 Molecular Design and Synthesis of New Electrochromic Polymers with Various Colors. Lu Liu, Chunye Xu, Dai Ning, Calen Kanelo and Minoru Tsyn; Mechanical Engineering, University of Washington, Seattle, Washington.

Electrochromic (EC) materials are those that can create a reversible and visible change in reflected or transmitted light upon electrochemical oxidation and/or reduction. The most extensively studied EC materials are based on inorganic systems such as tungsten trioxide (WO3) and iridium dioxide (IrO2). However, organic EC materials have attracted increasing attention. Among the organic materials, conducting polyners are a versatile so that the four arm molecules do not have to be identical. The placement of differing arms also affords the opportunity to study the effect of symmetry on the properties of these molecules. Recent results obtained with these materials will be described.

4:00 PM 12.6 Recent Work of the Organic Materials for Electronics Consortium of the EPSRC. Michael Grell1, Philip Hodg3, J. Emyr Macdonald2 and Stephen G. Yeates1; 1School of Chemistry, University of Manchester, Manchester, United Kingdom; 2Department of Physics, University of Sheffield, Sheffield, United Kingdom; 3Department of Physics, University of Cardiff, Cardiff, United Kingdom.

Recent work from the Organic Materials for Electronics Consortium of the Engineering and Physical Sciences Research Council, UK will be presented. The interdisciplinary consortium consists of research groups from the School of Chemistry, University of Manchester, the Department of Physics and Astronomy and the Department of Chemistry at the University of Sheffield, Department of Physics and Astronomy at the University of Cardiff and Avecia Ltd, Manchester. Recent work discussed will include: (i) The synthesis and characterisation of novel organic semiconductors (ii) The use of modified gate insulators in OFETs (iii) The fabrication of OFETs with organic ferroelectric gate insulators (iv) The use of phase image electrochromic force microscopy in organic electronics.
poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonic acid) on a glass substrate coated with indium-tin-oxide. The 80-nm-thick emitting layer was made by spin-coating from a 1,2-dichloroethane solution of the dendrimer. All the OLEDs exhibited bright green or yellowish-green emission when a positive bias was applied to the ITO electrode. Luminance reached 2,000-3,000 cd/m² at a voltage of 15 V. The electroluminescence (EL) spectra of the OLEDs were almost coincident with the PL spectra of the corresponding dendrimer films. The OLED using the dendrimer consisting of Ir(ppy)₃ core and hole-transporting phenylcarbazole-based dendrons exhibited an external efficiency of 7.6%, current efficiency of 26 cd/A and a power efficiency of 13 lm/W.

4:45 PM T2-9  
**Substituted Indolo[3,2-b]Carbazoles: A New Class of Stable, High Mobility Organic Semiconductors for Thin Film Transistors.** Yunying Li, Yiling Wu and Beng S. Ong; Materials Design and Integration Laboratory, Xerox Research Centre of Canada, Mississauga, Ontario, Canada.

Properly functionalyzed indolo[3,2-b]carbazoles represent a new class of stable, high-mobility organic semiconductors for thin-film transistors. Here we show that even conjugated polymer opens the way to organic low power field-effect transistors. Here, we demonstrate ambipolar charge transport in organic solid-state devices is very challenging since most of materials available and used during fabrication phase separation occurs and the semiconductor and insulating polymer from solution. SEM and EDS studies show that single-crystalline and multi-crystalline films can be formed by reaction of two different polymers. The morphology of the phase separated film was control such that the semiconductor material segregates to the top surface encapsulating the underlying semiconducting organic film. Conventional TFTs were fabricated with blends of semiconducting and insulating multilayers formed different phases in the film. The performance of polymer based electronic devices has shown great improvements over the past years. Polymer light emitting diodes (LEDs) show high luminance efficiency and thin film transistors (TFTs) show field effect mobilities of 0.1 cm²/Vs. These materials are easily processed from solution providing the potential of a vacuum free fabrication process. However, due to their poor environmental stability, polymeric devices are often fabricated and characterized under an inert atmosphere. The encapsulation of polymeric electronic devices is very challenging since most of materials available and used for encapsulation require process steps that involve high temperatures or solvents that may damage the polymeric semiconductor. Here we study the environmental stability of two polythiophene derivatives and a polyfluorene polymer, as well as flexible substrates.

**SESSION 13: Poster Session: Organic Based Materials and Devices**

**13.1 Ambipolar Charge Transport in Poly(3-hexylthiophene) (P3HT) Field-Effect Transistors.** Jana Zanussi¹, Lay-Lay Chua¹,², Peter K. H. Ho¹, Richard H. Friend³ and Hamming Siou²; ¹Cavendish Laboratory, University of Cambridge, Cambridge, United Kingdom; ²Department of Physics, National University of Singapore, Singapore, Singapore.

We have shown recently, that by using high-purity polymer gate dielectrics n-type field-effect conduction can be readily observed in a broad range of polymer semiconductors such as polyfluorenes (e.g. P3HT, F8) and polyphenylenevinylenes (e.g. MEH-PPV, OCA110-PV) which were previously believed to exhibit only p-type field-effect conduction. Here we show that even poly(3-hexylthiophene) (P3HT) which has been widely investigated as a p-channel semiconductor with high hole mobilities is equally able to conduct electron injection and very efficient type-selective behaviour in field-effect transistors. Moreover we demonstrate ambipolar charge transport in transistors based on high purity, regioregular poly(3-hexylthiophene) (P3HT) with balanced electron and hole mobilities. We use these ambipolar transistors to investigate the origin of shallow and deep traps in the bulk and at the semiconductor-dielectric interface represented by hysteretic current-voltage characteristics. This observation of balanced ambipolar field-induced charge transport in a conjugated polymer opens the way to organic low power complementary circuits and even light-emitting field-effect transistors.

**13.2 Molecular Dielectric Multilayers for Ultra-Low-Voltage Organic Thin Film Transistors.** Myung-Han Yoon, Antonio Facchetti and Tobin J. Marks; Chemistry, Northwestern University, Evanston, Illinois.

Very thin (2.3 - 5.5 nm) self-assembled organic dielectric multilayers have been integrated into organic thin-film transistor (OTFT) structures to achieve sub-1 V operating characteristics. These new dielectric layers are fabricated via modular, layer-by-layer solution phase deposition of molecular silicon precursors, resulting in smooth, nanostructurally well-defined, strongly-adherent, thermally stable, virtually pinhole-free, organosiloxane thin films having exceptionally large electrical capacitances (400-700 nFcm⁻²) and low leakage current densities. These multilayers enable OTFT function at very low source-drain, gate, and threshold voltages, and are compatible with a broad variety of vapor- or solution-deposited p- and n-channel organic semiconductors, as well as flexible substrates.

**13.3 Control of Thin Film Transistor Operation with Polar Self-Assembled Monolayers.** Yoshi Iwasa¹, Takao Nishikawa¹, Shin-ichiro Kobayashi¹, Taishi Takenobu¹, Tatsuya Shimoda¹, Tadaoki Mitani² and Michio Niwa³; ¹Institute for Organic Materials Research, Tohoku University, Sendai, Japan; ²School of Materials Science, JAIST, Ishikawa, Japan; ³Research Institute for Electrical Communication, Tohoku University, Sendai, Japan.

Organic thin film transistors (TFTs) show great promise as fundamental element devices for low cost and flexible electronics such as displays, radio-frequency identification tags, and mechanical or chemical sensors. From the viewpoint of both basic science and practical application, one of the central issues in organic TFTs is the interface of different materials inherent in the device structure. For example, the interface between organic semiconductors and electrodes controls the carrier injection, while the interface between organic semiconductors and gate insulators governs the trap and carrier densities. In late 1990s, Jackson and coworkers have demonstrated that the organosilane self-assembled monolayers (SAMs) on the SiO₂ gate insulators, most typically octadecyltrichlorosilane (OTS), improve the crystallinity of organic thin films deposited, and thus increase the field effect mobility. This technique has now become a standard to fabricate high mobility organic TFTs. Recently, we have demonstrated that the carrier density in the conduction channels can be changed by inserting polar SAMs between organic thin films and SiO₂ gate insulators. The effectiveness of SAMs has been also shown on organic single crystal field effect transistors. In this work we concentrated on SAMs under ambient conditions, an appealing characteristic for organic TFT applications.

**13.4 Self-Encapsulated Polymer Films: Improved Environmental Stability of Thin-Film Transistors.** Ana Claudia Arias, Fred Endicott and Robert A. Street; Falo Alto Research Center, Falo Alto, California.

The performance of polymer based electronic devices has shown great improvements over the past years. Polymer light emitting diodes (LEDs) show high luminance efficiency and thin film transistors (TFTs) show field effect mobilities of 0.1 cm²/Vs. These materials are easily processed from solution providing the potential of a vacuum free fabrication process. However, due to their poor environmental stability, polymeric devices are often fabricated and characterized under an inert atmosphere. The encapsulation of polymeric electronic devices is very challenging since most of materials available and used for encapsulation require process steps that involve high temperatures or solvents that may damage the polymeric semiconductor. Here we study the environmental stability of two polythiophene derivatives used to fabricate thin film transistors. The polymer films were self-capped by depositing the semiconductor blended with an insulating polymer from solution. SEM and EDS studies show that during film deposition phase separation occurs and the semiconductor and insulator materials form different phases in the film. The morphology of the phase separated film was control such that the semiconductor material segregates to the top surface encapsulating the underlying semiconducting organic film. Bottom gate TFT were fabricated with blends of semiconducting and insulating polymers at different concentrations and mobilities as high as 0.05 cm²/Vs were found. TFT devices were fabricated in air and showed stable sub-threshold voltages up to 21 days in air. This self-encapsulating process is compatible with inkjet printing techniques and improves the integration of TFT backplanes with display media.
Most of the organic semiconductors are the materials optically active in visible range. Operation of organic light-emitting diodes and solar cells is based on optical properties of these materials. This will show that optical effects may also play an important role in Organic Field-Effect Transistors (OFETs) - another key component of organic electronics [1,2]. Particularly, we report on an observation of light-induced switching of conductance in the back-gated OFETs with a built-in conduction channel [3]. Other results, including the demonstration of control of the OFET's characteristics with light, will be discussed. Supported by the NSF (DMR 0405208, ECE 0437932) and ARPA (I-R-99-1-0252). [2] V. Podzorov et al., Phys. Rev. Lett. 83, 3504 (2004). [3] V. Podzorov et al., cond-mat/0407638

13.6 Organic Thin Film Phototransistors: Materials and Mechanism. Dong-Yu Kim1, Yong-Young Noh1 and Kyiieshi Yase2; 1Dept. of Materials Science and Engineering, Gwangju Institute of Science and Technology (GIST), Gwangju, South Korea; 2Photonic Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Japan.

Conjugated organic oligomers or polymers have attracted a great deal of interest for use in applications of organic light emitting diodes (OLEDs), organic field effect transistors (OFETs), and organic photovoltaic devices. In particular, the fascinating photo-detection characteristics of conjugated organic compounds in the UV or visible region could lead to optoelectronic devices such as photovoltaic cells, photodetectors or photo-modulated OLEDs with a photocconducting layer. Among various organic phototransistors (OPTs) with thin-film transistor geometry are viable candidates for large area optical transducers because they combine light detection and signal amplification properties in a single device without the noise increment associated with conventional photodiodes. In this presentation, we will discuss on OPTs having a high responsivity and a ratio of photo-on-current to dark-off-current (IPh/IDark) fabricated by various organic conjugated oligomers. A main operating mechanism on OPTs will also be discussed.

13.7 Orientation of Organic Semiconductor Films on Photoreactive Polyimide Films and its Influence on Field-Effect Transistor Characteristics. Hiroshi Kikuchi1, Yuichi Uchida2, Yoshidile Fujisaki1, Hirotu Sat01, Taisieru Kurita1, Kuniharu Takizawa2 and Fumio Sat01; 1NHK Science & Technical Research Laboratories, Tokyo, Japan; 2Seikei University, Tokyo, Japan.

Control of the orientation of organic semiconductor films is one of the most important issues in the fabrication of field-effect transistors (FETs). In this study, we have investigated the effect of surface treatment on the orientation and mobility of pentacene by using a photoreactive polyimide film to modify the gate-insulator surfaces in organic FETs. A polyimide film based on a cyclotetrasilane tetracarboxylyphenylhydrazide (CBDA) component was used for this modification in order to induce orientation effects. Linear polarized UV light (wavelength range: 220-400 nm) was irradiated onto a polyimide film (80nm-thickness) on a glass substrate after baking (180°C for 1 hour) for the photo-alignment treatment. Polarized FT-IR and UV-visible spectra confirmed that alignment was induced by a photodecomposition of the polyimide. Moreover, optical anisotropy in the layer was confirmed using reflection ellipsometry. It is considered that linear polarized UV radiation in which the electric field is parallel to main chain of the polyimide causes anisotropic photodecomposition, and that this photodecomposition can cause the homogeneous alignment of organic semiconductor molecules on the film. To confirm this effect, X-ray diffraction was used to measure a pentacene film (50 nm-thickness) that was deposited on the polyimide after the photo-alignment treatment. The orientation of the pentacene film was greatly improved when the UV energy that was used to irradiate the polyimide film component was increased to 0.75 J/cm². Based on these results, we used this photo-alignment treatment to fabricate two types of pentacene FETs, with either silicon oxide (SiO2) or tantalum oxide (Ta2O5) as the gate insulator. We reliably and reproducibly improved the mobility of the device from 0.09 to 1.7 cm²/Vs for the SiO2 gate-insulator and from 0.5 to 1.9 cm²/Vs for the Ta2O5 gate-insulator under air-environment conditions. The current on/off ratio was over 105. Most of the characteristic parameters of the FETs, such as the best mobility, threshold voltage and on/off current were improved by using the UV treatment technique. We believe that this surface treatment method is generally applicable to any organic semiconductor that grows with a lamellar or plate-like habit, and that it is also general for any dielectric surface.

13.8 A Novel Concept of Vertical Organic Transistor with Low Working Voltage and High Output Current. Leping Ma and Yang Yang; MSE, UCLA, Los Angeles, California.

The major concept of conventional field-effect transistor is to create and control the channel by gate biases; hence it is the charge transport property being modulated. In this presentation, we report on an organic transistor with a unique device structure and device operating principle, i.e. low voltage driven field-effect transistor. The transistor consists of an active cell such as an organic diode, on top of a capacitor cell. When the capacitor cell is charged up, the top active cell is affected by the charged capacitor cell through a field effect, biasing the UV character cell. As a result, a novel organic field effect transistor is demonstrated. We have achieved organic transistors with low working voltages (less than 5 V), high current output (up to 10 mA or 4 A/cm²) and high On/Off ratio (six orders in magnitude). Discussions about the device characteristic will be provided. The demonstrated transistor with its enhanced operating characteristics creates new directions for organic transistors and their applications.

15.0 Low Voltage All-Polymer Transistor Utilizing a Hysrogroscopic Insulator. James G. Backlund1, Henrik G. O. Sandberg1, Ronald Osterbacka2 and Henrik Stubb1; 1Physics, Also Akademi, Turku, Finland; 2VTI Information Technology, Espoo, Finland.

Thin-film transistors (TFTs) based on solution-processed materials have many advantages compared to inorganic devices. The possibility of using direct printing techniques, flexibility, light weight, and low fabrication costs are all possible to achieve using polymer materials in TFTs. Controlling the TFT performance when using several layers of polymeric materials is a critical manufacturing task. We report on fabrication methods that can be used to improve the performance of TFTs. By using a hygroscopic insulator, polyvinylphenol (PV), in the TFTs we have fabricated high performance all-polymer transistors operating on voltages below two volts with distinct linear and saturated regimes. The transistors can be fabricated and operated in ambient air, but when operating the devices in controlled environments we show that the presence of moisture is essential for achieving the low voltage operation of these devices. However, the current modulation of the device is slower than expected and an explanation for the observed behavior incorporating ionic motion at the active layer interface is presented. There is also an interest of orienting the active layer in TFTs as it has been shown that improving the semiconducting material can have a favorable effect of the charge carrier mobility of the device. We here also present a new technique for accomplishing enhanced orientation in the polymer semiconductor layer. The orientation is obtained using no mechanical tools and the device structure is the same as in a top gate transistor. The semiconducting polymer, poly(3-hexylthiphene), is spin coated on a substrate with a spincoated PV (insulator film) mediator on top. A second polymer PEDOT:PSS (shrinker) is drop cast on the mediator. The shear force of the drying shrinker is used to orient the semiconductor beneath the mediator. Both the mediator and the shrinker can be removed to observe the obtained orientation. We have studied the devices operating using optical birefringence, x-ray diffraction, atomic force microscopy, and polarized absorption. [1] H. G. O. Sandberg et al. Adv. Mater. 2004, 16, 1112 [2] T. G. Bäcklund et al. Appl. Phys. Lett. 2004, 85, 3887 [3] T. G. Bäcklund et al. Adv. Funct. Mater. (in press)

15.1 Design and Synthesis of Functionalized Pentacene for Organic Field-Effect Transistors. Atibhi Basu Mallik, Maung-mang Ling and Zhanen Bao; Chemical Engineering, Stanford University, Stanford, California.

Organic field-effect transistors (OFETs) are of great interest because of their applications for plastic electronics such as electronic papers and flexible displays. Among organic semiconductors, pentacene has exhibited the highest field-effect mobility (close to 7 cm²/Vs) on polymer gate dielectrics) (1). However most of the efforts in improving the performance of pentacene-based OFETs have so far relaid on device physics and engineering techniques, rather than on pentacene functionalization. Prompted by recent efforts in the field (2), we are exploring the development of functionalized pentacene derivatives of both 1D and 2D types. In this presentation we further report on our continuing efforts (3) in the design and synthesis of pentacene-based derivatives with the aim of increasing their solubility, tuning their electronic properties, and improving their molecular ordering. Our strategy is to study the performance of OFET devices of these new materials. 1) Kelley, T. W.; Muyres, D. V.; Baude, P. F.; Smith, T. P.; Jones, T. D. Mat. Res. Soc. Symp. Proc. 2003, 771, L5.1- L5.6 2) Anthony, J. E.; Brault, D. S.; Hsu, H. C.; Lee, K.; J. Am. Chem. Soc. 2001, 123, 9482-9483. 3) Meng, H.; Beadlouk, M.; Mitchell, G.; Helgeson, R.; Wudli, F.; Bao, Z.; Siegert, T.; Kloc, C.; Chen, C.-H. Adv. Mater. 2003, 15, 1666-1603.
Fullerene Based n-type Organic Thin-Film Transistors.

Josiah N. Hajla, Bruno Domeneq, and Bernard Kieffer
School of Electrical and Computer Engineering, Georgia Institute of Technology, Atlanta, Georgia.

Significant progress has been made in the area of p-type organic field effect transistors while progress in developing n-type materials and devices has been comparatively lacking, a limiting factor in the pursuit to develop complimentary organic electronic circuits. Given the need for n-type organic semiconductors we have carried out studies using two different fullerene molecules, C60 and C70. Transistors were fabricated on heavily doped silicon wafers with thermally grown SiO2 as the gate oxide with Ti/Au bottom contact source and drain electrodes. Performance with these materials in similar geometries has shown field effect mobilities as high as 0.5 cm2/Vs for C60 [1] and 0.002 cm2/Vs for C70 [2], both reported for devices with organic films deposited and tested under ultra-high vacuum conditions. Here, we report mobilities ranging from 0.02 to 0.5 cm2/Vs up to 0.6 cm2/Vs (depending on channel dimensions), and mobilities from 0.003 cm2/Vs up to 0.04 cm2/Vs for C70. All devices were fabricated with organic films deposited under high vacuum but tested at ambient pressures under nitrogen. Devices performance (threshold voltage, on/off current ratio, etc.) will be presented and compared for both materials.


High Performance Organic Thin Film Transistors Based on Cyclohexyl-Substituted Organic Semiconductors.

Jason Locklin1, Zhean Bao2 and Rigoberto Advincula1
1Chemistry, University of Houston, Houston, Texas; 2Chemical Engineering, Stanford University, Stanford, California.

Various cyclohexyl end-capped oligomer semiconductors based on oligothiophene, oligothiophene-fluorene, and perylene diimide have been synthesized with Stille and Suzuki coupling. These materials exhibit increases in solubility over their unsubstituted or hexyl-substituted counterparts and have been successfully employed as the active component in organic field effect transistors. The morphology of vacuum deposited films of these oligomers has been investigated using TEM, AFM, and X-ray Diffraction. Field effect mobility as high as 0.17 cm2/Vs was observed in fluorine-thiophene oligomers deposited at elevated substrate temperatures. With the series of materials, a correlation between the size of the endgroup to the size of the inner semiconducting core is found to be an important factor in crystal growth in the thin film phase and directly related to charge transport in these materials.

Impact of Polymer Nanostructure on Performance of Regioregular Poly(3-hexithiophene) Thin Film Transistor.

Sujin Jia1, 2, Troy D. Hammond1, Shawn P. Williams1, Richard D. McCullough1 and Tomasz Kowalewski1

The use of regioregular head-to-tail polyalkylthiophenes in field effect transistors (FETs) is one of the most widely studied applications of these materials. While considerable amount of attention has been dedicated to control or improve the field effect carrier mobility in these devices, the results are not very consistent and are the subject of debate. One of the main reasons is that the formation of thin polythiophene thin films from solvents is highly sensitive to a variety of thermodynamic and kinetic factors, such as molecular architecture, molecular weight (MW) and its distribution, solvent, temperature, and external force field. In this study, atomic force microscopy (AFM) was used to monitor the morphology of thin films prepared from regioregular poly(3-hexithiophene) (HT-P3HT) and HT-P3HT based diblock copolymers of various MW, cast from several different solvents. Our results indicate that both the HT-P3HT homopolymers and their block copolymers with immiscible segments (e.g., poly(methyl acrylate) and polyesters) self-organize into two typical morphologies: (I) well-defined narrow, elongated aggregates ("nanowhiskers"), and (II) fine "granular" structures ("nanograins"). Type I morphology ("nanowhiskers") prevalent under conditions favoring film crystallization and long range aggregation in -/τ stacking direction. Such conditions can be achieved through the use of low volatile solvents and low MW polymers. In contrast, rapid solvent evaporation and high MW polymers favor formation of type II morphology ("nanograins"). Equilibrated HT-P3HT channels were cast under conditions favoring either of these structures indicate that granular morphologies lead to field effect carrier mobilities up to more than one order of magnitude higher than those observed for "nanowhiskers" structure. We propose that this difference is caused primarily by the difference in "sharpness" of grain boundaries between these two typical types of nanostructures.

Current charge carrier transport in field effect transistors based on Tricyanovinyl-capped Oligothiophenes. Xiuyu Cai1, Michael Borrad2, Christopher Newman3, Kent Mann and C. Daniel Friedb1
1Department of Chemical Engineering and Materials Science, University of Minnesota, Twin Cities, Minneapolis, Minnesota; 2Department of Chemistry, University of Minnesota, Twin Cities, Minneapolis, Minnesota.

Charge carrier transport in four tricyanovinyl (TCV)-capped oligothiophene compounds was studied with thin film field effect transistors. X-ray diffraction (XRD) and atomic force microscopy (AFM) both indicated that the films sublimed under high vacuum were highly crystalline. The films obtained from compound with three thiophene rings as the backbone showed highest electron mobility and on/off ratio of 0.005 cm2/Vs and 106 respectively and the activation energy of 90 meV. When the number of backbone thiophene rings increased to six, the majority charge carriers changed from electrons to holes with a hole mobility of 1.1x104 cm2/Vs.

High Performance Stable Thin Film Field Effect Transistors (TFTs) from Novel Organic Semiconductors Bis-thiophenyl-2,6-Anthracenes. Hong Meng, DuPont Company, Wilmington, Delaware.

Current research efforts have been focused on the stability and high performance of organic thin film transistors. We present our recent results on the design, synthesis, and device testing of a new class of stable organic semiconductors for OFETs. The mobility as high as 0.5 cm2/Vs and the on/off ratio over 107 have been achieved. We have investigated the device stability both in terms of shelf and the operating life time. Remarkably, the device demonstrated an average mobility of 0.4 cm2/Vs and on/off ratio above 106 after 2 years storage. Furthermore, there is no sign of decrease of the performance during the continuing operating the device for several thousands of times.

Surface and Interfacial Study of Organic Semiconductor Field Effect Transistor for Label-less DNA Biosensor. Melissa Stickles1, Sandrine Rivillon2, Yves J. Chabal1, Refik Kortan3, Zhean Bao2, Vitaly Podzorov2, Michael Gerashenson3 and Howard Katz1
1Biomedical Engineering, Rutgers University, Piscataway, New Jersey; 2Physics and Astronomy, Rutgers University, Piscataway, New Jersey; 3Chemical Engineering, Stanford University, Stanford, California; 4Materials Science and Engineering, Johns Hopkins University, Baltimore, Maryland; 5Rutgers University, Piscataway, New Jersey.

Label-less biosensors allow diagnostic DNA hybridization detection without the hindrance and complexity of fluorescent labeling. We are developing a label-less biosensor using a specialized organic field effect transistor (OFET). Our work currently focuses on characterizing organic thin films, and correlating their structure to charge transport using FTIR, X-ray diffraction, AFM, and current-voltage measurements. Organic molecules are selected from existing DNA immobilization properties such as hydroxyl-terminated groups (e.g. molecules with a bithiophene core). We deposit thin films of selected organic molecules on an insulating silicon dioxide layer using vacuum sublimation and solution deposition techniques. Due to organic molecule liquid crystalline complexity, we are likely to observe various molecular orientations. We believe such variation will affect organic charge transport properties. In order to study the relationship between crystalline structure and electron mobility, we begin by testing the influence of preparation methods, film thickness, and deposition temperature on layer structure. To understand the electronic sensing mechanism, we are studying the effect of the chemical and structural nature of surface-attached functional groups on the electrical performance of the organic field effect transistor. The chemical nature of the surface (composition and orientation) of the semiconducting organic thin film is determined using Fourier transform infrared spectroscopy (FTIR) in transmission geometry. The orientation of the molecules can also be extracted from polarization measurements, and the bonding to the substrate is evident from the formation of new peaks absent both on the original substrate and in the molecule itself. Supplementary structural information is obtained from X-ray diffraction studies at the X22A beamline of Brookhaven National Laboratories. We have measured both powder spectra of the organic compounds and thin film diffractions. Thin films exhibit a non-random preferential surface orientation. Equality of molecular model length predictions with the first diffraction peak layer spacing indicates near perpendicular orientation. Bragg peak indexing has been used to assign the unit cell organization in relation to substrate
temperature. A herringbone packing model is proposed for the more rigid molecule, while the organic semiconductor with flexible terminal groups shows an in-plane orientation with a monoclinic structure. Preliminary electrical data indicates that field-effect behavior can be achieved with mobility larger than 0.01 cm²/Vs, and correlation with film structure is under way. With X-ray diffraction and FTIR studies, we will be able to correlate film orientation with transport properties and affinity to biomolecules, making it possible to produce an optimal field-effect biosensor.

13.17 Single Molecular Layer Thin Film Transistors. Viet Wagner, Tobias Muck and Juergen Fritz; School of Engineering and Science, International University Bremen, Bremen, Germany.

Thin film transistors made of small organic molecules as active material show superior electrical characteristics in comparison with polymer based devices due to their ability of high crystalline ordering. Besides high mobility, other properties such as thermal stability, the optimisation of the insulator/organic interface and the proper preparation of ohmic contacts to the source and drain electrodes. In this context we present a study of thiophene-based thin film transistors, i.e. using α,ω-dihexylthiophene (DHHT) and α,ω-dihexyloxithiophene (DHOT) as active materials. Devices are prepared on oxidised highly doped silicon wafers. The silicon acts as source and drain contacts. Devices with systematically varied channel length (L = 2..50 μm) allow to determine the contact resistance via the transfer line method. Before deposition of the active layer, the silicon oxide (SiO₂) is cleaned with hexamethyldisilazane (HMDS) or octadecyltrichlorosilane (OTS) treatment. Firstly the transport layer thickness of the organic devices is determined experimentally. This is done by monitoring the drain current during the growth process of the organic layer via in situ electrical characterization under ultra-high vacuum conditions. The maximum of the drain current was found after growth of one or two molecular layers depending on the growth conditions. This result underlines the crucial importance of the insulator/organic interface preparation and the careful control of the initial stages of the organic layer growth. Secondly an in situ technique is applied to manufacture systematically organic field-effect transistors with a single molecular layer. The devices show rather high mobility values of about 0.03 cm²/Vs for DHHT on HMDS treated surfaces. Further growth beyond the first molecular layer results in oscillations of mobility values correlated to the completion of the first and second layer. Further layers tend to decrease mobility. In addition we observe an increase of the electrical contact resistance upon deposition of subsequent layers. Atomic force microscopy transistors after the growth process reveal a mass transport close to the electrodes. The number of thiophene molecules in the channel is reduced while an accumulation of molecules is found at the contacts. This mass transport over a length scale of one micron is considered to be one reason for the increase of contact resistance. These findings indicate, that single molecular layer devices are less affected by the growth disturbance caused by gold contacts in bottom contact geometry and that thicker layers are not required for successful transistor operation.

13.18 Effective Dopant Analysis for the High Performance Poly(3-Hexylthiophene) Field-Effect Transistors. Shigeki Komatsu, Masaharu Yoshida, Satoshi Horinouchi and Toshidhi Kamata; 1 R&D Center, RICOH, Yokohama, Japan; 2 Optoelectronic Industry and Technology Development Association, Tokyo, Japan; 3 National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan.

Organic field effect transistors (FETs) using a polymer semiconductor are one of the key technology for flexible and printable electronics, thus many research efforts have been devoted to the development of high performance polymer FETs. Recently α,ω-dihexylthiophene (P3HT) is a well known polymer semiconductor, which gives high field effect mobility (>10-1 cm²/Vs). It has been recognized that such a high mobility can be realized with a highly stacked and ordered structure of P3HT in the thin film. However, it has been revealed that such structural control is not sufficient to give the high mobility for the P3HT-FET. The structural control is not sufficient to give the high mobility for the P3HT-FET. In the past, some papers reported that the high mobility could be achieved by using single layer films. In this study, we have examined the origin of such an unclear doping effect for the P3HT-FET and discussed an effective dopant to give high performance polymer FETs. P3HT was prepared by a solution process. A detailed elemental analysis of the synthesized P3HT revealed that it contained halogens, terminal halogens, Zn, and Ni as impurities. Highly purification of the P3HT resulted in the decrease of the work-function of P3HT, and one or two orders decrease of high field effect mobility. It is suggested that the doping effect of each impurity species has been reported by several publications. The polymer P3HT shows superior electrical characteristics in comparison with the adjacent polymer molecules. The impurities seem to be original for the increase of hole mobility. Next, we have examined the effects of metal species dispersed in the P3HT film. Several kinds of ultra-fine metal particles was dispersed in the p-doped P3HT film with a purpose of controlling the intrinsic carrier density. Metal particles with lower work-function than P3HT acted as a donor, then de-doping effects could be observed. It is suggested that such a sub-threshold region, namely reduction of the on-off ratio, is due to the decrease of the carrier density. It resulted in keeping high mobility and activity of the on-off ratio. We will discuss the relation of the doping and de-doping effects for the high performance of polymer FETs in this presentation.

13.19 Programmable Polymer Thin Film and Nonvolatile Memory Device. Jin Yongng Oyang, Chih-Wen Chiu, Liping Ma and Yang Yang; Materials Science & Engineering, UCLA, Los Angeles, California.

We developed a novel organic memory device by taking the advantage of the organic electronics and nanotechnology. This device, made from a polystyrene film containing poly(3-hexylthiophene) (P3HT) and 8-hydroxyquinoline sandwiched between two metal electrodes, exhibited programmable electrical bistability. This device was fabricated by solution processing. The pristine device was in a low conductivity state and abruptly transited to a high conductivity state near 2.8 V. These two states differ in conductivity by about four orders of magnitude. Applying a negative bias of 1.8 V caused the device to return to the low conductivity state. The transitions are non-volatile and can be cycled for numerous times, so that the device can be used as low-cost, high-dielectric, nonvolatile memory. The mechanism for the electrical transition is attributed to an electric-field induced charge transfer between gold nanoparticles and 8-hydroxyquinoline. We speculate that this single-layer, solution processible and programmable thin film device presents a new direction for organic electronics.

13.20 High Mobility Pentacene Organic Field Effect Transistors Based on a Ferroelectric Polymer Gate Dielectric. Barbara Stanello1, Martin Zirkel1, Michael Beut1, Hames Marsch1, Georg Jakopic2, Guestrer Leising1, Simona Bauer-Gogonea3 and Siegfried Bauer2; 1 Institute of Nanostructured Materials and Photonics, Joanneum Research, Weiz, Austria; 2 Institute of Soft Matter Physics, Johannes Kepler University, Linz, Austria.

High-performance organic thin film transistors in top-contact geometry with pentacene as semiconductor and double layers of a ferroelectric polymer electrolyte poly(vinylidene-fluoride) containing tetrahydroxyethylenhexafluoropropanoic acid and the polymer poly(vinyl cinnamate) as gate dielectric are reported. The electrolyte is a high dielectric constant polymer with a dielectric constant ε=10 at 1 MHz. The other component of the gate dielectric, poly(vinyl cinnamate), is used as a seed layer for a correlated pentacene growth. The morphology and structure of the pentacene thin films were characterized by atomic force microscopy and X-ray diffraction. The film thickness and the optical constants of the double layer gate dielectric were determined by variable angle spectroscopic ellipsometry. As, depending on the preparation, the electrolyte thin film may appear in several crystalline compositions ranging from ferro- to paraelectric phases. Spectroscopic analysis was done in order to determine the actual phase composition which strongly determines the dielectric behavior. The detected electric bistability was extracted from the transistor characteristics and accounted for the paraelectric phase. The field-effect performance of the transistor characteristics was also accounting for the parasitic series resistance from the source and drain contacts. It is suggested that the dielectric effect and the morphology of the semiconductor layer is closely connected to the film structure and that in films having grain sizes above a critical value, intrinsic mobilities of 1cm²/Vs and more can be achieved. The use of ferroelectric layer high dielectric constant polymer dielectrics seems promising for lowering the operation voltage and for applications of organic field effect transistors in sensor systems and organic memories based on the ferro-, piezo- and pyroelectric properties of such polymers.

13.21 Surface and Solvent Mediated Molecular Ordering of Polythiophenes and Its Effects on Field-Effect Mobility in Thin Film Transistors. Kiwha Choi, Doh Woon Kim, Yeong Don
We have fabricated monochromatic organic light emitting diodes (OLEDs) using heavy heteroleptic iridium tris-cyclometalates. Arnold Tamayo1, Biwu Ma2, Peter Djurovic1 and Mark E. Thompson1,2,3,1Chemistry, University of Southern California, Los Angeles, California, 2Material Science, University of Southern California, Los Angeles, California, 3Department of Physics, UC Los Angeles, Los Angeles, California.

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Microcavity organic light emitting diodes (MOLEDs) are of great interest in recent years due to their spectral narrowing and color tuning ability. Organic materials usually have broad emission spectra, resulting in the inferior color purity of the devices. For example, photoluminescence spectra of tris(8-hydroxyquinoline) aluminum (Alq) have full width half maximum of ~85 nm. Narrowing of the emission spectrum can be achieved by using a microcavity structure. In addition, microcavity can be used to tune the position of the emission peak. In this work, we fabricated near-infrared emitting MOLEDs with two organic layers. The hole transporting layer was Alq, N" - d(naphthalene-1-y1) - N,N" - diphenylbenzilnic (NPB), and Alq was the emissive and electron transporting layer. The bilayer structure was sandwiched between two silver mirrors. In order to investigate the tunability of the microcavity Q-factor, devices with different thickness of bottom mirror (anode) were fabricated. The influence of the choice of the bottom mirror (anode) was also investigated, and the devices with copper and gold anodes were fabricated. The devices were characterized by angular dependent electroluminescence, photoluminescence, and transmittance measurements. Possible origins of the observed phenomena are discussed.

13.28
One and Two-Color Tandem Organic Photovoltaic Cells,  
Leguizamo C. Palacios 1,2, Gary K. Kunath 1, Wao-hong Kim 1,2, and Zakya H. Kafafi 1,2; 1Naval Research Laboratory, Washington, District of Columbia; 2SFA Inc., Largo, Maryland.

One and two-color tandem organic photovoltaic (OPVs) based on p/n (electron donor/electron acceptor) heterojunctions were fabricated and characterized on glass and plastic substrates. An ultra-thin layer consisting of Ag nanoclusters (Agx) served as the electron-hole recombination center between the two cells. Electron donors such as triarylmethines and N,N'-dis(4,4'-cyanobiphenyl-4-yl)-diphenylamine (BCP), electron acceptors such as C60 and 3,4,9,10-perylene-tetracarboxylic bis-benzimidazole (PTCBI) were used at the p/n junction. One-color OPVs/C60/Agx/NPD and two color OPVs/C60/Agx/CuPc/C60 OPVs exhibited relatively high fill factors of 0.4-0.45 and open circuit voltages of 1.30 and 1.05 V, almost equal to the sum of the open circuit voltages of the top and bottom cells. The paper will discuss the performance of tandem cells based on the absorption and charge separation/collection of the cells in the UV-Vis spectral range, the photovoltaic spectra of tris(8-hydroxyquinoline) aluminum (Alq) have full width half maximum of ~85 nm. Narrowing of the emission spectrum can be achieved by using a microcavity structure. In addition, microcavity can be used to tune the position of the emission peak. In this work, we fabricated near-infrared emitting MOLEDs with two organic layers. The hole transporting layer was Alq, N" - d(naphthalene-1-y1) - N,N" - diphenylbenzilnic (NPB), and Alq was the emissive and electron transporting layer. The bilayer structure was sandwiched between two silver mirrors. The bilayer structure was sandwiched between two silver mirrors.

13.29
Improving the Interface in Organic-Inorganic Hybrid Photovoltaic Cells,  
Yuxiang Liu 1,2, Lin Shu 1,2, Naiqing Huang 1,2, Michael McGlohe 1,3, Carine Edder 1, Jinving Liu 1,2, Jean Frechet 1, and Sean Shaheen 1; 1Stanford University, Stanford, California; 2Molecular Foundry, Berkeley, California; 3UC Berkeley, Berkeley, California; 4NREL, Golden, Colorado.

In organic-inorganic hybrid photovoltaic (PV) cells, photogenerated excitons diffuse to the organic-inorganic interface, where they are split by electron transfer. If the inorganic surface is modified by a thin coating of a third material before the organic semiconductor is incorporated, almost every property of the PV cell is affected. The interface modifier alters the packing of the organic molecules, which in turn affects the exciton diffusion length and the charge carrier mobility. The coating can increase the rates of forward and backward electron transfer by providing a covalent attachment between the organic and inorganic materials, which can lower down these rates by providing a barrier to electron transfer. Dipoles at the polymer/inorganic semiconductor interface can change the operating voltage of the device due to the shift of local vacuum level. If the energy gap of flat polymer is smaller than that of the light absorbing material, Förster energy transfer can be used to increase the distance over which excitons can be harvested. Furthermore, the thin coating can also help absorb light. To take advantage of the above hybrid PV cells, we have developed several conjugated polymers, which have thermally labile side groups, that interact with inorganic surfaces with a carboxylic acid moiety once the side group is removed. After attaching these polymers to a TiO2 nanoporous film, we are able to cover them with an additional organic semiconductor without removing the first polymer. Absorption measurements show that the interface modifier has a 36 % higher ability to absorb light once its side chains are removed. This enhancement in absorption coefficient enables more excitons to be formed within a diffusion length of the interface. This factor alone makes PV cells approximately 36 % more efficient. Photoluminescence measurements show that the energy levels of excitons for the conjugated polymers are chosen correctly most of the excitons formed within 15 nm of the interface are harvested due to efficient Förster energy transfer. We have been able to double the power conversion efficiency of hybrid organic-inorganic photovoltaic systems by using this method. Cyclovoltammetry measurements show that the carboxylic acid moieties lower the HOMO and LUMO of the polymers by 0.3 eV if they are attached directly to the conjugated backbone.

13.30
Hybrid Solar Cells based on Nanoporous TiO2 and a New Spirofluorene-Thiophene Copolymer with Oxidative Stability,  
Jang Jo, Doojin Yak, Seok-Soon Kim, Yong-Young Noh and Dong-Yu Kim; Dept. of Materials Science and Engineering, Gwangju Institute of Science and Technology (GIST), Gwangju, South Korea.

Recently, solar cells based on conjugated polymers have been actively researched for low-cost alternatives to conventional solid-state devices. Hole transport in the conjugated polymer is the limiting process in most hybrid nanocrystalline TiO2 solar cells with semiconducting polymers infiltrated. An efficient photo-induced charge transfer was required in a polymer p/n consisting of fluorene-based polymers such as poly 9,9-diocetylfluorene-co-bithiophene (F8T2). Therefore, F8T2 has emerged as a hole transporting material in high hybrid solar cells consisting of interpenetrating networks of TiO2 and polymer semiconductors (NPD/C60/Agx, NPD/C60, C60/Agx) to deliver PV cells with high hole mobility known in field effect transistors. However, most of devices fabricated from polymer-based polymers or oligomers suffer from photo-oxidative degradations as a result of UV illumination. We expected that this effect in photovoltaic cells, which are subject to be exposed to intense sunlight, will be more prominent than in other organic devices such as organic light emitting diodes and organic field effect transistors. In addition, heat treatments of a TiO2 nanoporous film in contact with a polymer film are needed for embedding the polymer into nanofibers less than 20 nm diameter in which excitons in organic materials can typically diffuse before recombining. This high temperature process could be another cause creating oxidative degradations. In this study, we propose new fluorene-based copolymers containing a spirooxazinecofluorene unit to avoid photo- and thermo-oxidative degradation, and report on greatly improved stability. We also present the effect of oxidative degradations on the device performance of photovoltaic cells consisting of these.

14.01
Absorption Quenching and Photovoltaic Effect in Poly(3-hexylthiophene) Thin Films Blended with Functionalized C60 Derivatives,  
Vishal Shrotriya, Jianyong Ouyang, Gang Li and Yang Yang; Materials Science and Engineering, University of California Los Angeles, Los Angeles, California.

Regioregular poly(3-hexylthiophene) based polymer photovoltaic cells have attracted a lot of attention recently because of their high power conversion efficiencies. To further enhance the device performance it is important to study the effect on the absorption spectra of the polymer when it is blended with C60 derivatives. In this study, the absorption spectra and the photovoltaic effect in thin films consisting of an admixture of p-type poly(3-hexylthiophene) and n-type acceptor [6,6]-phenyl C60 butyric acid methyl ester have been studied. A decrease in interband absorption in the wavelength range of 450-600 nm for the spun-cast films with different weight ratios of p-type and n-type components was observed and was explained by the two coupled electron and hole transfer processes. This two component film is attributed to the dis-regularity of the poly(3-hexylthiophene) chains and the charge transfer between poly(3-hexylthiophene) and [6,6]-phenyl C60 butyric acid methyl ester. The charge transfer was confirmed by photoluminescence and photoluminescence spectroscopy of the films. Finally, photovoltaic cells were fabricated utilizing different weight ratios of donor and acceptor in the blend as the active layer and device characteristics were studied. The effect of intermixed p-type donor polymer and the n-type acceptor was studied and the open circuit voltage ratio of the two components was achieved to give high power conversion efficiencies.

14.32
Advantages of a Novel Method for Direct-Write Fabrication of Polymer Devices,  
Paul Rughesiner, B. J. Larson, M. G. Lagally and Padma Gopalan; Materials Science and Engineering, University of Wisconsin - Madison, Madison, Wisconsin.
Due to their extremely low cost, polymers are a promising material to revolutionize the field of low-cost electronics, high-efficiency photovoltaics, and electronic applications. Most manufacturing methods for polymer devices utilize some type of spin-coating process for the polymer. After spin-coating, the polymer film is then typically patterned using conventional lithography, or in some cases a more exotic form of patterning such as stamp-lithography, to achieve the final desired pattern. We have developed an instrument capable of direct-writing the polymer into the final desired pattern by a process where the polymer is dispensed onto the substrate as compared to a neat film. We thermally evaporated high weight, spin-cast from chloroform solution onto hydrophobic Si wafers before and after annealing of the film. Changes in the optical absorption and electrical conductivity polymer films were confirmed previously reported changes in the structure of the polymer backbone. Interestingly, FTIR studies showed that the changes in backbone structure occurred without significant alteration of the structure of the alkyl side chains. In fact, the data indicate that the alkyl side chains remain disordered for films prepared from both molecular weight fractions, regardless of annealing conditions. Finally, our ongoing work to obtain a more detailed and comprehensive understanding of the structure of these systems through further analysis of the spectroscopic data is presented.

13.34
Carrier-Injected and Transport Mechanism of In-situ Polymerized Polyaniiline Films. Rodrigo Fernando Bianchi1,2, Silvan Antonio Travain1 and Jose Alberto Giacomeli1

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We present a study of the electric carrier-injection and transport mechanism in thin polyaniiline (PAni) films prepared by in-situ polymerization technique. The PAni material was prepared using the conventional chemical synthesis and deposited in-situ onto glass substrate having on its surface gold or aluminum lines as interdigitated gate electrodes. Electrical measurements were performed using a Solartron Impedance/Gain-Phase analyzer, in the frequency range from 0.1 Hz to 10 MHz (ac measurements) and a Keithley current source measuring unit (dc measurements) at different temperatures and under vacuum. A model is presented for describing the current vs. voltage and the Impedance measurements characteristics of PAni-electrodes systems that encompass: (i) the variable range hopping in a positionally random and energetically disordered system of localized states, (ii) the charge injection from the metal and PAni-AI and PAni-Au contacts, and (iii) the influence of space charge-limited current transport mechanisms and ac electrical characteristics are in agreement with experimental data. The dependence of the zero-field contact barrier (PAni-AI and PAni-Au interfaces) for carrier-injection, as well the carrier mobility on the electrical field and the influence of doping level on the polymer permittivity are obtained. This work was sponsored by Fapesp and MCT/IMMP from Brazil.

13.34
A Combined Optical Approach to Structural Determination of Semi-Conducting Polymer Thin Films. Marc Guran1, Dean DeLongchamp2 and Lee Richter1

1Surface and Microanalysis Science Division, National Institute of Standards and Technology, Gaithersburg, Maryland; 2Polymers Division, National Institute of Standards and Technology, Gaithersburg, Maryland.

Realization of the promise of organic electronics will requires advances in the associated materials and process chemistry along with improvements in the methodologies used to characterize the various components of such devices. Previous work on thin films of poly(thiophene) has demonstrated that changes in molecular weight and fabrication conditions can have significant effects on the performance of these films. Yet, these investigations have yet to show good correlation between the experiments characterizing the material (AFM and X-ray diffraction), and the observed changes in the transport properties of the films. Transmission UV-Vis spectroscopy, Variable Angle Spectroscopic Ellipsometry (VASE), and FTIR spectroscopy were used in concert to investigate poly-3-hexyl thiophene (P3HT) films of different molecular weights, spin-cast from chloroform solution onto hydrophobic Si wafers before and after annealing of the film. Changes in the optical absorption and electrical conductivity polymer films were confirmed previously reported changes in the structure of the polymer backbone. Interestingly, FTIR studies showed that the changes in backbone structure occurred without significant alteration of the structure of the alkyl side chains. In fact, the data indicate that the alkyl side chains remain disordered for films prepared from both molecular weight fractions, regardless of annealing conditions. Finally, our ongoing work to obtain a more detailed and comprehensive understanding of the structure of these systems through further analysis of the spectroscopic data is presented.

13.36
The Time Dependent Parallel Resistance in an Organic Schottky Contact. Arash Takshi am

We present a study of the electric carrier-injection and transport mechanism in thin polyaniiline (PAni) films prepared by in-situ polymerization technique. The PAni material was prepared using the conventional chemical synthesis and deposited in-situ onto glass substrate having on its surface gold or aluminum lines as interdigitated gate electrodes. Electrical measurements were performed using a Solartron Impedance/Gain-Phase analyzer, in the frequency range from 0.1 Hz to 10 MHz (ac measurements) and a Keithley current source measuring unit (dc measurements) at different temperatures and under vacuum. A model is presented for describing the current vs. voltage and the Impedance measurements characteristics of PAni-electrodes systems that encompass: (i) the variable range hopping in a positionally random and energetically disordered system of localized states, (ii) the charge injection from the metal and PAni-AI and PAni-Au contacts, and (iii) the influence of space charge-limited current transport mechanisms and ac electrical characteristics are in agreement with experimental data. The dependence of the zero-field contact barrier (PAni-AI and PAni-Au interfaces) for carrier-injection, as well the carrier mobility on the electrical field and the influence of doping level on the polymer permittivity are obtained. This work was sponsored by Fapesp and MCT/IMMP from Brazil.

13.36
Improving the Charge Carrier Mobility of Conjugated Polymers by Chain Alignment in Nanopores. Bhavani Srinivasan1, Kevin M. Coakley1, Chia Goh1, Yuixiang Liu2 and Michael D. McGehee1, 1Department of Materials Science Engineering, Stanford University, Stanford, California; 2Department of Chemistry, Stanford University, Stanford, California.

We have formed films of anodic alumina with arrays of straight nanochannels on indium tin oxide (ITO) electrodes. We made films of conjugated polymers with conjugated polymers, including poly (3-hexyl thiophene) (P3HT) and OC1C10-PPV, by spin casting the polymers over the pores and then melting the film. Scanning electron microscopy, photoabsorption spectroscopy and depth profiling confirm that the polymer fills the pores. Measurements of the transmission and reflectance of s and p-polarized light as a function of angle show that the polymer in the nanopores is partially aligned in the direction perpendicular to the substrate as compared to a neat film. We thermally evaporated high work function electrodes on top of the polymer to make hole-only diodes and measured the mobility in the direction perpendicular to the substrate by fitting the I-V characteristics to a space charge limited current (SCLC) model. In the case of P3HT this data is known to have anisotropic transport characteristics, we see a substantial (>50%) enhancement in current as compared to neat films of equivalently thick polymer. We have simulated the electrodynamics in the semiconductor (polymer) - insulator (alumina) nanostructure using the device simulation program Medici to account for a possible increase in current due to the dielectric environment in the nanopores. It was found that a correction factor between two and four was needed, depending on pore diameter and thickness, to get agreement with this correction, we obtained a mobility of greater than 0.006 cm2/Vs which is a factor of 20 higher than the highest diode mobility seen in neat films of P3HT. We believe a mobility as high as 0.1 cm2/Vs can be achieved if the chains are fully aligned since this value has been observed in field effect transistors where the chains lie in the plane of the film and current goes in the plane of the film. In the case of OC1C10-PPV, which is known to have isotropic charge transport characteristics, there was no correction needed, and the data indicated that the alumina-infiltrated polymer diodes. We are currently characterizing...
other polymers, polymers with varying molecular weight, the effect of treating the surface of the alumina pores before polymer infiltration, and different infiltration conditions to further optimize the structure. These results have important implications for bulk heterojunction photovoltaic cells, which are mainly limited by hole mobility in the polymer. Increased hole mobility in the diode geometry can enable photogenerated holes to reach the top electrode before electron recombination with electrons occurs. By replacing the insulating alumina with a semiconductor, such as titania, we should be able to make efficient ordered bulk heterojunction solar cells.

13.37 Ambipolar Charge Transport in a Methanofullerene. 
1Department of Physics, Imperial College London, London, United Kingdom; 2OSSAM, Opto Semiconductors, Inc., San Jose, California.

Blends of conjugated polymer with methanofullerences such as [6,6]-phenyl C 61 -butyryl acid methyl ester (PCBM) have proved to be one of the most promising material combinations for organic solar cells, yielding power conversion efficiencies of 3-4% [1]. The superior performance of fullerences compared to alternative electron transporters is attributed to their excellent electron transport properties and ability to form a conducting network within the polymer matrix. Recent studies, from our laboratory and elsewhere [2], have revealed an additional factor: that the addition of PCBM improves not only the electron transport but also the hole transport properties of polymer:PCBM blend films. This enhancement of the hole mobility in the presence of PCBM helps to explain why the short circuit current generated by these cells reaches a maximum at high PCBM fractions in the range of 65-85 wt %. [3], However, the mechanism by which PCBM enhances hole transport is not yet understood. We will report detailed experimental studies of the electron and hole transport in blends of poly-[2-methoxy-5-(3,7-dimethyloctyloxy)-1-4-phenylene vinylene] (MDMOPPV) with PCBM, and blend films of PCBM dispersed in an inert polymer matrix. Studies of the MDMO-PPV:PCBM blend films show that increased content successively increases both electron and hole mobility, as measured by Time of Flight (ToF) and results in less dispersive hole transport. The hole mobility in a blend of composition 1:2 by weight is at least two orders of magnitude greater than in the pristine polymer, which is confirmed by a range of measurements and techniques. Studies of charge transport by PCBM show that electron and hole ToF mobilities are similar in blend films of PCBM dispersed in an inert polymer matrix, therefore showing that PCBM is an ambipolar charge transport material. This is supported by quantum chemical studies of the intermolecular charge transfer in PCBM. With the aid of temperature and composition dependent transport measurements and quantum chemical calculations, we address the question of whether or not hole transport in blends of poly-[2-methoxy-5-(3,7-dimethyloctyloxy)-1-4-phenylene vinylene] (MDMOPPV) with PCBM, and blend films of PCBM dispersed in an inert polymer matrix is plausible to be responsible for the increase in hole mobility in MDMO-PPV:PCBM blends when PCBM is added to the blend. [1] E.g. Fig. 1. Fund Mater. 14, 425-434 (2003); [2] J. van Duren et al., Adv. Funct. Mater., 14, 425-434 (2003); [3] K. Pachos et al., Synth. Met. 137, 1469-70 (2003); S.A. Choulis et al., Appl. Phys. Lett. 83, 3812 (2003).

13.38 Charg Mobility in Packed Structures. 
Nicholas Prokopuk and Roselyn Bui; Chemistry and Materials Division, Naval Air Warfare Center, China Lake, California.

Intermolecular interactions play an important role in determining the charge carrier mobility in an organic film. Ordered arrays of molecules tend to provide conditions that are better suited for charge conduction. Greater overlap between the orbitals of neighboring molecules in crystalline films can yield high-performing organic thin-film transistors. Crystal structures of both diphenyl (DP) and decafluorodiphenyl (FDP) show a herringbone packing of the aromatic ring system. The present work focuses on the synthesis and introduction of the electron deficient oxadiazole unit into the hole transporting polymer backbone. The present work focuses on the synthesis and introduction of the electron deficient oxadiazole unit into the hole transporting polymer backbone. Small molecules with high hole mobilities in an ortho- and meta-position relative to each other - termed o-OXA-X and m-OXA-X, respectively. These molecules are able to form large wavelengths in an o-OXA-X and m-OXA-X, respectively. Comparison of related systems.

13.39 Control of Ferroelectric Poly (Vinylidene Fluoride-Co-Trifluoroethylene)/Metal Electrode Interfaces using Self-Assembled Monolayers. 
Cheolmin Park and Yoon Juoi Park; Materials Science and Engineering, Yonsei University, Seoul, South Korea.

As polymeric materials, poly vinylidene fluoride (PVDF) and its copolymers with trifluoroethylene (TFE) are of particular interest for their ferroelectric properties and the nonvolatile memory device applications. Ferroelectric polymer storage device includes a ferroelectric polymer sandwiched between two metal electrodes that achieve electrical signaling across the structure. In poly (vinylidene fluoride-co-trifluoroethylene) [P(VDF-TrFE) 72:28] polymer films, polarization behavior is mainly related to crystallinity and the orientation in the film. Thin films of P(VDF-TrFE) were deposited by spin coating on bare metal electrode, large drop of polarization switching was measured. This low polarization results from low crystallinity and the specific crystallographic orientation in this film. Difficulties associated with transport of charge carriers, however, have proven to be a barrier to improving the device efficiency. A polymer with charge delocalization over two or three dimensions should allow for faster carrier transport thereby improving device performance. Imbalance in charge injection/transport of electrons and holes has also presented a challenge to improving device operation. Our group has previously synthesized and characterized a 2-dimensional conjugated poly[2-methoxy-5-(3,7-dimethyloctyloxy)-1-4-phenylene vinylene] (MDMOPPV) with PCBM, and blend films of PCBM dispersed in an inert polymer matrix. Studies of the MDMO-PPV:PCBM blend films show that increased content successively increases both electron and hole mobility, as measured by Time of Flight (ToF) and results in less dispersive hole transport. The hole mobility in a blend of composition 1:2 by weight is at least two orders of magnitude greater than in the pristine polymer, which is confirmed by a range of measurements and techniques. Studies of charge transport by PCBM show that electron and hole ToF mobilities are similar in blend films of PCBM dispersed in an inert polymer matrix, therefore showing that PCBM is an ambipolar charge transport material. This is supported by quantum chemical studies of the intermolecular charge transfer in PCBM. With the aid of temperature and composition dependent transport measurements and quantum chemical calculations, we address the question of whether or not hole transport in blends of poly-[2-methoxy-5-(3,7-dimethyloctyloxy)-1-4-phenylene vinylene] (MDMOPPV) with PCBM, and blend films of PCBM dispersed in an inert polymer matrix is plausible to be responsible for the increase in hole mobility in MDMO-PPV:PCBM blends when PCBM is added to the blend. [1] E.g. Fig. 1. Fund Mater. 14, 425-434 (2003); [2] J. van Duren et al., Adv. Funct. Mater., 14, 425-434 (2003); [3] K. Pachos et al., Synth. Met. 137, 1469-70 (2003); S.A. Choulis et al., Appl. Phys. Lett. 83, 3812 (2003).

13.40 The Role of Symmetry and Charge Delocalization in Two-Dimensional Conjugated Molecules for Optoelectronic Applications. 
Hernansa Christian, Zakhrn I. Nazihmetova, and Mary E. Galvin; Materials Science and Engineering, University of Delaware, Newark, Delaware; 2Rohm and Haas Electronic Materials, LLC, Marlborough, Massachusetts.

In recent years, the development of efficient polymer based electroactive devices (PLEDs, transistors and solar cells) has been a widely studied area of research. Difficulties associated with transport of charge carriers, however, have proven to be a barrier to improving the device efficiency. A polymer with charge delocalization over two or three dimensions should allow for faster carrier transport thereby improving device performance. Imbalance in charge injection/transport of electrons and holes has also presented a challenge to improving device operation. Our group has previously synthesized and characterized a 2-dimensional conjugated poly[2-methoxy-5-(3,7-dimethyloctyloxy)-1-4-phenylene vinylene] (MDMOPPV) with PCBM, and blend films of PCBM dispersed in an inert polymer matrix. Studies of the MDMO-PPV:PCBM blend films show that increased content successively increases both electron and hole mobility, as measured by Time of Flight (ToF) and results in less dispersive hole transport. The hole mobility in a blend of composition 1:2 by weight is at least two orders of magnitude greater than in the pristine polymer, which is confirmed by a range of measurements and techniques. Studies of charge transport by PCBM show that electron and hole ToF mobilities are similar in blend films of PCBM dispersed in an inert polymer matrix, therefore showing that PCBM is an ambipolar charge transport material. This is supported by quantum chemical studies of the intermolecular charge transfer in PCBM. With the aid of temperature and composition dependent transport measurements and quantum chemical calculations, we address the question of whether or not hole transport in blends of poly-[2-methoxy-5-(3,7-dimethyloctyloxy)-1-4-phenylene vinylene] (MDMOPPV) with PCBM, and blend films of PCBM dispersed in an inert polymer matrix is plausible to be responsible for the increase in hole mobility in MDMO-PPV:PCBM blends when PCBM is added to the blend. [1] E.g. Fig. 1. Fund Mater. 14, 425-434 (2003); [2] J. van Duren et al., Adv. Funct. Mater., 14, 425-434 (2003); [3] K. Pachos et al., Synth. Met. 137, 1469-70 (2003); S.A. Choulis et al., Appl. Phys. Lett. 83, 3812 (2003).

M. Scott Bradley, Jonathan H. Yoon, and Vladimir Bulovic; Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, Massachusetts.

Thin films of J-aggregate cyanine dyes, deposited using a layer-by-layer (LBL) technique of polyelectrolyte multilayers, exhibit excitation-polariton dynamics, the limit of strong coupling between light and matter. LBL-j-aggregate thin films can be precisely deposited in a specific location in an optical microcavity, enabling the fabrication of previously unachievable unique optoelectronic devices, such as the recently demonstrated excitation-polariton light-emitting device. To gain insight into the physical properties of these films, we investigated the optical and morphological properties of 5,6-dichloro-2-[5,6-dichloro-1-ethyl-3-(3-sulfopropyl)-2-H]-
bulks of field-effect transistors and light-emitting diodes. The studies included photoelectron spectroscopy, photoluminescence, and photoconductivity measurements that provide insights into the electronic properties and excitations of these layered structures. The optical constants were calculated by fitting optical absorption measurements to determine the absorption coefficient and film thickness. We also report on the use of photochemical reactions, using solution probes, to measure charge transfer rates and evaluate the possibility of further enhancing the heterogeneous electron transfer rate at TCO surfaces.

Ion-doped surfaces can be used to modify the electronic properties of TCO surfaces, which is crucial for improving the performance of organic electronic devices. The reliable determination of carrier mobility in organic electronic devices (e.g., thin film field effect transistors) is of huge importance for future progress in the field. However, a comparison between experimental results obtained in different laboratories is often hampered by the variation of sample preparation and the local optoelectronic properties of phase-separated conjugated polymer films. The studies included photoelectron spectroscopy, conventional AFM, conductive probe AFM, and electrostatic force microscopy.

A new method is described for surface modification of ITO with an electrochemically self-assembled monolayer (SAM) to enhance hole injection in an organic electronic device. This procedure involves sequential electropolymerization and ultraviolet light exposure to form a thin film of conducting polymer on the ITO surface. The application of this technique to the fabrication of novel devices that utilize strong coupling of light and matter.


Charge injection at the interface between transparent conducting oxides (TCO) and organic molecular transport materials is a critical determinant in the efficiency of these devices. Charge injection can be enhanced by using small molecule organic donors (OLEDs) and organic photovoltaics (OPVs). We have recently shown that: (i) electronic heterogeneity (e.g., effective work function); (ii) wettability by non-polar organic materials; (iii) rates of charge transfer, must all be optimized in order for device performance to be fully enhanced. Small molecules and conducting polymers can be chemisorbed to the TCO interface, and it can be shown that at least wettability and charge transfer rates can be greatly enhanced with the appropriately chosen carrier. The approach to generating thin films with large absorption constants and small scattering is critical for the design of high-performance photovoltaic devices. The optical constants of the films, and find that at the peak absorption wavelength 594 nm, the films possess an absorption coefficient of $a = 1.07 \times 10^5$ cm$^{-1}$, among the highest ever measured for a neat thin film. The optical constants were calculated by fitting spectroscopic data to films in the layered growth regime to model based on propagation and matching matrices. We also report that a set of polyaniline- and poly(3.4-ethylene dioxythiophene)-based film structures can be chemisorbed to the ITO surface and reduces the electronic heterogeneity of the ITO surface. The presented method is a general approach to generating thin films with large absorption constant and promises to be an enabling step to the fabrication of novel devices that utilize strong coupling of light and matter.


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 Organic materials are of great interest for incorporation into electronic components. Their unique advantages, such as simplified processing, tunable properties, and low cost make them attractive for both existing and emerging technologies. Devices such as transistors, light-emitting diodes, and memory devices certainly stand to benefit from these advantages, while new applications such as flexible displays and circuits may exploit them specifically. The success of these technologies is largely dependent on the electronic properties of the organic active layer material. To date, the highest-performance organic semiconductors have been those that conduct current via positive charge carriers, suitable for incorporation into p-channel devices. While the discovery of materials that approach the performance of inorganic semiconductors is encouraging, n-channel devices are key to developing organic electronics applications, such as organic CMOS circuits and rectifying elements. While many efforts have been made to synthesize new n-type materials, their performance has been hindered by a poor understanding of both film growth mechanisms and energy level requirements, specific problems never being addressed for n-type semiconductors. The purpose of this work is to systematically design, synthesize, and characterize new high-performance n-channel semiconductor materials. In addition to the obvious contribution to the efficiency of organic devices and circuits, this study carries the potential to elucidate fundamental relationships between molecular structure, film morphology, and electronic characteristics. In this paper, we will present the synthesis and transistor results of new n-channel organic semiconductors containing electron deficient side groups. We have employed a variety of techniques, such as x-ray diffraction, atomic force microscopy, and thin-film transistor characterization to investigate these relationships within novel families of organic molecules that appear promising for n-type devices.

**Abstract Withdrawn**
analysing expression for the mobility, leading to an accurate compact model. We demonstrate the importance of including the concentration dependence of the mobility in single-LED structures and the limitations of assuming a fixed mobility. We show that a model which takes into account the instantaneous polymer concentration during the injection process provides a more accurate description of the charge transport properties.

In conclusion, our study highlights the significance of accounting for the concentration dependence of the mobility in organic electronic devices. This approach improves the predictive capability of models and offers a more realistic representation of the charge transport mechanisms in organic materials.


2. A. Madsen, P. W. M. Blom, and B. de Boer, Materials Science Centre, University of Groningen, Groningen, Netherlands.

3. Conjugated polymers are promising materials for applications in light-emitting diodes (LEDs), organic field-effect transistors, and solar cells. Given the fact that most of them are p-type semiconductors, the hole transport has been widely investigated in the past in this type of materials. One of the most studied materials is poly (diacetylene-1,4) (PDA). The hole mobility in PDA-based LEDs has been reported to be on the order of 10^{-4} cm^2/Vs at room temperature.


5. Understanding the mechanism of charge transport in organic electronic materials is critical to the development of improved organic solar cells, LEDs, and other optoelectronic devices. Transport in organic electronic materials is traditionally studied using time-resolved (e.g., time-of-flight and dark-injection) or steady-state (e.g., current-voltage) techniques and evaluated within frameworks such as the Gaussian DOF and its variants. Although useful for many applications, these approaches may not be applicable for identifying the microscopic transport mechanism or for relating the charge transport properties to the chemical or physical structure of the materials. We will thus progress in the study of microscopic models of charge transport in molecular solids using both Monte Carlo simulation techniques and quantum-chemical methods.

We apply the models to experimental data for hole transport in several materials including poly(3-methylthiophene) (P3M)

higher applied voltages the hole injection is assisted by the presence of electrons in the device, leading to an enhanced electric field near the anode. This enhanced hole injection is responsible for the weak temperature dependence of the earlier observed ‘electron’ currents. As a next step we lowered the workfunction of Ag from 4.3 eV to 3.7 eV by applying self-assembled monolayers (SAMS) of hexadecanethiol, which increases the injection barrier for holes towards 1.5-1.6 eV. With this strong suppression of the hole current we have for the first time observed intrinsic electron currents which have a stronger temperature dependence as compared to holes. The electron current in these SAMS coated electron-only devices can be consistently described with a trapping model, which provides further insight in the origin of the reduced electron currents in many conjugated polymers.

11:15 AM 14.9
Organic Electron Mobility in Field-Effect Transistors using Fullerene Thin Films. Birendra Thokcho1, Nenad Marjanovic3, Gebhard Josef Mat1, Serap Gunes1, Niyazi Serdar Sariciftci2, Alberto Montaigana Ramı1,2, Andrei Andreev2, Helmut Sitter2, Reinhard Schwoediauerr and Siegfried Bauer3, 1Linz Institute of Organic Solar Cells(LOIS), Physical Chemistry, Johannes Kepler University, Linz, Austria; 2Institute of Semiconductor- and Solid State Physics, Johannes Kepler University, Linz, Austria; 3Soft Matter Physics, Johannes Kepler University, Linz, Austria.

Hot wall epitaxy (HWE), working close to thermonuclear equilibrium is a well known technique for growing highly ordered organic thin film transistors from solution. Recent mechanistic studies of field-effect transistors (OFETs) with HWE grown fullerene thin films. These devices exhibit high electron mobilities up to 2.5 cm²/Vs with an on/off ratio >10⁶. In addition, non-linear transport phenomena at high electric fields were observed. Solution processed [6,6]-phenyl C₆₁-butyric acid methyl ester (PCBM) OFETs show lower mobilities up to 0.2 cm²/Vs. Improvement of device performance by using novel polymeric dielectrics, optimized channel length and film growth conditions will also be outlined.

11:30 AM 14.10
Organic CMOS Technology Based on Interface Doped Pentacene. Maciej Sitar, Reinhard Schwoediauer 2, and Heinz von Seggern; Materials Science, T.U. Darmstadt, Darmstadt, Germany.

The realization of an n-type organic field effect transistor (OFET) based on interface-doped pentacene is demonstrated. The doping is performed by depositing traces of Ca onto the gate insulator before the organic semiconductor layer is applied. Electron field effect mobilities of 0.19 cm²/Vs are achieved. The field effect, i.e. the electron accumulation behaviour, is studied by impedance and charge measurements on a metal-insulator-semiconductor (MIS) diode. A good correlation between the physical properties of the transistor and the MIS diode can be reported. This new device concept allows for an integration of the n-channel on the same substrate utilizing only one organic semiconductor, laying a headstone for organic complementary-metal-oxide-semiconductor (CMOS) technology. A CMOS circuit consisting of an n- and p-type pentacene OFET on the same substrate with variable mobilities is realized and its properties will be discussed.

11:45 AM 14.11
Electric Field Dependent Transition from Dispensive to Non-Dispersive Transport in Conjugated Polymers. Lucas Pugikawa Santos1, 2Gregorio Couto Faria1, Antonio Rafael Andrade1,2, Sergio Mergulho1 and Roberto Mendonca Faria1; 1Instituto de Ficas de Sao Carlos, Sao Carlos, SP, Brazil; 2Departamento de Física, Universidade Federal de Sao Carlos, Sao Carlos, SP, Brazil.

Time-of-flight measurements in polystyrene (PSt) and poly(3-hexylthiophene) (P3HT) devices. The transient photocurrent response under short excitation wavelengths (above the absorption peak) and in a low electric field regime (below 10⁵ V/cm) was characteristic of dispersive charge carrier transport. On the other hand, for excitation wavelengths below the bandgap and in a high electric field regime (above 10⁵ V/cm), the hole mobility values evaluated for all excitation wavelengths apparently converge to a definite value (about 10⁵ cm²/Vs). A detailed discussion of the photocarrier generation and transport processes in conjugated polymers is realized by analyzing the electric field, temperature and excitation wavelength dependence on the carrier mobility and on tail broadening parameter of the transient photocurrent response.

SESSION 15: Photovoltaics
Chair: Lukas Burgi
Wednesday Afternoon, March 30, 2005
Room 201 (Moscone West)

1:30 PM 15.1
Development of Nanostructured Oxide Electron Conductors for Organic Photovoltaic Cells. David S. Ginley1, Sean Shahen 2, Matthew White2, Calvin Curtis1, Alex Miedaner1, Rueben Collins3 and Dana Olson3; 1PVAM, NREL, Golden, Colorado; 2Physics, University of Colorado, Boulder, Colorado; 3Physics, Colorado School of Mines, Golden, Colorado.

Organic photovoltaic (OPV) cells offer the potential for low cost, readily processable solar energy conversion devices. Due to the short exciton diffusion lengths and low mobilities in the organic components, the devices need to be integrated at the nano-scale. The development of a low-cost large-area devices with key dimensions on the order of 10-20 nm is a daunting challenge. To accomplish this requires the development of new processing approaches that produce appropriate nano-materials at this length scale. Two approaches are possible: (1) the use of nano-particulate materials to form a structure analogous to the bulk heterojunction cell first developed using fullerenes as the electron acceptor or (2) the development of nano-carpet materials with surface bound organized nanostructures. Here we present results on the synthesis of both nano-particulate oxide materials of ZnO, SnO2 and TiO2 and nano-carpets of ZnO and TiO2 and their incorporation into OPV devices. Key is that by controlling nucleation and the surface capping agents, the size of nanoparticles and the spacing of the ZnO or TiO2 nano-fibers can be controlled. Initial devices have shown efficiencies from 0.3-0.5% with Voc near 0.5V and currents up to 3.5 mA/cm². These results demonstrate the viability of the approach. We will discuss the surface and oxide properties that need to be optimized to achieve higher efficiencies.

2:00 PM 15.2
Performance of Pentacene-C60 Heterojunction Photovoltaic Devices. Sergey Mezentyi1, Mihaela Breban1, Vince B. Ballaroti1, John E. Anthony2, Ellen D. Williams1, Warren Herman1 and Danilo B. Romero1; 1Laboratory for Physical Sciences, University of Maryland, College Park, Maryland; 2Department of Chemistry, University of Kentucky, Lexington, Kentucky.

We investigate the effects of the structure of the active layer on the photovoltaic device characteristics of small molecular weight organic photocells. The active layer consists of donor-acceptor heterojunctions formed by pentacene (Pn) and fullerene (C60) molecules. Photovoltaic devices with sandwich geometry of comprising transparent indium-tin-oxide (ITO) / [Pn]/[C60] / Al and ITO / [poly(3-hexylthiophene) iodide (PEDOT):[PSS] / [Pn]/[C60] / lithium fluoride (LiF) / Al) with bilayer (n=1) and multilayer (n=18) have been fabricated using layer-by-layer growth of the Pn and C60 from separate organic MBE effusion cells. Devices with Pn/C60 bulk heterojunctions were obtained either by co-deposition of Pn and C60 molecules or by spin-casting of blends of soluble Pn and C60 derivatives. The multilayer devices with the PEDOT:PS and LiF electrodes manifest an increase of the short-circuit current and quantum efficiency. Several orders of magnitude increase in the current with the number of layers while the bulk heterojunction devices revealed an average value (Voc ~ 0.25 V) for the bilayer and ~ 1.0 V for the multilayer, which the number of layers while the bulk heterojunction devices revealed an average value (Voc ~ 0.45 V). Electroabsorption measurements of the built-in potentials in the corresponding devices revealed an average value (Voc ~ 0.25 V) for the bilayer and ~ 1.0 V for the multilayer device. This work is supported by the Polymer and the Nanophysics and Devices programs of the Laboratory for Physical Sciences (MD) and by ONR and NSF-CAREER (J.E.A., KY).

2:15 PM 15.3
Ganome Charge Separation in Bulk Heterojunction Photovoltaic Cells. Shashin Zhao1, and Peter Pearsall; 1Materials Science and Engineering, Stanford University, Stanford, California; 2Electrical Engineering, Stanford University, Stanford, California.

Organic bulk heterojunction photovoltaic cells provide a solution to the exciton diffusion efficiency bottleneck of organic donor-acceptor solar cells. However, the bulk heterojunction geometry also suffers from the additional loss pathways of ganome (both carriers originate...
from the same exciton) and non-geminate (both carriers originate from different excitons) recombination. It is usually assumed that non-geminate recombination is the recombination process that can be minimized by increasing the carrier mobilities. We have modeled the separation of the geminate charge-pair at a donor-acceptor interface of arbitrary geometry using Monte Carlo simulations. We find that the geminate separation probability and fill factor. These results are consistent with the intensity- and voltage-dependent photocurrent measurements on planar and bulk heterostructures. Our studies of the effect of the bulk heterojunction geometry indicate that for fine-grained morphologies, fill factors approximately greater than 0.1 are required to prevent geminate recombination under normal operation (i.e. moderate forward bias). Only after this condition is met can one start to minimize the non-geminate recombination process. Our model explains why not all donor-acceptor pairs form high-efficiency solar cells. Furthermore, it provides precise guidelines for increasing the efficiency of bulk heterojunction photovoltaic cells.

2:30 PM 15.4
Surface Photovoltage in Polyfluorene-based Polymer Blends: Correlation between Morphology and Electronic Properties.

Marco C. Giunti, Marcus Benedictus, Jean-Didier Fontaine, Richard H. Friend, and Henning Sirringhaus. C2:30 PM 15.4
Cornell University, Cambridge, United Kingdom; 2CEM, Zuerich, Switzerland.

The performance of organic materials-based solar cells is strongly dependent on the morphology of the device on the nanoscale. We present a microscopic study of charge generation and recombination in polyfluorene-based photovoltaic structures. Surface photovoltage has been measured using Scanning Kelvin Probe Microscopy enabling to locally resolve photoinduced charge generation, transfer and recombination in thin films of blends of poly-(9,9'-dioctylfluorene-co-bis-N,N'-bis(N,N'-4-butyphenyl)bis-N,N'-phenyl)-1,4-phenylenediamine) (PF1) and poly-9,9'-bis(N,N'-bis(4-butyphenyl)bis-N,N'-phenyl)-1,4-phenylenediamine) (PF2) with a resolution better than 100 nm. The surface photovoltage and the blend morphology appear strongly correlated, with three regions clearly identifiable: This allows to extract information about the conduction pathways for photogenerated charges and factors limiting the efficiency. The long time decay of surface photovoltage in the dark shows that trapped charges are always present in real devices and play an important role towards the device performance. We propose a simple model describing the morphology of the devices, with a particular emphasis on the vertical phase segregation of the two polymers, and its correlation with the optoelectronic properties.

2:45 PM 15.5
Exciton Migration and Quenching in Polymer Light-Emitting Diodes and Solar Cells.

Dinizinho Pires, Denis Van Woudenberg, Alexander B. Sieval, Jan C. Hummelen and Paul W. M. Blom; Materials Science Centre, University of Groningen, Groningen, Netherlands.

Application of conjugated polymers in polymer light-emitting diodes (PLEDS) and solar cells is currently attracting much attention, due to easy and low-cost manufacture of these devices, their flexibility and light weight. The most efficient solar cells based on bulk heterojunctions of conjugated polymers and fullerenes have a characteristic power-conversion efficiency of 2.5%-3%. After photoexcitation of the polymer phase the photoexcitations migrate towards the polymer/fullerene interface electron transfer from the polymer (donor) to the fullerene (acceptor) takes place. Consequently, the diffusion of excitons towards the polymer/fullerene heterojunction is an important process with regard to the efficiency of the device. In PLEDs excitons are formed in the cathode layer and recombine in the anode layer. In order to disentangle these effects we have first investigated exciton diffusion in polymer/fullerene heterojunctions using time-resolved photoluminescence. It is observed that heterostructures consisting of a spiro compound (spiro-1,1'-spirobiindane) (SPI) based derivative and evaporated C60 are ill-defined due to diffusion of C60 into the polymer, leading to an overestimation of the exciton diffusion length. This artefact is resolved by the use of a newly developed high-purity spiro-polymerizing fullerene, which allows to study the electron acceptor layer. From the decay curves of polymer layers with varying thickness an exciton diffusion constant of 3x10^-7 cm^2/s has been obtained. Subsequently, bilayers of metals and various poly(phenylenevinylene) (PPV) derivatives have been systematically investigated. The time-resolved luminescence was numerically simulated in an exciton diffusion model assuming quenching by long-range dipole-dipole interaction at the metallic mirror. From these simulations the exciton diffusion length is directly obtained. The exciton diffusion length is then quantitatively established, taking redistribution of the exciton population due to diffusion into account. The quantitative understanding of exciton quenching has been applied to double layer PLEDs, where an additional polycarbonate film is inserted between the active layer and the cathode. Application of a 20 nm ELT leads to a pronounced improvement of the PLED efficiency. For ELTs with thickness of 40 nm or larger, the correlation efficiency is independent, indicating a dependence of exciton quenching as predicted by our luminescence measurements results.

3:15 PM 15.6
A Study of Exciton Diffusion and other Factors that Limit the Performance of Organic Photovoltaics.

Shawn R. Scully, Yuxing Liu, Michael Howell and Michael D. McGehee; Materials Science and Engineering, Stanford University, Stanford, California.

The dynamics of exciton diffusion play a fundamental role in the operation of organic devices such as LEDs, biosensors, and photovoltaics. In organic photovoltaic devices, excitons usually diffuse to a donor-acceptor interface where they dissociate by electron transfer. It is therefore critically important to understand exciton diffusion in detail in order to optimize device architectures. Despite its enormous importance in determining the power conversion efficiency of photovoltaic cells, not much is currently known about exciton diffusion in organic semiconductors. While hundreds of papers describing charge transport in organic semiconductors have been published, there is only a few that address the dynamics of exciton diffusion. It is often assumed that the exciton diffusion length (Ld) is ~10 nm, while in fact, Ld has been shown to vary over a wide range from 3 nm to 2 µm. We have measured the exciton diffusion length of various organic materials, including MDMO-PPV and RR-PoHT, using steady-state photoluminescence quenching in well-defined polymer/titania bilayer heterostructures. We address how processing conditions can affect the exciton diffusion length in the investigated systems and suggest ways to engineer new materials with larger exciton diffusion lengths. Care was taken to account for optical interference effects, which if ignored can lead to either gross underestimation or overestimation of the diffusion length. Using the measured diffusion lengths, we model the theoretical quantum efficiency of bilayer organic/inorganic photovoltaic devices and compare these with experiment. We systematically address possible loss mechanisms, including poor optical engineering of excitations by surface plasmons in the metal electrode, and non unity charge collection efficiency, and show how they can be overcome. Our data suggests that materials with even modest exciton diffusion lengths can lead to high efficiency photovoltaics.

3:30 PM 15.7
Solar Cells of Low-Bandgap Polyfluorenes.

Mats R. Andersson, Erik Perzon, Vendimegan Mammo, Xiangjun Wang, Fengbing Zhang, Frederick Oswald, Juan Luis Delgado, Pilar de la Cruz, Fernando Langa and Olle Inganas; 1Materials and Surface Chemistry, Gothenburg, Sweden; 2Bimolecular and Organic Electronics, Linkoping, Sweden; 3Facultad de Ciencias del Medio Ambiente, Toledo, Spain.

The development of conjugated polymer solar cells is still in an early phase, and many issues of materials and device development remain to be solved. One of our goals is to prepare efficient and stable solar cells and our efforts are presently concentrated on preparing polyfluorenes with extended absorption to cover the important parts of the solar emission. Polyfluorenes normally have high mobility and stability, which is desired for the use in solar cells. However, they normally also have a relatively large bandgap. To decrease the bandgap we have synthesized several polymers based on planar conjugated segments with internal donor-acceptor functions in between the substituted fluorene groups. One of the polymers prepared is an alternating polyfluorene copolymer with an onset of absorption at 980 nm (1.27 eV) and shows liquid crystalline like properties at elevated temperatures. Thin film transistors prepared of this polymer show photovoltaic properties similar to regioregular PPV. Sandwich solar cells have been prepared of the polymers blended with C60 and C70 derivatives with high electron affinity. So far our best solar cells derived from the low-bandgap polymer exhibit a maximum external quantum efficiency of 28% at 400 nm extending to 8% at 800 nm. Under simulated solar
Device Operation of Polymer-Fullerene Bulk Heterojunction Solar Cells.

A fundamental limitation of the photocurrent of solar cells based on a blend of poly(2-methoxy-5-(3',7'-dimethoxynaphthoxy)-1,4-phenylene vinylene) (MDMO-PPV) and [6,6]-phenyl C61-butyric acid methyl ester (PCBM) is provided by the mobility of the slowest charge carrier species, the holes in the MDMO-PPV. In order to electrostatically allow the experimentally observed photocurrents, a hole mobility of at least 10−8 m2/Vs is required, which exceeds the observed hole mobility in pristine MDMO-PPV by more than two orders of magnitude. From space-charge injection, admittance and transient electroluminescence measurements a hole mobility of 2×10−8 m2/Vs was found for the MDMO-PPV phase in the 20:80 wt. % MDMO-PPV:PCBM blend at room temperature. Consequently, the charge carrier transport in these MDMO-PPV:PCBM based solar cell is much more balanced than previously assumed, which is a necessary requirement for the disclosed high fill factors of above 50 %. We demonstrate that for this composition the photocurrent in conjugated polymer/fullerene blends is dominated by the dissociation efficiency of bound electron-hole pairs at the donor/acceptor interface. A model based on Onsager’s theory of charge recombination explains the observed field- and temperature dependence of the photocurrent in the MDMO-PPV:PCBM blend. At room temperature only 60% of the generated bound electron-hole pairs are dissociated and contribute to the short-circuit current, which is a major loss mechanism in photovoltaic devices on this material system. Another intriguing question is why for optimal performance 80 wt. % of a non-absorbing (PCBM) species is required. For this we have investigated the dependence of the performance of OCI100-PPV:PCBM based bulk heterojunction solar cells on their composition. With regard to the charge transport we demonstrate that with increasing PCBM weight ratio the electron mobility gradually increases up to 80 wt.% and subsequently saturates to its bulk value. Surprisingly, the hole mobility in the PPV phase shows an identical behavior and saturates beyond 67 wt.% PCBM at a value which is more than two orders of magnitude higher than the one of the pure polymer. The experimental electron and hole mobilities are used to study the photocurrent generation of OCI100-PPV:PCBM BHJ solar cells. From numerical calculations it is shown that for PCBM concentrations exceeding 80 wt.% the reduced light absorption is responsible for the loss of device performance. From 80 to 67 wt.% the decrease in power conversion efficiency is mainly due to a decreased separation efficiency of bound electron-hole (e-h) pairs. Below 67 wt.% the performance loss is governed by a combination of a reduced generation rate of e-h pairs and a strong decrease of the hole transport.

Utilization of low-bandgap polymers that absorb light extending into red and infrared range is one way to harvest more solar energy in polymer and fullerene based solar cells. Reducing the bandgap of the polymer will cause a shift in the lowest unoccupied molecular orbital (LUMO) and/or highest occupied molecular orbital (HOMO), possibly resulting in energetic mismatch between the polymer and a acceptor fullerene, thereby weakening the driving force for charge separation. A lack of optical absorption of the low-bandgap polymer in the visible wavelength range may be another consequence when the absorption extending to the infrared wavelengths. By selecting the proper fullerene we can realize energetic match and compensate the deficient absorption of polymer in the visible wavelength range. We report the broadening of photocurrent spectral response window in the wavelength range at 300 < λ < 1000 nm, using a low-bandgap polymer blended with C70-fullerene derivative. The low-bandgap copolymer contains fluorene and a donor-acceptor-donor moiety (APFO-Gl) and has an onset of optical absorption at λ = 1000 nm. Solar cells consisting of APFO-Gl blended with 3’(3,5-Bis-trifluoromethylphenyl)-1’-(4-nitrophenyl)pyrazolino[70]fullerene (FO147), are fabricated. Photovoltaic properties of these solar cells as well as the photophysics properties of these films are determined and discussed. The highest performance is achieved by the APFO-Gl:FO147 (1:4 by weight) based devices. The devices exhibit a pronounced photocurrent spectral response in a broad range, where the external quantum efficiency covers the solar spectrum at wavelengths of 300 < λ < 1000 nm. It has a maximum of ~78% at wavelength λ = 400 nm and as high as ~8.8% at λ = 850 nm as well as 7% at λ = 900 nm. A photocurrent density of 3.4 mA/cm², open circuit voltage of 0.85 V and power conversion efficiency of 0.7% is achieved under the illumination of AML 1.5 (1 000 W/m²) from a solar simulator. The performance is attributed to better energetic match between the LUMO of APFO-G1 and that of the FO147, and also the enhanced optical absorption in FO147. Reference [1] X. Wang, E. Perzon, J.L. Delegado, Pd I Cruz, F. Zhang, P. Langa, M. Anderson, O. Inganas, Appl. Phys. Lett. 85, xxxxx, (2004). In press.

**4:45 PM 15.11**

**Broad Photocurrent Spectral Response Window of Solar Cells with Low-Bandgap Copolyfluorene and C70-Fullerene.**

Xiangjun Wang⁴, Erik Perzon⁵, Jassu Luis Dolgado⁶, Fernando Langa⁶, Mais Anderson⁷ and Olle Inganas⁸; ¹Biomolecular and organic electronic, Linköping University, Linköping, Sweden; ²Materials and Surface Chemistry, Chalmers University of Technology, Sweden; ³Facultad de Ciencias del Medio Ambiente, Universidad de Castilla-La Mancha, Toledo, Spain.

We present an analytic description of the loss of photocurrent efficiency as moderate light intensities and demonstrate a simple technique for extracting the mobility of electrons in semiconducting polymer layers. The underlying theoretical analysis, which is based on a simple drift-recombination scheme, shows good agreement with the measured intensity dependent photocurrent. The electron mobility extraction is demonstrated for pristine polymers (MEH-PPV, Yellow-PPV) as well as polymer nanocrystal composites. The same physical framework is then used to describe the switch on of the photocurrent and the buildup of electron and hole concentrations inside the device. By analyzing the time evolution of the measured photocurrent transient we find an independent verification of the results extracted from the intensity dependence measurements. We use the combination of experimental and numerical approach for understanding and analyzing morphologies of organic heterostructure photodetectors and solar cells, both in bulk heterostructure blends and bi-layer devices. We present the method and preliminary experimental results.

**SESSION 16: Poster Session: Organic Based Materials and Devices**

*Chairs: Ana Claudia Arias, Lukas Burgi, John Enlerson and Nir Tesler*

*Tuesday, March 30, 2005* 8:00 PM

**8:15 (Marriott)**

**16.1**

**A Structural Investigation of PF-74 Doped Polyppyrole as a Function of Oxidation State.**

Mya R. Warren¹, J. D. Madden² and B. Bergersen³; ¹Physics and Astronomy, University of British Columbia, Vancouver, British Columbia; ²Electrical and Computer Engineering, University of British Columbia, Vancouver, British Columbia, Canada.
Many applications of conducting polymers, such as supercapacitors, electrochromic devices, and lightweight actuators make use of electron injection during their operation. These devices will intrinsically depend on the polymer structure during redox cycling. In this study, X-ray diffraction is used to investigate the structure of highly conducting polypropylene as a function of oxidation state. Polypropylene was electrochemically deposited with the PF$_6^-$ counter ion at a constant current density of 0.125 mA/cm$^2$ and a temperature of -40 °C. The films had a conductivity of 300 S/cm and a thickness of 25 μm. Films were reduced at constant current to remove the counter ion. The diffraction patterns of both show short-range order in the form of several broad crystalline peaks with d-spacings of 1.75 nm, 0.65 nm, and 0.34 nm and one amorphous peak at 0.44 nm. X-ray patterns were obtained in the transmission and reflection geometries. Differences in these patterns are attributed to film anisotropy in the thickness direction; the chains preferentially align perpendicular to the plane of the film. Comparison of the oxidized and reduced patterns shows that the ions expelled during reduction contribute only to the amorphous peak, which is greatly reduced in amplitude in the reduced film. The remaining intensity of this peak is similar to the crystalline peaks and may be due to amorphous regions in the polymer. The peaks belonging to the polymer crystallites are largely unaffected by reduction. Most notably, there are no significant shifts in the peak positions. Peak shifts would be expected if ions were expelled from the crystallites as this would cause a contraction along certain crystal axes. Since the polymer crystallites do not take up regular positions in the crystals, but are distributed in the amorphous regions of the polymer instead.

### 16.2 Pentacene Transistors with Polymer Gate Dielectrics on Metallized Optical Fibers

**Jimmy Erik Granstrom and Howard Katz; Materials Research. Bell Labs, Lucent Technologies, Murray Hill, New Jersey.**

It is difficult to deposit a very thin polymer layer onto a fiber-shaped substrate from solution because the high interfacial energy can lead to dewetting. We present a dip coating process that applies a gate dielectric to conductive fiber substrates during the fabrication of fiber transistors for use in applications such as electroluminescent devices. We will demonstrate the feasibility of dip-coating this gate dielectric on micrometer scale fiber substrates. This technique is used to coat a layer of polymer with the same composition as the transistor gate dielectric. This layer is then reduced electrochemically to form a neutral polymer layer with a reduced thickness. Electrochemical deposition of a metal gate layer occurs, and the dielectric passivation film is etched from the exposed polymer gate film. The polymer is then deposited to form a second dielectric layer. A final metal layer is electrochemically deposited to form a metal gate. This process can be repeated to form multi-layered transistors. The process is compatible with mechanical handling of polymer coated fiber substrates and is applicable to both thermal and optical fiber substrates.

### 16.3 Morphology, Optical Properties and Field-Effect Transistors Based on Electrotantis Nanofibers of Conjugated Polymers

**Kazuhiro Takeda; Material Research. Bell Labs, Lucent Technologies, Murray Hill, New Jersey.**

Semiconductor nanowires, nanodots and other nanostructures have a variety of unique optical, electronic and magnetic properties arising from confinement effects. These properties can be precisely controlled and tuned during the fabrication of the nanostructures. We have prepared high quality nanofibers from conjugated polymers, such as poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) and its blends with poly(3-hexylthiophene) (P3HT) or poly(3-octylthiophene) (P3OT), using electrospinning technique and investigated the effect of one-dimensional (1-D) confinement on the optical and electronic properties of conjugated polymer nanofibers. Morphological and spectroscopic analyses revealed that the MEH-PPV/P3HT blend nanofibers exhibit a new phase separation and improved efficiency for energy transfer compared to the neat thin films. However, MEH-PPV/P3OT blend nanofibers showed reduced energy transfer from P3OT to MEH-PPV as compared to the copolymers. Field-effect transistors based on the MEH-PPV/PHT blend nanofibers exhibited p-channel transistor characteristics with hole mobility in the range of (0.05-1) x 10$^{-4}$ cm$^2$/V·s. Our results demonstrate that conjugated polymer nanofibers are promising 1-D system to study confinement effects on charge transport and optical properties.
Axially oriented anthracene thin films were grown on oxidized silicon surfaces by a new process, with domain sizes in the centimeter range. The morphology consists of tilted, or standing-up, at deeply buried interfaces. The high-energy X-ray beams can penetrate through a conductive silicon electrode and x-ray beam scattering. Pentacene layers are found to be highly oriented. Epitaxial organic heterostructures have the potential to produce materials and devices with improved properties and performance. Electrical transport measurements of films fabricated by these methods are underway.

16.8 Modeling the Organic Thin Film Transistors. Viorel Olariu, Robert Rotzoll, Siddharth Mohapatra, Robert Wenz, Michèle Grigas, Oleg Shchekin, Klaus Dimmler and Anantha Dodabalapur. 1, 2 Design, Organic ID, Inc., Colorado Springs, Colorado; 2R&D Laboratory, OrganicID, Inc., Austin, Texas; 3The Department of Electrical and Computer Engineering, The University of Texas at Austin, Austin, Texas.

In spite of their low performances, organic thin film transistors (OTFTs) appear to be a strong contender to the silicon based MOS FET devices whenever low-cost and low (but reasonable) performance circuits are required in applications such as RFID devices for large volumes. In order to design competitive circuits based on OTFTs, the designers need circuit models that predict the operation of OTFT with a reasonable accuracy. Although generally, the OTFT operation is similar to the regular MOS FET device, there are several characteristics that clearly differentiate them. One important difference between the operation of the OTFT and the silicon MOS FET (that is a direct consequence of the physical implementation of OTFT) is that the organic transistor is normally operated in the accumulation mode, while the silicon transistor operates in the inversion mode. Due to the molecular nature of the semiconductor, the carrier mobility is of order magnitude lower than for the silicon MOS FET. But probably the most challenging effect, from the design as well as the modeling point of view, is the hysteresis effect that many researchers reported. This effect is explained by two most likely causes: the slow charges in the dielectric near the semiconductor-insulator interface and also by the possibility of polarization of the asymmetrical molecules in the gate dielectric. Variable carrier mobility law, low on/off ratio, and the Schottky barrier at the interface between the source/drain metal contact and the organic semiconductor are among other important effects that had to be considered for the development of an accurate circuit model of the organic transistor. The developed model has been used to simulate DC characteristics and also simple circuits such as logic gates, ring oscillators, rectifiers, etc. This presentation shows the equations that govern the described behavior as well as a comparison between the simulated and experimental data. The experimental circuits were fabricated on flexible plastic substrate and employed a solution-cast dielectric. The pentacene was the semiconductor of choice with the carrier mobility in the range of 0.1 - 1.5 cm²/Vs.


Molecular electronics is broadly defined as electronic devices whose properties are dominated by both the molecule and the molecule/molecule interactions of their self-assembled monolayer (SAMs) films. The fabrication of these junctions, which are usually less than 10 nm in length, has posed a remarkable challenge and once they are assembled, it is still difficult to determine how the molecules interact with each other. Therefore, to gain a better understanding of the SAMs structure and phase, either lying down, tilted, or standing-up, at deeply buried interfaces. The high-energy X-ray beams can penetrate through a conductive silicon electrode and thus resolve the conformation of molecules in the electronic junction, both before and during electrical operation.


Organic photovoltaic cells (OPV) and organic light emitting diodes (OLEDs) depend critically on the interfaces between the layers in the devices. One key area is the contact formation where PEDOT:PSS, a conducting polymer, is commonly used as an intermediate layer to improve the electrical contact. We report here on the inkjet printing of PEDOT:PSS using various surfactants and other additives with the aim of improving the electrical contact through better control of the wetting, surface roughness, work function and conductivity. PEDOT:PSS was synthesized and printed using a variety of surfactants, as well as added dimethyl sulfoxide (DMSO). The surfactants modify the sheet resistance, surface roughness, and work function of inkjet printed PEDOT films and can also increase the range of printable film thicknesses. Added DMSO can increase the conductivity of the initial PEDOT:PSS from 4 S/cm to 133 S/cm. The surface roughness could be reduced to 86 angstroms with appropriate surfactants. A Kelvin probe was used to measure the work function which could be varied more than 0.5 V depending on the additives used. Inkjet printing is shown to be a powerful tool for exploring contact formation as well as for direct writing of contacts on a variety of important materials for organic devices.
attractive approach to modify and improve metal/organic contacts in organic electronic devices like LEDs, photovoltaic cells, and FETs.


Stijn De Vos1,2,3, Asmer Henriquez1,2, Stijn De Jonge1,3, Jan Groene1 and Paul Heremans1,2, 1MCP, IMEC, Heverlee, Belgium, 2ESAT, KULeuven, Leuven, Belgium.

Organic semiconductors have been incorporated in a number of devices, such as organic thin-film transistors (OTFTs), organic solar cells, and organic light-emitting diodes (OLEDs). Display applications are a particularly important driver for the further development of this organic technology. Recently, an organic light-emitting field-effect transistor (OLEFET) was reported. A coevaporated film of o-CTA (a p-type organic semiconductor) and N,N'-Ditridicyclo-p-4,9,10-tetracarboxylic diimide (PTCDI-C14H17) (an n-type organic semiconductor) was used. OLEFETs might be useful in microelectronics, as they combine electrical and optical functionality in a single device. Here, we report on an OLEFET based on the subsequent deposition of p-type tetracene and n-type PTCDI-C14H17. Bottom contact devices were fabricated on a highly doped Si substrate with 100 nm thermally grown SiO2, acting as the gate electrode and the gate dielectric, respectively. We used standard lithography for patterning 20 nm Au as source and drain electrodes. Next, a profile of photoresist was created that covers part of the electrodes. After a surface treatment, the sample was mounted on a 45° triangular sample holder. During the first deposition, the sample was in a 45° angle with respect to the flux of tetracene, which thus created an interesting structure, because of the photoresist profile. One electrode was fully covered with tetracene. Part of the channel was covered as well, while the other part of the channel and the other electrode were in the shadow region, hence no tetracene was deposited there. The sample was then tilted 180° on the sample holder. During the following deposition of PTCDI-C14H17, the previously uncovered electrode was covered, as well as part of the channel. Inside the channel, an overlapping region of tetracene and PTCDI-C14H17 is present after these two depositions. By applying an appropriate bias to the gate, source and drain electrodes, equal currents of electrons and holes are injected from the source and drain contacts, and a number of organic semiconductor films. In the overlapping region, recombination of electrons and holes occurs, and excitons are formed. This generates light emission. The width of the light-emitting overlap region, as well as the distance from the overlap region to the metal electrodes can be freely chosen within certain limits by adjusting the photoresist dimensions. This is important, as it is known that exciton quenching occurs at metal contacts. We have fabricated a 10μm channel length device in which the light-emitting overlap region is 3μm wide, and is located at a distance of more than 3μm from both the source and the drain. As a conclusion, we have demonstrated a light-emitting field-effect transistor using 2 patterned organic semiconductors. In the overlapping region of these 2 materials, light can be generated.

16.14 Conductive Polymer Deposition by Inkjet Printing

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This work describes polyaniline deposition process using a commercial and inexpensive printer - Epson Stylus Photo R200. Ink-jet printing was used to directly pattern polyaniline as interdigitated electrodes onto a glass substrate. We describe the process used to form a patterned thin film involving inkjet-related technologies, the self-patterning behavior of a polymeric solution on the substrate, and the drying process. Each layer defines the thickness profile and film properties. Special emphasis is placed upon the utilized polymers and conditions, such as polymer structure, molar mass, solvents and concentration. Multiple layers must be printed such that they mix and react to form a solid material such that they form discrete unixed layers. By fully utilizing these unique properties of microfluidics, we have succeeded in fabricating gas sensors by direct patterning of polymer solutions.

16.15 Patterning of Conjugated Polymer Films for Flexible Electrochromic Devices

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New conjugated polymers with high electron affinity are of great interest for applications in photovoltaics and in interdigitated thin film transistors. A series of poly(2,7-diphenylpyrazino(2,3-g)quinoline) (poly(pyrazinoquinoxaline)) based conducting polymer light emitting diode (PLED) devices and conducting polymer and metallic interdigitated electrodes (IDEs) for electrochromic devices (ECDs). Complementary colored, dichroic aromatic based electrochromic (EC) polymers were deposited on polymer electrodes using a roll coating process. ECDs containing the 2-lane, 4-lane, and 6-lane devices, respectively. The extent of interdigitation noticeably improves the switching performance of lateral ECDs due to shorter diffusion distances for dopant ions and minimal electrolyte resistance. In these devices, we have reported the improved device performance on PLED devices (A/PFO/PVK/ITO) by using the electrochemically cross-linked polyfluorene films. This work describes the use of electrochemical nanolithography (ECN) to pattern features, objects, and wires at the micrometer level on polyfluorene films and conducting polymer light emitting diode (PLED) devices.

16.16 Electro patterning and Nanopatterning of Conjugated Polymers using the Precursor Polymer Approach

Rigoberto Advincula, Chemistry, University of Houston, Houston, Texas.

In this talk, we present interesting results and strategies for the fabrication and patterning of conjugated polymer ultrathin films using the precursor electrochemical cross-linking approach. The application of these nanomaterials to electro-optical devices, e.g. polymer light emitting diode (PLED) devices and conducting polymer nanowires will be described. The potential for higher performance of lateral ECDs was discussed. In this experiment, we have recently reported the improved device performance and durability of lateral ECDs due to shorter diffusion distances for dopant ions and minimal electrolyte resistance. In these devices, we have reported the improved device performance on PLED devices (A/PFO/PVK/I TO) by doping the electrochemically cross-linked polyfluorene films. In this talk, we present interesting results and strategies for the fabrication and patterning of conjugated polymer ultrathin films using the precursor electrochemical cross-linking approach. The application of these nanomaterials to electro-optical devices, e.g. polymer light emitting diode (PLED) devices and conducting polymer nanowires will be described. The potential for higher performance of lateral ECDs was discussed. In this experiment, we have recently reported the improved device performance and durability of lateral ECDs due to shorter diffusion distances for dopant ions and minimal electrolyte resistance. In these devices, we have reported the improved device performance on PLED devices (A/PFO/PVK/I TO) by doping the electrochemically cross-linked polyfluorene films. In this talk, we present interesting results and strategies for the fabrication and patterning of conjugated polymer ultrathin films using the precursor electrochemical cross-linking approach. The application of these nanomaterials to electro-optical devices, e.g. polymer light emitting diode (PLED) devices and conducting polymer nanowires will be described. The potential for higher performance of lateral ECDs was discussed. In this experiment, we have recently reported the improved device performance and durability of lateral ECDs due to shorter diffusion distances for dopant ions and minimal electrolyte resistance.
poly(prazinoquinoxaline) as the electron transport materials. The experimental and theoretical results demonstrated that the pyrazinoquinoxaline is an excellent building block for realizing high electron affinity organic semiconductors for electronics.

16.18 Conjugated Oligoquinolines: n-Type Organic Semiconductors for Highly Efficient Blue Electroluminescence.
Abhishek P. Kulkarni, Angela P. Gifford, Christopher J. Touzola and Samson A. Jenekhe; Chemical Engineering, University of Washington, Seattle, Washington. We report the synthesis of a new class of conjugated organic semiconductors, which we term oligoquinolines. This new class of materials is designed to combine the optical and electronic features of both conjugated polymers and small molecules. The oligoquinolines exhibit strong blue luminescence, high crystallinity, and high solubility in common organic solvents.

Achievement of pure blue electroluminescence (EL) with high efficiency, color purity, and stability remains an elusive goal. The promise of EL displays has drawn increasing interest over the past two decades. The discovery of optically-active polymers, with the promise of cheap solar cells and light emitting diodes, drew increased attention to the field in the early 1990s. Unfortunately, stability remains an unsolved problem for these devices. Despite intensive research efforts, most of these devices are plagued by short life-spans, poor efficiencies, and reliability issues. These shortcomings underscore a need for greater understanding and better modeling of the underlying fundamental processes involved in device formation and degradation. There exist gaps and discrepancies in the published literature of even the most studied of these polymers. One such heavily studied optically-active polymer is MEH-PPV. In this paper, we present novel research results that explore the basic molecular structure, orientation, and electrical properties of this popular light emitting polymer. The HOMO-LUMO structure of MEH-PPV, based on band-gap theory, was investigated through absorption and emission spectra, computer simulated semi-empirical modeling, and ultraviolet photoemission spectroscopy (UPS). Using a synchrotron, the relative change in photoemission cross-section for various electron states was measured and used to determine the partial density of states. The UPS measurements include both angle-resolved (ARUPS) and incident energy dependent spectra. ARUPS was used to determine the band structure of the material under investigation and to identify molecular species on the surface responsible for the photoemission energies associated with the bands of the molecules. Some indication of bulk film orientation was inferred by dispersion of incident energy dependent UPS. The results from these various methods of characterization are compared. In addition, some implications regarding the role of defect states, extrinsic carrier involvement, and Fermi-level pinning at the interface are discussed.

Janelle Leger and Sue Carter, Physics, UC Santa Cruz, Santa Cruz, California.

We study light-emitting electrochemical cells (LEC) employing poly(2-methoxy,5-(2-ethylhexyloxy) paraphenylene vinylene) (MEH-PPV) in both planar and vertical geometries in an effort to understand the factors affecting emission profiles and to gain information that will allow us to model electroluminescence spectra in vertical LEC structures. Specifically we explore salt type and electrode dependence. For the vertical structure LECs (ITO/MEH-PPV/PEO; salt/electrode), we observe very similar EL spectra in forward and reverse bias and for various salts and electrode materials under steady state conditions. However, significant electrode-dependent dynamic changes are observed for certain structures, suggesting a redistribution of the recombination profile. In general, devices using an Au electrode establish steady state emission profiles in reverse bias more closely as compared to devices employing an Al electrode. Devices also display spectral dependence on salt concentration along with increased voltage dependence for lower salt concentrations. Results suggest that emission in vertical LEC structures is highly delocalized across the thickness of the device. Salt type, in contrast, did not appear to noticeably affect EL spectra, though it is noted that devices employing Li salts showed significantly improved emission in reverse bias in comparison to those with TBA salts. This appears to be due to an irreversibility electrochemical reduction of ITO caused by the TBA cation. To understand some of these results, we studied changes in the PL and EL profiles of planar LEC structures for which these quantities can be directly imaged. We observed significant p-type doping as evidenced by PL quenching at the anode for all devices and emission that was typically fairly uniform over the non-quenched region. Variations in salt type apparently did not have an effect on either the PL quenching or emission profile. Preliminary results suggest a similar insensitivity to electrode material. However, significant PL quenching was observed at the anode for high work-function electrodes. We do not observe evidence of n-doping in these structures, suggesting either that n-doping results in ineffective PL quenching in MEH-PPV or that dopant effects may be critical to understanding the EL. A simple model to account for the observed EL spectra was developed utilizing a bandgap function of the work-function electrodes. We do not observe evidence of n-doping in these structures, suggesting either that n-doping results in ineffective PL quenching in MEH-PPV or that dopant effects may be critical to understanding the EL. A simple model to account for the observed EL spectra was developed utilizing a bandgap function of the work-function electrodes.
These results can be interpreted by the dipole caused by the electron transfer from the substrate to TNP. IRRAS spectra show that TNP is adsorbed on Au, but the orientation of TNP molecule is random on both Ag and Cu substrates. This indicates that the chemical interaction between TNP and metal substrates has an impact on the morphology of the organic film. It will be discussed in the following sections at the charge transfer between the molecule and metal substrate on the electronic structure and morphology of deposited organic film. [1] H. Ishii, et al., Adv. Mater. 11, 685 (1999).

To improve efficiency of polymer light-emitting diodes (PLEDs), balance of charge injection and transport from each electrode is important. For charge balance, multilayer architecture is required. In case of a PLEDs, [poly-(3,4-ethylenedioxythiophene)] (PEDOT) doped with [poly(styrene-sulfonate)] (PSS) were developed and optimized for hole transporting layer (HTL). Introduction of PEDOT:PSS often improves luminous efficiency. However, interface of ITO/PEDOT:PSS is not stable in the PLEDs structure. When PEDOT:PSS is coated onto indium-tinoxide (ITO), ITO could be etched by sulfonic acid and some indium could be diffused into PEDOT:PSS. PEDOT:PSS HTLs are also involved in the oxidative doping of polyfluorene emitting layer components, leading to reduced luminous efficiency. Effective transport polymer requires good resistance, thermal and electrochemical stability. In addition, the highest occupied molecular orbital (HOMO) of the HTL has to be close to, or even below, the HOMO of the emitting polymer. These polymers showed high transparency, high $T_{\text{on}}$, HOMO level tunability, excellent stability, resistance and surface properties. We also fabricated EL devices using new hole transporting polymers and compared the performances and stability with PEDOT:PSS based devices.

The Effect of Atmospheric Doping on the Interfacial Electronic Structure of Phthalocyanine Thin Films as Studied by UPS. Toshihisa Nishitani 1, Kazunori Kanai 1, Takanori Araki 1, Masahiro Uehara 1, Martin R. Willis 2 and Kazuhiko Seki 3, 4. 1Department of Chemistry, Graduate School of Science, Nagoya University, Nagoya, Japan; 2School of Chemistry, The University of Nottingham, Nottingham, United Kingdom; 3Research Center for Materials Science, Nagoya University, Nagoya, Japan; 4Institute for Advanced Research, Nagoya University, Nagoya, Japan.

Recently, small molecule organic semiconductors have attracted considerable attention due to their potential for applications as electronic devices such as organic light emitting diodes (OLEDs) or organic field effect transistors (OFETs). It is well known that the electronic and optoelectronic properties of organic semiconductors is very sensitive to the ambient atmosphere. Especially, presence of oxygen and water in organic films has a large effect on their conductivity. Electrical properties of titanium phthalocyanine (TiOPc) were investigated by means of the field-effect (FE) measurements, which revealed that TiOPc films fabricated in ultrahigh vacuum (UHV) condition exhibited an n-type semiconductor behavior, while the exposure of the film to oxygen causes a clear conversion from n-type to p-type behavior. For getting further insight into such atmospheric doping, in this work we investigated the effect of exposing TiOPc film to oxygen by ultraviolet photoelectron spectroscopy (UPS). The dependence of the energy of molecular electronic levels on the film thickness probed by UPS was clearly different for films prepared in UHV and in oxygen atmosphere. The film deposited in UHV condition showed an n-type alignment between the highest occupied molecular orbital (HOMO) and the Fermi level ($E_F$) of the substrate, while a p-type alignment was observed in oxygen atmosphere. This conversion of the energy level alignment can be ascribed to the hole doping by oxygen and excellently corresponds to the above mentioned change of the FE properties. Another important factor of doping is the $E_F$ alignment between TiOPc thin film and the substrate. In order to examine this, the energy of the TiOPc HOMO relative to the $E_F$ of metal substrates was determined for various substrates. For films prepared in UHV condition, the HOMO positions scatter by about 0.8eV, indicating that $E_F$ alignment between substrate and TiOPc was not achieved, probably because of insufficient carrier density in the TiOPc thin film. The exposure of the film to oxygen makes the HOMO level positions for all substrates coincident with each other, that is, the HOMO position relative to metal Fermi level is independent of the substrate. These results indicate that $E_F$ alignment was achieved by the hole doping by oxygen. The effect of other gases such as ammonia will be also discussed.

Spin Self-Assembled Layer-by-Layer Films for Electrochromic Devices. Yoon-Chae Nah and Dong-Yu Kim, Dept. of Materials Science and Engineering, Gwangju Institute of Science and Technology (GIST), Gwangju, South Korea.

Electrochromism (EC) is defined as reversible changes in optical properties under an applied electric field. Because of their low power consumption and high coloration efficiency, EC devices have many potential applications such as smart windows, mirrors and displays. There are several methods to prepare EC materials, physical (sputtering and evaporation), chemical (chemical vapor deposition and sol-gel method), and electrochemical (electro or electrophotochemical deposition) processes. These methods are very useful to make flexible electrodes, but have also some difficulties in controlling the deposition of the electrodes in nano-scale. In contrast, a layer-by-layer (LbL) technique which is to form films by sequential adsorption of charged molecules presents many advantages in control of the electrode structure even within a single molecule by alternating pH or additives. There are two methods to prepare the self-assembled LbL films; dipping and spin coating. A dipping method (dip self-assembly) is based on the self-diffusion of charged polyelectrolytes by an electrostatic force, which leads to a time-consuming process for a monolayer formation. In addition, this method requires careful washing and drying steps. On the other hand, a spin self-assembly is a method to use centrifugal force and air shear during the spin process in addition to electrostatic interactions between the charged polyelectrolytes. Therefore, it takes shorter time to form the monolayer compared to dip self-assembly. Furthermore, this method is reported to provide highly ordered film structure by an effective elimination of water molecules or weakly adsorbed polyelectrolyte during the spin process. In our presentation, EC materials are prepared by spin self-assembly using anionic and cationic polyelectrolytes and the prepared film structure is investigated as a function of deposition conditions. Their electrochemical and electrochromic properties are also discussed.

Organic Thin Film Transistors Obtained using Atomic Layer Deposited Al2O3 as High-k Dielectric. Sandro Ferrari 1, Elisabetta Peron 1, Francesca Perissinotti 1, Giovanna Scarel 1, Dario Natali 2, Mario Cairoli 2, Luca Fulinagalli 2, Marco Sampietro 2, Alessandra Angiulli 2 and Paolo D. Gianvivace 2, 1Lab. MDI - INFAM, Agrate Brianza (MI), Italy; 2Dipartimento di Elettronica e Informazione, Politecnico di Milano, Milan, Italy; 3ISMAC-CNR, Milan, Italy.

Organic thin film transistors promise to boost the diffusion of electronic components in low cost items. Among them hybrid organic-inorganic transistors have shown several advantages. In particular, the use of high-k oxides as gate dielectrics allows to reduce the threshold gate voltage significantly, enabling low voltage operation of the devices. Among the high-k oxides, Al2O3 appears to be a good candidate, since it is low cost, non-toxic and easily processible. In this paper we report on transistor characteristics obtained using Al2O3 deposited with Atomic Layer Deposition (ALD). The films were grown using Al(CH3)3 as Aluminum and Oxygen sources respectively. ALD allowed to obtain extremely smooth Al2O3 films with very good electrical properties in terms of high breakdown voltage of 8-10 MV/cm, and low leakage currents, in contrast to Al2O3 obtained by PVD or anodic oxidation. Using poly-3-lexyl-thiophene as active layer, Al2O3 was compared to SiO2 as a dielectric for organic transistors. Hole carrier mobility resulted to be lower in Al2O3 devices, probably because of disorder at the semiconductor-dielectric interface. To improve the quality of this interface, instead of capping the dielectric surface, functionalization of the organic semiconductor with a spin-coated layer of poly-thiophene with and without substitution in the side chain to improve the affinity with the polar Al2O3 surface. Comparisons among the different techniques will be reported.

Large-Area Wet Micro-Printing for Organic Device Patterning. Zhongzheng Jin 1, 2 and James C. Sturm 1, 2, 3. 1 Department of Electrical Engineering, Princeton University, Princeton, New Jersey; 2 Princeton Institute for the Science and Technology of Materials (PRISM), Princeton University, Princeton, New Jersey.

An important challenge for Organic Light-Emitting Diodes (OLEDs) manufacturing is the patterning method of the organic materials used for different-colors. Ink-jet printing has been widely developed for polymers, but it suffers from potential drawbacks, such as nozzle clogging, repeatability of the direct droplet coverage and throughput. In this talk, a large-area wet micro-printing technique is
proposed and demonstrated for organic device patterning. In this method, a printing plate is first prepared by surface engineering so that a designed high-energy (wettability) pattern is achieved. The printing plate is then coated with "ink", a solvent solution with dissolved organic materials to be printed. Guided by the wettability pattern, ink sticks only to selected regions of the printing plate. The printing plate is then brought into contact with the deposited materials, during which ink is transferred to desired locations. Following printing, the solvent is allowed to dry, leaving a patterned organic film on the target substrate. With this approach, the Red, Green and Blue (R, G, B) sub-pixel arrays have been patterned, using the host polymer poly-(9-vinylcarbazole) (PVK) doped with 2-(4-biphenyl)-5-(4-tert-butyphenyl)-1,3,4-oxadiazole (PBD) for electron transporting doped layers and coumarin 6 and coumarin 47 [1] for R, G, B color tuning, respectively. The entire blend was printed on each sub-pixel using chlorobenzene as a solvent. A controlled vapor pressure was used to adjust the drying rates. In these first experiments, 300 x 300 cm² pixels were printed over an area of ~2 x 2 cm. Monochrome OLED devices were tested for their electrical and electro luminescence properties, including J-V-L characteristics and external quantum efficiency. The devices show efficiencies comparable to those by spin coating. The results suggest that large-area wet micro-printing is a promising patterning technique for low-cost full-color OLED displays. [1] C.C. Wu, J.C. Sturm, R.A. Register, J. Tian, R.P. Duna, and M.E. Thompson. IEEE Trans. Elec. Dev. 44, pp. 1269-1281 (1997).

Electronic Structure and Charge Transfer Dynamics of Alq3/Al and Alq3/LiF/Al Interfaces. Stina G. M. Jonsson¹, Michel P. de Jong², William R. Salanek³ and Mats Fahlin¹;
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An explanation for the fact that Alq3/LiF/Al interfaces exhibit better device performance than Alq3/Al interfaces is sought in the electronic structure and charge transfer characteristics at the interfaces. Monolayers of Alq3 have been grown on Al and LiF/Al substrates by physical vapour deposition. In the case of Alq3/Al there is a covalent interaction between the metal substrate and the organic monolayer (evidenced by an interfacial state observed in the UPS spectra), which is also supported by a vacuum level shift indicating dipole formation at the interface, in analogy with previous results [1]. In contrast, for the Alq3/LiF/Al system, there are two new interfacial states appearing in the Alq3 spectrum for LiF layers up to ~20 Å. XPS and UPS results show that these interfacial states originate from charge transfer between the Al substrate and the Alq3 monolayer across the inert LiF sandwich layer. The Alq3 molecules at the interface are then doped. Furthermore, the UPS results indicate that Alq3 is n-doped for Alq3 that is obtained when deposited on LiF/Al substrates, not the commonly found mer-Alq3 isomer. This is important to device design since the two isomers have distinctly different electronic and optical properties. These UPS results are consistent with UPS results obtained by photoelectron spectroscopy. The core-hole clock technique (2), which is based on resonant photoemission spectroscopy, can be used to study the charge transfer dynamics of organic/metal interfaces. We present core-hole clock data for both interfaces and the differences observed for insertion of a LiF layer of variable thickness are discussed. (1) Yokoyama, T., Yoshimura, D., Ito, E., Ishii, H., Ouchi, Y., Seki, K., 2003, Jpn. J. Appl. Phys. 42, 3666. (2) Brouwer, P.A., Karis, O., Martensson, K., 2002, Rev. Mod. Phys. 74, 793.

New Functionalized Oligo-Acene Derivatives for Organic-Field Effect-Transistors. Matthias Rehahn and Michael Roth; Macromolecular Chemistry, Darmstadt University of Technology, Darmstadt, Germany.

The production of flexible and cheap electronic devices requires the development of novel semiconductor materials, processable from solution via spin coating or ink jet printing techniques. The strategy we apply is the incorporation of various functionalities. The advantages of conventional polymers (rapid film formation, high film stability, good solubility) with those of small semiconducting organic molecules (highly efficient ordering, high charge carrier mobility). Therefore, we synthesized oligo-acene derivatives bearing functional groups which can be used to attach them as lateral substituents to appropriate precursor polymers. Finally, we build up organic field effect transistors (OFETs) from the resulting polymer via solution-based processes as well as reference transistors from the original low-molecular-weight semiconductors via vapor deposition techniques. Comparison of the devices allows estimation of the performance of the respective materials, and to optimize the polymer coating process under the conditions. In a proof-of-concept demonstration, we grew the polymer onto silicon wafers and characterized them with respect to their electronic, their electronic and solid state properties. The characterization showed that it is possible to shift the HOMO/LUMO levels over a wide range. This allows adapting the organic semiconductor properties to the levels of the source/gate electrodes. The new materials were used to fabricate organic field-effect transistors. Some of these OFETs exhibit a very high degree of ordering in the solid state, and some of them have charge carrier mobilities in the range of 0.1 - 0.6 cm²/Vs. In conclusion, the presented modular strategy allows the fabrication of a wide variety of organic semiconductors and the fine tuning of their electronic and solid state properties.
Ultrathin SiO₂ Layer. Koshi Okamura 1, Masanori Nakamura 2 and Kazuhiro Kudo 3, 1 Graduate School of Science and Technology, Chiba University, Chiba, Japan; 3Department of Electronics and Mechanical Engineering, Faculty of Engineering, Chiba University, Chiba, Japan.

The characteristics and control of carrier injection into organic materials are key issues for designing organic devices. It has been reported that introducing ultrathin insulating layer, such as LiF or Al₂O₃, between metal and organic layers shows a significant reduction of the threshold voltage and an enhancement of carrier injection in organic light emitting diodes (OLEDs). Although some explanations have been given, the contribution of the direct tunneling and mechanism for the improved carrier injection are not fully understood. In this study, therefore, we propose a diode structure including an insulating layer, thin enough to enable electrons to tunnel directly, between metal and organic layers to accomplish the following two points: the role of the insulating layer between metal and organic layers, and applicability of the knowledge of the energy level alignment in organic/metal interfaces, which have been extensively studied by ultraviolet photoelectron spectroscopy (UPS), to practical devices. The proposed devices are equivalently fabricated by using the silicon micro-process technology, and consist of a n-Si(100) substrate, a thermally grown ultrathin SiO₂ layer of about 2nm, an organic layer, such as CuPc, pentacene or Alq₃, and an Al electrode. When a positive voltage is applied to the top Al electrode, energy levels of the organic material are pulled down with respect to the Fermi level of the Si substrate, therefore electrons can tunnel into unoccupied energy levels, such as LUMO and LUMO-1, of the organic layer. When a negative voltage is applied to the Al electrode, on the contrary, energy levels of the organic layer are pulled up, therefore electrons tunnel from occupied energy levels, such as HOMO and HOMO-1, of the organic layer into the Si substrate. By controlling the biasing voltage, carriers are injected into desired energy levels of the organic layer. Detailed characteristics of the tunnelling current and energy relaxation accompanying the light emission will be presented in the session.

16.34 Spin-Conserve Carrier Recombination in Conducting Polymeric Materials. Manfred J. Walter 1, M. Reufer 1, P. G. Lagoudakis 1, U. Scherf 2, J. M. Lupton 3 and J. Feldmann 3; 1Photons and Optoelectronics Group, Physics Department and CeNS, Ludwig-Maximilians-Universität, Munich, Germany; 2FB Chemistry, Universität Wuppertal, Wuppertal, Germany.

According to simple statistics the intrinsic quantum efficiency η of polymeric light emitting diodes (PLEDs) is limited to 25%, as generally only singlet excitons contribute to the electroluminescence of the device while triplets mostly decay nonradiatively. In contrast to this, several publications in the last few years suggested that this limit might not be true but that intrinsic quantum efficiencies exceeding this limit could be reached. Bound polaron pairs (PPs) that are precursors to exciton formation play a major role in the respective argument as η>25% holds only if a negligible energy difference between singlet and triplet PP-states is assumed [1]. However, it is now known experimentally about the crucial energy of polaron pairs and the role of spin-lattice-relaxation in the PP-state. Tackling this problem of spin dependent exciton formation we use a novel class of polymers containing traces of metallic complexes that makes it possible to observe singlet and triplet excitons simultaneously for the first time. The phosphorescent decay channel of generally invisible triplets is activated [2]. This way we can efficiently differentiate between spin states by spectroscopic means and directly observe changes of the total spin of the bound polaron pairs. By applying an external electric field the PPs can be stabilized over timescales relevant to the operation of PLEDs. Fast spin-lattice-relaxation between isoenergetic PP-states of different spin multiplicity should be observable. Astonishingly, during the electrostatic storage such effective mixing of spin-states cannot be observed even at room temperature, suggesting an exceptionally strong exchange interaction between carriers constituting the PP. We conclude that the assumption of fast spin-lattice-relaxation when arguing in favour of η>25% may not be founded. Besides this, we provide direct experimental evidence for the presence of triplet PPs. It is also shown that even under the influence of strong electric fields only a small number of excitons is dissociated into free electrons and holes. The strongly spin-conserving recombination pathway in PPLEDs means that the fill factor exceeding the 25% is most likely only surfacemountable using phosphorescent triplet emitters. However, on the up side we note that the strong long-range exchange interaction observed in polymers bares considerable potential for future room temperature spintronics applications as the exchange splitting of the bound carrier pair is much larger than KT [1]. [2] J. M. Lupton et al., Phys.Rev.Lett. 89, 167401 (2002).

16.35 Electronic Structure Calculation and Multiscale Simulation of Acene Functionalized Polyhedral Oligomeric Silyloxanes (POSS) Molecular Crystals. Feng Qi 1, Murat Durandurdu 2, 3 and John Kieffer 1; 1Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan; 2Department of Physics, University of Texas at El Paso, El Paso, Texas.

Ab initio calculations were used to investigate the electronic structure of a series of polyhedral oligomeric silyloxanes (POSS), functionalized with acene molecules. Moreover, classical MD simulations were used to predict the structures that result from self-assembly of these molecular groups. These structures were characterized in terms of their melting and crystallization behavior, and mechanical properties. Our calculations reveal that these acene-functionalized POSS compounds have a much lower gap at the gamma point than pure acene molecular crystals, but have superior thermal and mechanical properties. Our results indicate that these acene-functionalized oligomers are potential new candidates for both conducting organic molecules, which are useful for future organic electronic applications. This work provides an example of the design and synthesis of new materials based on building block assembly.

16.36 Trap-Assisted Hole Injection and Quantum Efficiency Enhancement in Poly(9,9-Dietylfluorene-Co-Benzothiadiazole) Polymer Light-Emitting Diodes. Alexander Seeley 1, Richard Friend 2, Jeremy Burroughs 2 and f!Seon Kim 1; 1Physics, University of Cambridge, Cambridge, United Kingdom; 2CDT Ltd, Cambridge, United Kingdom.

We report a reversible many-fold quantum efficiency enhancement during electrical driving of polymer light-emitting diodes (PLEDs) containing poly(9,9-diethylfluorene-alt-benzothiadiazole) (F8BT), developing over several minutes or hours at low applied bias and remaining in similar timescales after device switching. This phenomenon is only observed in devices containing F8BT as an emissive layer in pure or blended form, regardless of anode and cathode choices and even in the absence of a poly(styrenesulfonate)-doped poly(3,4-ethylene-dioxythiophene) (PEDOT:PSS) layer. We report detailed investigations using a standardised device structure containing PEDOT:PSS and a calcium cathode. Direct measurements of trapped charge recovered from the device after driving significantly exceed the unipolar limit, and thermally activated relaxation suggests a maximum trap depth around 0.6 eV. Neither photoluminescence nor electroluminescence spectra reveal any change in the bulk optoelectronic properties of the emissive polymer nor any new emissive species. During the quantum efficiency enhancement process, the bulk conduction of the device increases. Reverse bias treatment of the device significantly reinforces the QE enhancement. Based on these observations, we propose a simple model in which interfacial dipoles are generated by trapped holes near the anode combining with injected electrons to produce a narrow tunnelling barrier for easy hole injection. The new injection pathway leads to a higher hole current density and thus a better charge injection balance. This produces the relatively high quantum efficiency observed in all F8BT LEDs.

16.37 Acene Polymer N-channel FET fabricated by Drop-On-Demand Inkjet Printing Technique. Rohit Dikshit, Yi Su, Rajneek Khillan, Razat Nohria and Kody Varahramyan; Institute for Micromanufacturing, Louisiana Tech University, Ruston, Louisiana.

Organic and polymer field effect transistors have received a prominent attention due to their potential applications in low-cost and low end of electronic devices like large area flexible displays, smart cards, radio frequency identification (RFID) tags and optoelectronic devices. Conventional vacuum-deposition and photolithographic techniques are expensive fabrication processes which should be avoided for fabrication of organic and polymeric electronic devices [1]. Many organic or polymer materials are soluble in some solvents such as chloroform, toluene, DMF, THF, xylene and water. This offers a convenient means for solution processing like spin-coating, solution self-assembly and inkjet printing [2, 3]. Inkjet printing technique offers a simple, low cost, low temperature and mask-free micro-fabrication for polymer electronics [4]. In this paper we report an all-polymer n-channel field effect transistor fabricated by drop-on-demand inkjet printing technique. Semi-conducting organic materials such as P3HT or Me-PCBM (methyl lithium fullerene II oligomeric 2,5-dibromo-3-ethyl) are used as an active channel material, conducting polymer polypyrrole (PPY) is used as source, drain and gate electrodes and FVP as insulating layer. All these polymers were inkjet printed to form the n-channel field effect transistor. These transistors were fabricated on heavily doped n-type Si wafer as a gate and silicon dioxide as gate dielectric material. Source, drain and active channel material were inkjet printed using the above mentioned polymers. Polymer FETS with channel length in the range of 30 μm to 100 μm.


Thermal effects such as heat generation and dissipation are increasingly important in micro- and nanoelectronics and provide a substantial barrier to further miniaturisation. Molecular semiconductors such as conjugated polymers are often advocated as building blocks for nanoscale electronic devices, but the intrinsically low mobility of these materials implies that most of the electrical energy passing through the material is converted into heat. Consequently, there remains considerable interest in techniques for thermal measurement on organic devices. We recently presented a highly sensitive molecular thermometer based on dual emission from the commonly used semiconducting polymer poly(phenylene vinylene) (PPV). This enables contact free optical thermometry of very thin films of conjugated polymers, such as in light-emitting diodes, and provides direct information on non-radiative decay channels in organic semiconductors. [1]

We have now improved our detection scheme and are able to demonstrate the exceptional time resolution achievable with PPV molecular thermometers by measuring the instantaneous temperature of a conducting strip line on the nanosecond time scale [2]. As the molecular thermometer works by thermally activating emission from a long-lived meta-stable state, we are able to achieve fluorescence-based thermal imaging without the potentially perturbing influence of the exciting light source. Our method, which relies on gated fluorescence spectroscopy, therefore allows absolutely non-invasive characterisation of a totally thermally isolated system. Besides the technological implications and applications of adiabatic fluorescence thermometry to, for example, organic displays, the observation of externally triggered fluorescence bursts from organic semiconductors is of considerable fundamental interest. An external stimulus, in this case an electrically generated heat pulse, is used to flip the spin of the excited electron through reverse intersystem crossing from the singlet state to the triplet state. Although the spins remain unpolarised, the control over spin correlation may provide a basis for molecular spintronic devices. [1] J. M. Lupton, Appl. Phys. Lett. 81, 2478 (2002). [2] J. Stehr et al., Adv. Mater., in press.


Within the class of organic semiconductors, ionic transition metal complexes (iTMCs) such as ruthenium(II) tri-bipyridine have recently prompted extensive photophysical and electrochemical study. Devices based on these compounds have been shown to balance ease of fabrication and efficient emission, with power efficiencies for single layer iTMC devices as high as 10 Lm/W. Their operation is dominated by the conduction of mobile ions, which permits the use of air stable electrodes. As a result, devices based on iTMCs are being developed for flat-panel displays and solid-state lighting applications. In order for these devices to be considered viable for display applications, the half lives of the device radiance must approach 10,000 h. To date, the best ruthenium(II) tri-bipyridine devices have half lives on the order of 1,000 h under nitrogen atmosphere. Even with air stable contacts, iTMC devices undergo an irreversible degradation of the complex when operated in a nitrogen-filled drybox or air. However, the specific chemical identities of the predominant degradation products have not been identified. It has been shown to suppress the photoluminescence quantum yield of these devices. We have quantitatively investigated the influence of moisture on ruthenium(II) tri-bipyridine device performance. By running devices under controlled humidity levels, we have shown that the rate of degradation of the device radiance versus time is first order in water concentration. In this report we also discuss recent efforts in mass spectrometry to identify the specific quenching species formed from running these devices under atmospheric conditions.

16.40 Efficient RGB and White OLEDs Using Platinum Dinuclear Complexes as Phosphorescent Emitters. Brien Ma1, Peter I. Djuricovic2, Jian Li3, Simona Garon2, Arnold Tamayo2 and Mark E. Thompson2; 1 Materials Science, USC, Los Angeles, California; 2Chemistry, USC, Los Angeles, California.

Highly efficient organic light emitting diodes (OLEDs) have been achieved by using heavy metal complexes as phosphorescent emitters. The strong spin-orbit coupling from the heavy atom readily interconverts all three spin states leading the quantum efficiency close to the theory limit of 100%. Most of these metal complexes (such as iridiun and platinum derivatives) applied in devices are mononuclear species. This presentation will describe the application of platinum dinuclear complexes in monochromatic red, green, blue (RGB) and white OLEDs. Two types of dinuclear complexes will be introduced: one is bisacetylacetonate-bridged complexes and the other is pyrazolate-bridged complexes. For the former type, emission color tuning can be achieved by changing the identity cyclometalated ligands, while for the latter one, controlling the Pt-Pt separation modifies the emission energy. White OLEDs have been fabricated using these dinuclear complexes in different device architectures, which include a multiple emissive layer structure, a single-doped double-layer structure utilizing monomer and the aggregation emission. In addition, other approaches to get white emission by using platinum dinuclear complexes will be addressed.

16.41 Correlating Structure Development to Performance Enhancement in Organic Semiconductor Films. Dean Michael DeLongchamp1, Sharadha Sambasivan2, Daniel A. Fischer1 and Eric K. Lin2; 1Polymers Division, National Institute of Standards and Technology, Gaithersburg, Maryland; 2Materials Science and Engineering Laboratory, National Institute of Standards and Technology, Gaithersburg, Maryland.

Measuring the structural development of organic semiconductor films and correlating it to the electrical characteristics of organic field effect transistors (OFETs) are critical steppingstones to commercialization. Good correlation will guide development of new materials and processing methods. Synchrotron-based Near-Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy is a technique that can non-destructively reveal the structure and chemistry of thin organic films. The density of bonds involving low-Z elements (Carbon, Nitrogen, Oxygen, and Fluorine) can be quantified, the composition depth profile can be developed with nanometer precision for the top (2-10) nm of the film, and the average surface-relative bond orientation can be determined. We employ NEXAFS spectroscopy to investigate chemical, substrate-relative orientation development in thin organic semiconductor films. These structural quantities are then correlated to OFET performance. Semiconducting materials to be presented include small molecule soluble precursors, thermally evaporated small molecules, and polymers. Examples include classical model systems such as pentacene and regioregular poly(3-hexylthiophene), as well as recently designed new molecules. Heat processing-induced increases in substrate-relative molecular orientation can be described. Structure and performance enhancement by hydrophobic substrate preparation will be discussed. Finally, the role of the semiconductor chemical structure itself will be considered. NEXAFS provides excellent correlation of processing to structure to performance that allows us to optimize an emission, which can be fruitfully pursued to develop next-generation materials.

16.45 An Efficient Polymeric Light-Emitting Device with Aluminum Cathode. X. Y. Deng and K. Y. Wong; Department of Physics, Chinese University of Hong Kong, Hong Kong, China.

Polymer light-emitting devices (PLEDs) using aluminum as the cathode normally have poor light-emitting efficiencies due to the high work-function of aluminum, which impedes electron injection at the cathode contact. In a previous work[1], we discovered that through modifying the emissive polymer by blending it with poly(ethylene glycol)[(H(OCH2CH2)n)O]H, the electroluminescent (EL) efficiency of a PLED with aluminum cathode can be enhanced by more than two orders of magnitude. A device efficiency exceeding 2.6 cd/A was achieved for an orange-color-emitting PLED. This scheme is
unique among other methods of enhancement, such as the employment of a lithium fluoride interlayer[2], since PEG contains no metallic component in its structure. We have subsequently found that similar enhancement was observed by introducing PEG as an ultrathin interfacial layer between the emissive polymer and the cathode, which shows that the mechanisms underlying the enhancement are largely of interfacial origin. The enhancement mechanism is apparently not dependent on the structure of the emissive polymer, as enhancement was observed for different species of emissive polymers such as MEH-PPV and PFO. On the other hand, the enhancement was observed when using other metals beside aluminum as the cathode. The result indicated that the enhancement mechanism is specific to the interaction between aluminum and PEG.

We report a joint theoretical and experimental study of several new thiophene-based poly(azomethine)s. Five soluble new conjugated polymers were obtained from the poly(azomethine)s. Theoretical band gaps of the new thiophene-based poly(azomethine)s were in the range of 2.33-2.67 eV, which are smaller than that of the phenylene-based polymer. The variation of the backbone ring (fluorene, carbazole, or naphthalene) or donor/acceptor side chain on the phenylene ring significantly affected the dihedral angles and resulted in the variation of electronic properties (ionization potential, electron affinity, and band gap) of poly(azomethine)s derived from the polymerization of 2,5-diformyl-3-b-hexylthiophene (DFHT) with various diene monomers. The optical and electrochemical band gaps of the polymer films were in the range of 2.21-2.28 and 2.13-2.24 eV, respectively. The trends on the effect of the backbone ring or side chain on the electronic properties is in good agreement with the theoretical results. Our study demonstrates how the electronic properties of conjugated poly(azomethine)s can be tuned by the backbone ring or side group, which could be important for electronic or optoelectronic applications of the materials.

16.43
New Thiophene-Linked Conjugated Poly(azomethine):

Cheng-Liang Liu1, Fu-Chuan Tsai2, Chao-Ching Chang4, Wen-Chang Chen1 and Samson A. Jenekhe1; 1Department of Chemical Engineering and Institute of Polymer Science and Engineering, National Taiwan University, Taipei, Taiwan; 2Departments of Chemical Engineering and of Chemistry, University of Washington, Seattle, Washington.

We develop a new family of branched di(alkyl) and dialkoxy substituted poly(3,4-propylenedioxythiophene) (PProDOT) polymers, where the substituents are symmetrically placed at the 2 position of the propylene bridge. The polymer synthesis was carried out using Grignard Metathesis to yield PProDOT-(CH2=O-2-ethylhexyl)2, PProDOT-(2-ethylhexyl, PProDOT-(2-ethylbutyl)2, PProDOT-(2-methylbutyl)2, PProDOT-(CH2=O-(2-methylbutyl))2, PProDOT-(CH2=O-(2-ethylbutyl))2, PProDOT-(2-methylbutyl)2, PProDOT-(hexyl)2 and PProDOT-(CH2=O-(2-ethylhexyl))2. The polymers obtained have high molecular weights (Mn = 20,000-50,000 g mol-1) and dispersity around 1.7. All of the polymers are highly soluble in chloroform, while the ethyl branched polymers, as well as the octadecl substituted polymer, are also highly soluble in DCM, toluene and THF. The methyl branched derivatives, as well as polymers substituted with short linear alkyl chains have moderate solubility in these solvents. Solutions of these polymers display thermochromic and solvatochromic behavior. Spray-cast films from polymer solutions are electrochromically switchable from a strongly absorptive blue-purple (alkyl) or red-purple (alkoxy) color in the neutral state to a highly transmissive sky-blue color. The optical band gap varies between 1.84 to 1.96 eV, which is typical of substituted PProDOT derivatives, and enhanced switching behavior was observed using the propylene chain as the switching group.

16.44
Photogeneration and Electronic Transport Mechanisms in Thin Films of Amorphous 2,4,7-Trinitro-Nine Fluorenone.

Iliia Mikhailovich Kachirski, Physics, Peoples Friendship University, Moscow, Russian Federation.

The photogeneration process in thin films of vacuum evaporated amorphous 2,4,7-trinitro-N-ninefluorenone (a-TNF) is investigated by steady-state photodetection measurements and by photoinduced discharge method. It was found that in the intrinsic spectral range of absorption (wavelength < 400 nm) the charge carrier photogeneration mechanism includes several steps. The final step, thermal dissociation of light generated electron-hole pairs occurs according to the Onsager mechanism. The effect of the trapping centres on the conductivity of thin films of a-TNF is investigated by Space Charge Limited Current (SCLC), Steady-State Photocconductivity methods. It was suggested that the transport of charge carriers in a-TNF is controlled by traps. Some parameters of traps were determined.

16.45
Abstract Withdrawn

16.46
Patterned Organics with Photolithography.

John Andrew DeFranco1, Bradley Schmidt2, Ricardo Ruiz1, Michal Lipson3 and George Malliaras1; 1Materials, Cornell University, Ithaca, New York; 2Electrical and Computer Engineering, Cornell University, Ithaca, New York.

The realization of organic electronic technologies requires the availability of patterning techniques that are compatible with chemically sensitive materials. We demonstrate an approach that allows the photolithographic patterning of organic films without their exposure to harmful solvents, and achieves micrometer resolution. Examples of additive and subtractive patterning of polymers as well as small molecules show this approach to be quite generic.

16.47
Abstract Withdrawn

16.48

We have developed a new family of branched di(alkyl) and dialkoxy substituted poly(3,4-propylenedioxythiophene) (PProDOT) polymers, where the substituents are symmetrically placed at the 2 position of the propylene bridge. The polymer synthesis was carried out using Grignard Metathesis to yield PProDOT-(CH2=O-2-ethylhexyl)2, PProDOT-(2-ethylhexyl, PProDOT-(2-ethylbutyl)2, PProDOT-(2-methylbutyl)2, PProDOT-(CH2=O-(2-methylbutyl))2, PProDOT-(CH2=O-(2-ethylbutyl))2, PProDOT-(2-methylbutyl)2, PProDOT-(hexyl)2 and PProDOT-(CH2=O-(2-ethylhexyl))2. The polymers obtained have high molecular weights (Mn = 20,000-50,000 g mol-1) and dispersity around 1.7. All of the polymers are highly soluble in chloroform, while the ethyl branched polymers, as well as the octadecl substituted polymer, are also highly soluble in DCM, toluene and THF. The methyl branched derivatives, as well as polymers substituted with short linear alkyl chains have moderate solubility in these solvents. Solutions of these polymers display thermochromic and solvatochromic behavior. Spray-cast films from polymer solutions are electrochromically switchable from a strongly absorptive blue-purple (alkyl) or red-purple (alkoxy) color in the neutral state to a highly transmissive sky-blue color. The optical band gap varies between 1.84 to 1.96 eV, which is typical of substituted PProDOT derivatives, and enhanced switching behavior was observed using the propylene chain as the switching group.

16.49
High-Mobility Polymer Thin-Film Transistors and Solvent Effects. Joohyung Park, S. Young Park, M. Joon Kim, Tae Il Kim and Hong H. Lee; School of Chemical Engineering, Seoul National University, Seoul, South Korea.

A polymer gate dielectric of poly(2-hydroxyethyl methacrylate) (PHEMA) is introduced to the polymer thin-film transistor (TFT) with poly(3-hexylthiophene) as its active layer. The mobility of the polymer TFT with the PHEMA gate dielectric is 0.1 cm2V-1s-1, which is much higher than any mobility reported for polymer TFT with polymer dielectric. The solvent used in forming the dielectric layer on the polymer dielectric film and the mode of casting have pronounced effects on the device performance. It has been found that the effect on the mobility has to do with the surface roughness, the mobility decreasing with increasing surface roughness. The physical parameter that can be related to the roughness is solubility parameter. We have found that a solvent with a solubility parameter closer to that of PHEMA causes more roughening of PHEMA surface and as a result leads to a poorer device performance. Therefore, the solvent with the solubility parameter that is furthest away from that of PHEMA should be used for the best device performance. This conclusion should be valid for any polymer gate dielectric with a polymer semiconductor.

16.50
Photoresponse of Organic Field-Effect Transistors based on Soluble Semiconductors and Dielectrics. Nenad Marjanovic, Birendra Singh Thokchom, Serap Gunes and Serdar Niyazi Sariciftci; Physical Chemistry, Johannes Kepler University Linz, Austria, Linz Institute for Organic Solar Cells (LIOS), Linz, Austria.

Photocative organic field-effect transistors, photOFETs based on soluble semiconductors and dielectrics with top source and drain electrodes are fabricated and characterized in the dark and under illumination. Gate insulating layers are based on photovoltaic dielectrics that are spin coated on ITO coated glass substrates. The semiconductor layers of the transistors are based on conjugated polymers as electron donors and materials of high electron affinity as
Two polymer dielectrics are made cooperative in acting as the gate insulator for organic thin-film transistors (OTFTs). The bilayer insulator consists of a thin polymer dielectric in contact with the active layer that can induce good electrical properties and a much thicker dielectric with good dielectric properties. These dielectrics are cooperative in combining the best each can offer for better device performance. To demonstrate the concept, a bottom-gate OTFT structure was used where pentacene is the active material. The polyvinylphenol (PVP) is the thin dielectric in contact with the pentacene layer, and polyvinylacetate (PVAc) is the thick dielectric in contact with the PVPH layer. The performance of the OTFT with the bilayer insulator shows that the good electrical characteristics induced by PVP are retained while the hysteresis is eliminated with the presence of PVAc.

16.51
Polymer Gate Dielectric Formulation for Organic Thin-Film Transistors. S. Young Park, Joonyung Park, M. Joon Kim, Ta Il Kim and Hong H. Lee; School of Chemical Engineering, Seoul National University, Seoul, South Korea.

Two polymer dielectrics are made cooperative in acting as the gate insulator for organic thin-film transistors (OTFTs). The bilayer insulator consists of a thin polymer dielectric in contact with the active layer that can induce good electrical properties and a much thicker dielectric with good dielectric properties. These dielectrics are cooperative in combining the best each can offer for better device performance. To demonstrate the concept, a bottom-gate OTFT structure was used where pentacene is the active material. The polyvinylphenol (PVP) is the thin dielectric in contact with the pentacene layer, and polyvinylacetate (PVAc) is the thick dielectric in contact with the PVPH layer. The performance of the OTFT with the bilayer insulator shows that the good electrical characteristics induced by PVP are retained while the hysteresis is eliminated with the presence of PVAc.

16.52
Direct Measurement of Surface Complex Loading and Surface Dipole, and their Effect on Simple Device Behavior. Jing Guo1, Norbert Koch2, Jeffrey Schwartz2 and Steven L. Bernasch1; 1Chemistry, Princeton University, Princeton, New Jersey; 2Physics, Humboldt University Berlin, Berlin, Germany.

The complex nature of phenoxy ligands having a range of dipole moments were prepared on the surface of ITO. Surface complex loadings and stoichiometries were measured by Quartz Crystal Microgravimetric (QCM). Work functions of ITO substrates treated with these various surface complexes were measured using a Kelvin probe. Surface complex dipole moments were then calculated based on measured surface loadings. Changes in the ITO work function, resulting in a shift in $V_{th}$, is only around 1.0 cm$^{-2}$.

16.53
Feedback Enhancement in Photonic Crystal Lasers with an Organic Gain Material. Rik Harbers1,2, Nikolaj Moll1, Rainer F. Mahrt2, Daniel Erni1 and Werner Baechtold1; 1Swiss Federal Institute of Technology, Zurich, Switzerland; 2IBM Research, Ruschlikon, Switzerland.

Photonic crystal lasers with an organic gain material are improved by using a photonic crystal that consists of a thin layer of a high-index material to enhance the mode coupling. The use of high-index material increases the index contrast in the photonic crystal and the confinement in the waveguide. The mode coupling is thus increased, which results in larger feedback given to the lasing modes. This allows for thinner lasers.

16.54
Charge Carrier Mobility Measurements in Tetracene Single Crystals. Jens Plaum, Jens Niesmak and Ashutosh K. Tripathi; Physics Department, University of Stuttgart, Stuttgart, Germany.

To study the electronic properties of organic thin films, ultra-pure single crystals of the respective material define reference systems for the charge carrier transport. Therefore, we have studied the electron and hole mobility of tetracene single crystals by time-of-flight (TOF) spectroscopy and field-effect transistor (FET) characteristics in the temperature range from 300K to 450K. The centimeter-sized single crystal of tetracene were grown from purified pentacene crystals by Bridgman growth in a continuous gas stream of e.g. H$_2$ or Ar, or from saturated gas phase in a modified Bridgman setup. Whereas by sublimation techniques only platelet-shaped crystals could be obtained, the single crystal prepared by vapor-Bridgman is cone-shaped with a rotational axis of about 2cm in length. By TOF spectroscopy, the mobilities for electrons and holes can be estimated separately without injection-limited effects at the contacts, in contrast to techniques based on current measurements. Studies in the FET geometry yield information on the transport at the crystal surface, i.e. the (ab)-plane. For the preparation of the FET gate insulators, various setups and materials such as polymers have been tested and their individual problems and advantages will be described. By use of a polymethylphenyloxide-gate insulator, we could achieve an electrical breakdown-field strength of 3MV/cm. For holes a defined Dopf transient is observed along the c-direction of the crystals, whereas the electrons obey a standard dispersive transport behavior caused by inhomogeneities. From temperature dependent mobility measurements a thermally activated multiple trapping and release transport for holes can be concluded with a maximum of the mobility at room temperature (RT) of about 1.0cm$^2$/Vs. Fitting the experimental data by a model, we estimated the density of traps as well as their respective energy can be adjusted. By complementary Auger photodiffraction and gas-chronatography (GC) studies the structure and the chemical impurities related to the observed trap distribution were distinguished. From these data we can conclude that trapping is mainly caused by chemical inhomogeneities in the molecular crystals. Photoluminescence measurements, a molecular spectroscopy technique, observed for holes moving in the (ab)-crystal surface. The maximum mobility of 0.8cm$^2$/Vs at RT agrees well with the one obtained by TOF. Again, GC of the chemical composition of the crystal surface indicated contamination by oxid products of tetracene strongly correlated to the observed transport behavior. Finally, we will discuss impacts on the transport in organic thin film devices made of...
9:00 AM 17.3
Organic Based Magnetic Thin Films by Low Temperature CVD. R. Shima Edelstein,1 J. W. Yoo,2 N. P. Raju,3 J. D. Bergeson,4 K. I. Pokhodnya,4,5 Joel S. Miller2 and Arthur J. Epstein2,5,6 1Department of Physics and Department of Chemistry, Ohio State University, Columbus, Ohio; 2Department of Chemistry, University of Utah, Salt Lake City, Utah.

Spintronic devices4 use the spin property of electrons in applications such as giant magnetoresistance based magnetic read heads, spin valves, and spin light emitting diodes. The introduction of organic based materials to replace conventional ceramics, metals or alloys offers some advantages: versatility of substrate materials (lower processing temperatures), control over the magnetic ordering temperature (by tailoring the composition), and improved spin injection across interfaces5. In this work we describe how the composition and physical properties of an organic based magnet can be controlled by varying the Chemical Vapor deposition (CVD) conditions. An elaborate study has been performed for the CO2(CO)10 / TCNE system to form cobalt tetracyanobenzene [Co(TCNE)2], x=2 - a paramagnetic compound. This work has been implemented to the V(CO)12 / TCNE system to form vanadium tetracyanobenzene [V(TCNE)2], x=2. Thick (~5-10 µm) CVD made films were reported to be ferrimagnetic with an ordering temperature, Tc, of up to ~400K, and room temperature conductivity ~10-4 S/cm. This work towards the synthesis of the CVD process parameters are controlled to make films (~0.05-0.5 µm) of known composition (and room temperature conductivity ~10-2<σ<10-2 S/cm) which may be incorporated in spintronic devices. 6

9:15 AM 17.4
A New Architecture for Nanoscale Field-Effect Transistors. Daniel Fige, Liang Wang and Anantha Dodabalapur. The University of Texas at Austin, Austin, Texas.

There have been many reports of nanoscale field-effect transistors with deposited semiconductors such as organic molecules, organic and inorganic semiconductors, carbon nanotubes, etc. In such devices, the gate is almost always at the bottom and is unpatterned. The gate metal (often doped silicon) is then deposited over the gate insulator, and the patterning of source/drain electrodes with a very small gap above the gate insulator. Many innovative techniques have been used to get the source/drain gap, which defines the channel length, between the semiconducting layer and the metal. Many reports have then deposited above the gate insulator to connect to the source and drain either by covering it or by some kind of self-assembly. In this work, we have created a new type of nanoscale field-effect transistor that is suited to a wide range of semiconductors including organic/polymer semiconductors as well as recently reported inorganic semiconductors with high mobility that can be cast from solution. With suitable scaling it may also be used to implement molecular scale three-terminal devices that cannot be achieved with the previous approach outlined above. The devices are fabricated on an insulating substrate (SiO2 in our case). In the first step, tapered Al electrodes are defined by electron beam lithography and lift-off. The aluminum functions as the gate and it oxidizes upon exposure to air to create the gate insulator. The thickness of Al2O3 is estimated to be in the range 5-10 nm. Ti/Au source/drain regions are then defined in close proximity to the gate with a second exposure and lift-off. The semiconductor is then deposited on top of such a structure. The channel length in these devices is estimated to be about 50 nm, but can be reduced to the 5-10 nm range as recent work in our labs shows to be possible when using device architecture outlined above. The device has been demonstrated can be implemented with a range of semiconductors including inorganic nanowires, nanotubes, and inorganic and organic thin-film semiconductors. More interestingly it is a very suitable geometry for measuring mobility, film thickness and channel dimensions. For example it can be used for measuring mobility, film thickness and channel dimensions that can be as low as 5 nm, it will be possible to cause some deposited macromolecular self-assembly upon synthesis of a suitable class of molecular materials. Another example of a possible future application is in chemical and biological sensing. This device has an extremely small input capacitance. This means that a small number of gate charges can produce significant channel conductivity modulation. This is a very desirable feature for a range of sensitive bio-sensing applications.

9:30 AM 17.5
*Stacked N-Channel Organic Semiconductors with High Electron Mobilities in Organic Thin Film Transistors. C. Daniel Frohlich, Chem Eng and Mat Sci, University of Minnesota, Minneapolis, Minnesota.

This talk will describe multi-investigator efforts to develop crystalline organic semiconductors with improved n-channel (electron conduction) performance in organic thin film transistors (OTFTs). A major focus is on understanding the effect of structure at all length scales- including molecular packing, crystal packing, and the band mobility- on critical device parameters such as the electron mobility, the threshold voltage for conduction, and the on-off current ratio. In our best devices based on p-stacking perylene diimide derivatives, we achieved electron mobilities over 1 cm2/Vs and on-off current ratios above 10^7. We use a four-pronged strategy for the development of n-channel organic semiconductors, including (1) synthesis of new materials; (2) OTFT fabrication and testing as a function of temperature; (3) visualization of charge transport bottlenecks by high-resolution scanning probe methods; and (4) experimental and theoretical determinations (with Jean-Luc Bredas at Georgia Tech) of intermolecular electronic overlap and charge induced reorganization energies. This talk will focus on each of these components and will emphasize recent success we have had with p-stacked oligothiophenes and perylene diimides. Topics covered will include semiconductor film growth, structure characterization by X-ray diffraction and atomic force microscopy, device I-V characteristics, stability, carrier trapping, and O2/H2O sensitivity.

10:15 AM 17.6

We describe a transport model for ordered polyalkylthiophene semiconductors, which differs from previous models in that it explicitly considers how the polycrystalline lamella structure influences the transport mechanisms and density of states (DOS). The model is based on first principles calculation of the electronic structure, which calculates the shift in the valence band energies due to hole delocalization, and provides estimates of the density of states, and the band mobility. We construct a two-dimensional density of states appropriate to the polycrystalline lamella structure, from which a numerical calculation yields the temperature dependence of the effective mobility for comparison with transistor data. The DOS includes disordered grain boundary material, which is influenced by the shift in the band edge due to hole delocalization. Model calculations of mobility are compared to experiments on high mobility thin-film transistors made from regioregular PQT-12. The model gives a good qualitative representation of the transport and at least semi-quantitative agreement with data on PQT-12, although many details of the structure are not known precisely. The model reproduces the high mobility prefactor and the activation energy of the high temperature regime. The change in mobility activation energy below 250K is explained by low mobility states within the band tail distribution. The model also helps to put limits on the value of the microscopic mobility in lamella, and what needs to be known to extend an improved value from the TFT data. The results of the model are consistent with a free mobility of about 10 cm2/Vs, which is in line with theoretical expectations.
Information technology is the impetus of today’s life, where integrated organic electronics, optoelectronics, and sensors are providing important key technologies of the near-future due to the possibility to generate low-cost, flexible devices. A key element of organic electronics is the organic field-effect transistor (OFET). As organic semiconductor, the aromatic hydrocarbon small molecule (oligomer) pentacene is a very prominent candidate: it forms highly ordered, polycrystalline thin films, with the highest mobility of all in-film-deposited organic semiconductors, and it is also stable in ambient conditions than other poly-mer-based semiconductors. However, the mobility of charge carriers in the organic semiconducting layer is determined not only by the intrinsic properties of the semiconducting material, but also by the dielectric layer due to inter- and extralevels. Besides general growth conditions (e.g. substrate temperature, deposition rate), the growth is also dependent on the substrate material, its surface roughness and chemistry, and the pre-treatment. The permittivity of the dielectric material influences the charge carrier mobility, and the semiconductor-di-electric interface can be responsible for trapping states, thus influencing the performance of the OFET device. Driven by the wish of producing all-organic devices, the need for custom-designed dielectric materials was generated. Particularly, materials are searched for which can be applied and patterned with a variety of methods, enabling one to achieve high-performance, low-cost integrated organic electronic devices. Recently, inorganic-organic hybrid polymers such as ORMOCERs have attracted considerable attention for application in polymer electronics. They consist of organically functionalized inorganic-oxidic units, where methacryl, styryl, or epoxy groups can be used as organic moieties. Their physical/chemical mate-rial properties can be tuned over a wide range. Their synthesis can be controlled such that the resulting polymers possess a high glass transition temperature (Tg), a large variety of application and patterning methods can be applied. The fabrication of OFETs using pentacene deposited on various ORMOCER thin-film dielectric layers will be presented. OFETs in top-contact geometry show a charge carrier mobility up to 0.23 cm2/Vs, an On-Off ratio up to 105, and positive onset voltages in the range of 20 V. The performance of the de-vices with respect to the crystallinity and thus to the mobility of the pentacene films as well as the influence of the dielectric ORMOCER layers will be discussed.

11:15 AM AM 17.9

Morphological Effects on Charge Transport in Conjugated Polyelectrolytes, B. J. Hackel,1,2 Michael D. McGehee, and Michelle F. Toney,1 1 Material Science and Engineering, Stanford University, Stanford, California; 2Stanford Synchrotron Radiation Laboratory, Menlo Park, California.

Conjugated polymers include some of the most promising candidates for the active layer of low-cost thin-film transistors (TFTs) and bulk heterojunction photovoltaic (PV) cells. The charge carrier mobility of these conjugated polymers is the key material property limiting the performance of these devices. In addition to assessing the charge carrier mobility, an understanding the factors that affect it is therefore critically important. We have shown previously that the charge carrier mobility in TFTs increases by four orders-of-magnitude as the molecular weight (MW) of regioregular poly(3-hexylthiophene) (P3HT) is increased from 3000 g/mol to 36,000 g/mol. We find that the mobility also increases with MW in diodes, but only by a factor of 1.5. Studying films of P3HT with different MWs provides an ideal system for correlating morphological changes in conjugated polymers to the resulting changes in charge transport. To accomplish this, we have varied the spin-casting solvent, annealing conditions and drop-casting to modify the morphology at a common electronic force microscopy (AFM) images show a narrow structure that increases in length and appears to be better connected after annealing, using a higher boiling point solvent, and drop-casting, corresponding to a factor of 100 improvement of the mobility. The AFM results show that a constant MW of low-MW films are not due to variations in amount of in-plane π-stacking, and is most likely due to chain-length-dependent electronic properties and/or grain boundaries effects. Switching to low-MW P3HT improves the overall crystallinity and the intensity of in-plane π-stacking, but the mobility is more than a factor of 100 lower than high-MW P3HT. These counterintuitive results clearly show that the charge carrier mobility of conjugated polymers is coupled to several different aspects of the morphology. In the case of the low-MW films, the strong driving force for ordering creates grain boundaries that isolate the ordered regions from their neighbors. Whereas in high-MW films, the long chains can connect the small ordered regions and provide a clear pathway for charges to move through the film.
measured, evidence of p-doping. An order of magnitude increase in current density is also obtained at high bias, indicating reduction of the effective barrier at the contact. Nondoping in organic materials is a difficult challenge because of the relatively high energy of the lowest unoccupied molecular orbital of most materials of interest (electron affinity ~1.5–2.5 eV). Donors must have very low ionization energy and are nonvolatile and incompatible with the host materials and are used as efficient donors introduced through the decomposition of materials like LiF, CsF, or NaF. However, the alkali cation is mobile and diffuses through the organic layer. Furthermore, the small size of the alkali cation can result in a fairly tight bond between the host molecule, resulting in strong electron localization. Larger, less mobile donor are therefore being pursued. We review here work on pyronin B chloride co-vaporized with NTCDA. The energetics of this donor-acceptor pair, as well as the energetic and electronic properties of the alkali cation in the crown ether in principle reduces its diffusivity and increases its distance to the acceptor (host) molecule, allowing higher depletion within the electron. 1. J. Blochwitz et al., Organic Electron. 2, 97 (2001); X. Zhou et al., Appl. Phys. Lett., 78, 410 (2001) 2. W. Gao et al., Appl. Phys. Lett. 78, 4040 (2001); W. Gao et al., J. Appl. Phys. 94, 359 (2003)

2:00 PM 18.2 Charge Carrier Transport Studies of Organic Single Crystal Field-Effect Transistors using Nondestructive, Reversible Methods. Mang-mang (Miko) Lng, Alejandro L. Briones and Zhanen Bao; Chemical Engineering, Stanford University, Stanford, California.

Organic semiconductor single crystals are ideal systems for charge transport studies. However, due to their fragility it is challenging to fabricate and characterize these devices. In this talk, we report methods for fabricating single crystal field effect transistor fabrication and characterization, prompted by recent progress in this field (1). First, a simple and yet reliable method to study the correlation between charge carrier mobility and crystal orientation has been demonstrated. Both top and bottom contact device configurations have been realized. Our method would provide a quick, easy way of studying intrinsic electronic properties of a large spectrum of organic semiconductors. It is also known that the properties of the interface between organic semiconductors and either gate insulator or the source/drain electrodes have impact on device performance, as shown by recent experimental evidence (2). Therefore, a second method of direct investigation of the correlation between the mobility and the organic semiconductor-gate insulator interface morphology has been demonstrated. We examine the interfacial changes before and after device operation, with or without interfacial chemical surface treatment. Overall, our methods make it possible for facile characterizing organic single crystal devices.

2:15 PM 18.3 Interface Transitions in Polymeric Thin Film Transistors Studied Using Laminated Films. Michael Chabing1, Alberto Salles2, Yiliang Wu2, Ping Liu2, Beng Ong2, Martin Heeney3 and lain McCulloch2; 1Chemical Engineering, Stanford University, Stanford, California; 2Electronic Materials Laboratory, PARC, Palo Alto, California; 3Xerox Research Centre of Canada, Mississauga, Ontario, Canada.

One of the most important factors contributing to the performance of polymeric thin-film transistors (TFTs) is the nature of the interface between the semiconducting polymer and the gate dielectric. There has been much work studying the effects of chemical modification of dielectric layers on the performance of TFTs made with spin-coated semiconductor thin films. Interpretation of these studies is complicated by the fact that transport occurs within ~1 nm of the surface of the dielectric making structural analysis difficult. We will describe a simple method of fabrication that can be used to separate microstructural changes from effects such as the chemical structure of surface-modifying layers. We have fabricated supported films of conducting polymers, such as poly[5,5'-bis(3-dodecyl-2-thienyl)-2,2'-bithiophene] and poly(3-hexylthiophene), onto microfabricated coplanar electrodes structures to form TFTs. The effective field-effect mobilities of the films were identical (~0.03 cm2/Vs) if they were laminated onto either bare silicon dioxide dielectrics or ones coated with a self-assembled monolayer to form a hydrophobic coating. In contrast, spin-coated films on hydrophilic and hydrophobic surfaces have mobilities less of three orders of magnitude. These results directly demonstrate that the lower mobility obtained for semiconductor films spun on bare silicon dioxide is likely due to molecular ordering in the interfacial layer. We will discuss the details of the lamination process and the results obtained for different dielectric layers.

2:30 PM 18.4 Investigation of the Insulator-Metal Transition in Poly(3-hexylthiophene) Induced in Field-Effect Transistor. Daniel Moses, Anoop Singh, Guangming Wang and Alan J. Heeger; Physics, University of California, Santa Barbara, California.

We report on the temperature dependence of the channel conductance in a field-effect transistor (FET) fabricated with regioregular poly(3-hexylthiophene) (RR-P3HT). The conductance in both, pristine polymer as well as chemically doped polymers was measured at various gate voltages. It appears that the devices made of the chemically doped polymers exhibit larger mobility, apparently due to the higher compensation ratio. Comparing the FET channel conductance to the one deduced from two probe conductance measurements reveals the metallic electrode-polymer interface contact resistance at various temperatures. We will discuss the implications of our data to the insulator-metallic transition in RR-P3HT.

2:45 PM 18.5 Mechanical and Charge Transport Properties of Self-Assembled Organic Monolayers. Imma Rtena1, Jeong Y. Park2, Jeff Neaton2, Gerard Smith1, Alexander Liddle1, D. Frank Ogletree3 and Miquel Salmeron3; 1Materials and Surface Science, Lawrence Berkeley National Laboratory, Berkeley, California; 2University of California, Berkeley, Berkeley, California. Metal-molecule-metal junctions are useful devices for exploring the structural and electronic factors affecting electrical transport in molecules. In these junctions individual molecules or molecular assemblies are contacted by two metal electrodes. In applications where a number of molecules have to be addressed as an ensemble, control over intermolecular interactions would be very valuable. Since deformation of molecules would affect the self-assembly influencing their collective behavior and hence the electronic transport through them. We are interested in measuring and correlating electronic and mechanical properties of organic molecules. Traditionally electronic measurements have been conducted on molecular structures and nano-objects situated between metal electrodes with large aspect ratios which prevents any atomic scale (STM, AFM) characterization of the molecular geometries and the atomic structure (geometrical, electronic) at the junction. Therefore we need to employ state-of-the-art nanofabrication techniques to fabricate insulating test substrates with embedded coplanar metallic nanoelectrodes that will act as source and drain. 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. Our approach provides a unique way to control the quality and structure of the molecular films between the electrodes (< 1 nm) the molecules are accessible at the nanoscale to an STM/AFM tip and thus allows us to clarify the ambiguities of the unknown contact structure. An important aspect of our work is to show how electronic flow through organic molecules is important in several areas: rationalizing electron transfer in organic and biological molecules; fabricating molecular electronic devices, such as qSELs and also for developing molecular devices.

3:15 PM 18.6 Interface and Gate Bias Dependent Response of Sensing Organic Thin-Film Transistors. Maria Cristina Tanese1, Daniel Fine5, Ananth Dodabalapur3 and Luisa Torsi1; 1Chemistry, Universita di Bari, Bari, Italy; 2PRC/MER, University of Texas at Austin, Austin, Texas.

Organic thin-film transistors (OTFTs), when operated as multi-parameter responsive systems [1], can be a viable alternative to existing chemiresistor based systems. OTFTs are semiconducting organic/polymer based sensors that offer the advantage of a reproducible response repeatability and stability [2]. The response of the sensor, within 2%, for 20 subsequent exposure to the analyte because full device recovery can be achieved (operating the OTFTs at room temperature) by strategic use of the gate bias. Selectivity is being pursued by choosing ad hoc chemically or biologically functionalized semiconducting polymer active layers. This new technology can take also great advantage of the rapid developments occurring in the field of organic electronics where OTFTs have been integrated in complementary-metal-oxide-semiconductor (CMOS) circuits and in flexible plastic displays. Organic based CMOS circuits have been proposed also as sensing systems [3]. The rapid development of organic electronics along with the OTFTs combined with microfluidics, opens wide horizons for the use of OTFT in portable sensing systems or even in bio-chips. This work proposes a systematic study of OTFT responses dependence on important parameters such as the chemical nature of the semiconducting polymer layer, the gate-dielectric/organic-semiconductor interface and the analyte.
concentration. The effects of exposure of organic thin film transistors, comprising different organic semiconductors and gate dielectrics, to several analytes were investigated. The transistor sensors exhibited an increase or a decrease of the transient source-drain current in the presence of the analyte, most likely as a result of doping or of a trapping process of the organic active layer. The occurrence of these transient effects can also consist, depend on the transistor structure and the gate-electronic/organic-semiconductor interface and on the applied gate field. A weak dependence also on the analyte concentration has been observed. Evidences of a sizable response and probably also sensitivity enhancement for an OTFT are also produced. This result is significant for sensing applications as it indicates that an OTFT can exhibit a sensitivity higher than that achievable with the same organic semiconductor based on carbon-type sensors. [1-12] B. Crone, A. Dodabalapur, H. E. Katz, J. Appl. Phys., 91, 10410, 2002.

3:30 PM 18.7
Investigation of Annealing Effects and Film Thickness of Polymer Solar Cells. Gang Li, Vishal Shrotriya and Yang Yang; Materials Science and Engineering, University of California at Los Angeles, Los Angeles, California.

Regioregular poly-(3-hexylthiophene) (RR-P3HT) is one of promising candidates for polymer photovoltaic research due to its stability and absorption in red region. In this presentation, polymer photovoltaic devices based on synthesized [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) (1:1 weight ratio) were prepared. The device structure consists of ITO/PEDOT:PSS (30 nm)/RR-P3HT:PCBM/Ca (30 nm)/Al (100 nm). The effects of annealing temperature and time on the devices were characterized before and after cathode deposition. Thermal annealing shows significant improvements in the performance of both types of devices, with post-production annealing showing slightly better. In the devices with 43 nm active layer, maximum power conversion efficiency (PCE) of 3.1% and fill factor (FF) up to 67% was obtained under AM1.5, 100 mW/cm2 illumination. By keeping optimized thermal annealing condition and varying active layer thickness, devices with PCE up to 3.84% have been fabricated. We found that the organic/organic (O/A) and organic/inorganic (O/I) interfaces of the polymer layer exhibit a higher recombination level than the O/A interface. Solution-processing a second component with favorable enthalpic interactions does not give bilayer structures, but instead forms a composite with mesoscale order. We find substantial uptake of CdSe nanocrystals (with diameter in the range 2-3 nm), with a weight composition of up to 2% nanocrystal/polymer. These structures give distinct vertical pathways in each component, show lateral organisation on a length scale of 10-20 nm, and are therefore particularly suited for photovoltaic devices, since they provide the correct length scale for migration of photoexcited electrons to heterojunctions and very effective conduction pathways for electrons and holes to charge collection electrodes. Quantum efficiencies for charge collection of 80% are found. This combination of surface-tethered polymers and nanocrystals offers a general strategy for scalable processing of nanostructured composite films.

4:15 PM 18.9
Micro-Structural Effects on the Optical and Charge Transport Properties in Polylenses (9,9-diptylfluorene-co-Benzothiadiazole). Carrie L. Dougal, Jason J. Yuan, Hsin-Chun Wu, Andrea S. Greenblatt, Mariam M. Nielsen, John Seon Kim and Richard H. Friend; 1Department of Physics, University of Cambridge, Cambridge, United Kingdom; 2Risø National Laboratory, Roskilde, Denmark.

Spin-coated poly (9,9-diptylfluorene-co-benzothiadiazole) (F8BT) films of different molecular weights (Mn = 9K - 255K, The Dow Chemical Company) both in the pristine and annealed state have been studied in an effort to elucidate changes in the polymer micro-structure and the effects this structure has on the optical and charge transport properties of these films. A structural model was developed based on Raman spectroscopy, X-ray diffraction, atomic force microscopy, and optical microscopy under cross-polarizers, describing the restructuring of the polymer film as a function of polymer molecular weight and upon annealing. In pristine films the micro-structure is such that the BT units in neighboring chains are adjacent to one another. As the temperature is increased, the transition temperatures allows for a restructuring of the packing geometry into a lower energy configuration in which the BT units in one polymer chain are adjacent to the F8 units in a neighboring chain ("alternate structure") due to a decrease in the efficiency of interchain electron transport in this structure. In addition, interchain excitation migration to low energy weakly emissive states is also reduced for these "alternate structure" films, as observed in their luminescence spectra, resulting in higher luminescence efficiencies.

4:45 PM 18.111
Surface Structure of Conjugated Polymer Thin Films: The Measurement of Surface Dichroic Ratios by NEXAFS and their Correlation with Field-Effect Conduction Properties.
The structure (chain packing and orientation) of the top- and bottom-most layers of a semiconducting organic thin film is expected to exert a strong influence on the field-effect mobility of charge carriers. This film is used as the channel layer in the field-effect transistor. 

In this work, we report for the first time a fully encapsulated self-assembly (ESA) method. The results show critical information on backbone and side-chain orientation. This method is general and can be applied to other organic semiconductors. We found that the frontier structures of the polymer thin films are in fact different at the top and bottom surfaces, and these in turn are markedly altered depending on the quality of the deposition solvent. These results help rationalize the scatter in the measured field-effect mobilities from different laboratories, particularly as different solvents are used. We will also discuss the conclusions in relation to bulk field breakdown tests were performed at 1000 Hz, 15% relative humidity and varying temperatures and voltages. The test results showed that the dielectric constant values were between 1.8 and 2.4 and breakdown field values were 9 kV/cm. The test results, it is concluded that this is a technique that might prove useful the estimate the capacitance, dielectric constant and breakdown field values of nanocrystalline EAs films.

This paper reports on a new organic thin film transistor (OTFT) based on a dual-gate configuration. This dual-gate OTFT lends itself as a highly functional test structure for characterization of density of states at the interfaces of the active organic and dielectric layers. In addition, it is useful in circuits from the standpoint of providing control over the threshold voltage as well as to shield parasitic effects in vertically integrated backplanes. The device is fabricated using poly(3-hexylthiophene) (P3HT) as the organic semiconductor layer. The bottom-gate employs silicon dioxide (SiO$_2$) as the gate dielectric, whereas the top-gate employs amorphous silicon nitride (Si$_3$N$_4$) as the gate dielectric. This design provides a means of characterizing the density of states of the bottom P3HT/SiO$_2$ and top P3HT/Si$_3$N$_4$ interfaces, to evaluate the interface integrity and provide insight into the underlying transport mechanism. The bias on the bottom-gate has a distinct influence on the threshold voltage, subthreshold slope, on-current, and leakage current of the top-gate TFT. Similar dependence of the bottom-gate TFT characteristics on the top-gate bias is observed. The ability to control selected TFT parameters (e.g., threshold voltage) using the dual-gate OTFT structure is attractive for circuit integration applications in active-matrix displays and imagers.
should be carried out for good interface stability), polymer spin coating, and preparation of device quality a-SiN films by 75°C PECVD.

10.5 The Effect of Gate Dielectric Surface Energy on Pentacene Morphology and OTFT Characteristics

Kwonoo Shin and Chan Eon Park; Polymer Research Institute, Chemical Engineering, Pohang University of Science and Technology, Pohang, Gyeongbuk, South Korea.

The effects of surface energy of polymer gate dielectrics on pentacene morphology and the electrical properties of pentacene field-effect transistors (FETs) are reported using surface energy controllable poly(methoxy-siloxane) as gate dielectric layers. The surface energy of gate dielectrics strongly influences the pentacene film morphology and growth mode, producing layer-by-layer growth with large and dendritic grains at high surface energy and 3D island growth with small grains at low surface energy. In spite of the small grains (<300 nm) and decreased ordering of pentacene molecules vertical to the film, the high surface energy dielectric FETs are larger by a factor of about 5 compared to their high surface energy counter parts. In pentacene growth on the low surface energy dielectric, interconnection between grains is observed and gradual lateral growth of grains causes the vacant space between grains to be filled. Hence, the larger mobility of low surface energy gate dielectric FETs can be achieved by interconnection and tight packing between pentacene grains. On the other hand, the high surface energy dielectric forms the first pentacene layer with some voids and then successive incomplete layers over the first which can limit the carrier movement in the lower carrier mobility in spite of the formation of large grains (~1.3 μm).

10.6 Dielectrics for Organic Transistors with Low Threshold Voltage. Jochen Brill; Silke Goettling and Eduardo Margallo; Chair of Display Technology, University of Stuttgart, Stuttgart, Germany.

To achieve a large transistor current, the mobility and the gate capacity should be large, the threshold voltage low enough. The capacity is determined by the thickness of the dielectric layer and its dielectric constant. As these parameters can be influenced by the choice of materials and processing, inorganic and organic dielectrics have been examined. In the table the materials are listed. Only anodic oxidation can overcome the difficulty of the thermal budget completely. The schematic principle will be explained. The role of the electrolyte is to provide oxidizing anions and the conduction of the electric current. Usually aqueous solutions with salts are used. The ions resulting of the salts are too large to migrate through the oxide. But once the process takes place at the surface of the oxide, a reaction between the metal ions and these characteristic ions might occur and they are integrated into the oxide and defining its later properties. This might result in carrier traps and increased leakage currents. To avoid this effect we investigated dielectrics like hydrogen peroxide 30% H2O2 (AI and Ta). Aq. sol. with 0.01% citric acid (Ta), Ethylene glycol sol. with NH4BSO8 (AI) From Kiesiog interferees (x-ray diffraction) the film thickness was calculated and roughness evaluated. Also it was found by atomic force microscopy that the roughness is lowered by 35%. The results clearly favor H2O2. For electrical characterization capacitors were built. Results will be shown and leakage currents and breakdown will be evaluated. Substrates with different insulators were coated with pentacene and the surface was observed with an AFM. Only on SiO2 and on PI large grains can be found. This results were confirmed by x-ray diffraction.

Unfortunately the excellent texture of the pentacene on PI could not be realized in transistor structures. It was found, that the deposition of the gold contacts and their photolithographic structuring influenced the surface in a disadvantage way. Therefore the anodic oxidized dielectrics are favored to build transistor devices. For this we use a standard bottom contact structure. For the drain and source contacts gold was used, deposited by sputtering. Directly after deposition of purified pentacene the characteristics were measured with a parameter analyzer. Input and output characteristics will be shown. For T2O5 mobilities in the range of 102 cm2/Vs and threshold voltages -4.8V could be achieved. VDS was -5V.


Recently, we have experimentally demonstrated a dual-gate organic thin film transistor (DG-OTFT) technology [1]. The devices are made by adding an insulator layer and a top gate (TG) electrode to a conventional bottom gate (BG) p-type transistor. The bottom gate (BG) is the electrically active layer, made of 50 nm thick pentacene, and the transistor is fabricated onto SiO2/Si substrates which served as the transistor gate electrode. Gold electrodes were deposited onto the PbPc layer through a shadow mask using electron-beam evaporation to form the source and drain contacts. The I-V characteristics of the PbPc OTFTs were measured using a HP 4155A semiconductor parameter analyzer in ambient air. The mobility of the PbPc TG strongly depends on the substrate temperature for deposition. When deposited onto octadecyltrithoxysilane-treated substrate at room temperature or lower, the mobility of the PbPc TG is less than 10-6 cm2/Vs. However, the mobility increases with increasing the substrate temperature. At temperature around 140 °C, the mobility becomes larger than 10-4 cm2/Vs. In addition, the mobility of the PbPc TG strongly depends on kinds of self-assembled monolayer (SAM) on the surface of SiO2 layer. Alkylsilane layers with different alkyl chain length on SiO2 were prepared. We investigated the effect of alkyl chain length of SAM on the PbPc OTFT performance. The mobility increased with increasing the alkyl chain length. The PbPc TG fabricated on tricetyltrichlorosilane-treated substrate have field-effect mobility larger than 0.1 cm2/Vs·s and current on/off ratio greater than 105. Furthermore, the mobility of the PbPc TG should be high in air, where it does not almost change after exposure to air more than three months.

10.8 High Performance and High Stability of Lead Phthalocyanine Thin-Film Transistors in Ambient Air. Hisomi Iwazumi1 and Yoshinori Tokura1,2,1Correlated Electron Research Center (CERC), AIST, Tsukuba, Japan; 2University of Tokyo, Tokyo, Japan.

Metal phthalocyanines (Pcs) are attractive materials for device applications in various fields such as optoelectronics for the design of field effect transistor (FET), organic light-emitting diode (OLED), gas sensors. The coordinate metals in Pcs are important factors for the optoelectronic properties. Copper phthalocyanine thin-film field-effect transistor (TFT) has been reported to show good performance with hole mobilities larger than 0.01 cm2/V·s and on/off current rations greater than 106. Among many Pc families, lead phthalocyanine (PbPc) with a shutterlike-shape structure, is the most promising candidate for practical applications, because it has a high flexibility and electronic properties such as one-dimensional conduction nature, electrical switching, and high sensitivity to gas. The properties depend on the film structures, because two phases, monoclinic phase and triclinic phase, exist in the crystal structures. In the monoclinic phase, lead atoms form a onedimensional chain with a relatively short interatomic distance. On the other hand, in the triclinic crystal phase the lead atoms are far from each other and the overlap of the neighboring PbPc molecules is small. We report here on the high performance and high stability of PbPc TFTs in ambient air. For the PbPc TFT fabrication, first PbPc layer was thermally evaporated onto SiO2/Si substrates which served as the transistors gate electrode. Gold electrodes were deposited onto the PbPc layer through a shadow mask using electron-beam evaporation to form the source and drain contacts. The I-V characteristics of the PbPc TFT were measured using a HP 4155A semiconductor parameter analyzer in ambient air. The mobility of the PbPc TG strongly depends on the substrate temperature for deposition. When deposited onto octadecyltrithoxysilane-treated substrate at room temperature or lower, the mobility of the PbPc TG is less than 10-6 cm2/Vs. However, the mobility increases with increasing the substrate temperature. At temperature around 140 °C, the mobility becomes larger than 10-4 cm2/Vs. In addition, the mobility of the PbPc TG strongly depends on kinds of self-assembled monolayer (SAM) on the surface of SiO2 layer. Alkylsilane layers with different alkyl chain length on SiO2 were prepared. We investigated the effect of alkyl chain length of SAM on the PbPc OTFT performance. The mobility increased with increasing the alkyl chain length. The PbPc TG fabricated on tricetyltrichlorosilane-treated substrate have field-effect mobility larger than 0.1 cm2/V·s·s and current on/off ratio greater than 105. Furthermore, the mobility of the PbPc TG should be high in air, where it does not almost change after exposure to air more than three months.
19.9 Flexible Pentacene/PMMa Thin-Film Transistors Fabricated on Aluminium Foil Substrates. Cristobal Voz, Istdro Martin, Albert Orgella, Michael Vetter and Ramon Alcubilla; Enginyeria Electronica, Universitat Politècnica Catalunya, Barcelona, Spain.

Pentacene thin-film transistors (TFT) were fabricated on aluminium foils using the polymer polyethylene molybdenum (PMMA) as a gate dielectric. Then, the aluminium substrate acts as a gate electrode itself. A bottom-gate TFT structure is used to study the influence of the dielectric and aluminium substrate on the device performance. Pentacene thin-films were deposited by thermal evaporation in high vacuum at deposition rates around 3 Ås⁻¹ and substrate temperatures below 100 °C. The maximum process temperature was 170 °C, corresponding to the baking of polyethylene molybdenum. The thickness of spin-cast PMMA layer was 700 nm, whereas pentacene films were 650 nm thick. The TFTs channel length and width were 120 and 800 nm, respectively. Devices show p-type characteristics with on/off ratios over 10⁴ for VGS ranging from -30 to +30 V. The field-effect mobility and threshold voltage were around 0.01 cm²V⁻¹s⁻¹ and -15 V, respectively. It is important to point out that these devices were off for zero-applied VGS voltages. X-ray diffraction measurements seem to indicate that pentacene molecules prefer growing more vertically on PMMA surface. This fact could be related to the methyl ending groups (CH₃) present on PMMA, which promote the growth of highly ordered pentacene layers [1, 2]. In addition, topographic images obtained by atomic force microscopy (AFM) reveal grain dimensions that reach sizes of a few hundred nanometers. As a summary, it could be concluded that the use of PMMA as a gate dielectric layer in pentacene TFTs have several advantages: (a) It can be deposited at low temperatures over large area by spin coating on expensive substrates (plastic, aluminium foil...), (b) the methyl ending groups improve the pentacene ordering like a SAM does; the structure, the substrate temperature on the structural and electrical properties of pentacene layers will be discussed in detail. [1] S.H. Jin, J.S. Yu, J.W. Kim, C.A. Lee, B.G. Park, J.D. Lee, J.H. Lee, Society for Information Display International Symposium (SID 2003), Baltimore, Maryland (USA). [2] J. Puigdollers, C. Voz, A. Orgella, R. Quidant, I. Martin, M. Vetter, R. Alcubilla, Organic Electronics 5(1-3), 67 (2004).

19.10 Evaluation of the Self-Assembly and Transistor Performance of a Soluble Oligothiophene Series. Amanda R. Murphy¹, Jean M. J. Fréchet⁵, Paul C. Chang⁶, Vivek Subramanian⁷ and Dean M. DeLongchamp³; ¹Chemistry, UC Berkeley, Berkeley, California; ²Electrical Engineering and Computer Science, UC Berkeley, Berkeley, California; ³Polymer Division, National Institute of Standards & Technology, Gaithersburg, Maryland.

A series of symmetrical a,w-substituted oligothiophenes with four to seven thiophene rings was synthesized using Stille cross-coupling methods. The oligomers contain solubilizing groups allowing them to be solution processable at room temperature. The solubilizing groups can then be removed by thermolysis in a post-processing step. Characterization of the bulk materials by UV-vis and thermogravimetric analysis is presented, as well as AFM and NEXAFS spectroscopic analysis of spin-cast films. The largest oligomers were found to self-assemble into crystalline terraces after thermolysis, resulting in high charge mobilities as measured in top-contact thin film transistors.

19.11 Room Temperature Deposition of TiO₂ Thin Films on PET(poly-ethylene teraphthalate) by using UV-enhanced Atomic Layer Deposition. Myung Mo Sung; Chemistry, Kookmin University, Seoul, South Korea.

We have deposited titanium dioxide thin films on PET(poly-ethylene teraphthalate) substrates at room temperature by UV-enhanced atomic layer deposition using titanium(IV) iso-propoxide and water. The atomic layer deposition relies on alternate pulsing of the precursors gases onto the substrate surface and subsequent cheluisorption of the precursors. In many cases, the surface reactions of the atomic layer deposition are not completed at low temperature. In this experiment, the surface reactions of the atomic layer deposition of the TiO₂ thin films were enhanced by using UV irradiation at room temperature. The structure, chemical composition, morphology and thickness of the TiO₂ thin films were investigated by XRD, XPS, AFM, UV and Ellipsometry.

19.12 Effective Integration of Organic Light-Emitting Diode and Organic Transistor. Chih Wei Chu; Material Science and Engineering, University of California, Los Angeles, Los Angeles, California.

Flexible Pentacene/PMMa Thin-Film Transistors Fabricated on Aluminium Foil Substrates. Cristobal Voz, Istdro Martin, Albert Orgella, Michael Vetter and Ramon Alcubilla; Enginyeria Electronica, Universitat Politècnica Catalunya, Barcelona, Spain.

High performance organic active matrix pixel is fabricated by using a metal oxide (VO25) coupling unit, which effectively integrates the organic light-emitting diode (OLED) on top of organic field effect transistor (OFET). The field effect mobility of the OFET approaches 0.1 to 0.5 square centimeters per volt second and ON/OFF current ratio >10⁶. The brightness of the OLED is on the order of 3,000 cd/m², with an efficiency above 3.3 cd/A. The present work describes in detail a unique methodology for sizing and stacking OFET in bottom-emitting active matrix pixel circuits. The confinement of pixel dimension ensures the uniformity of light emission. Results presented allow selection of the coupling material for maximizing device efficiency. The unique active matrix pixel circuit is proposed which renders both the OFET and OLED their individual performance after integration.

19.13 Optical Interference as a Tool to Describe the Spectral Changes Created by a Tunable and Controllable Excitons. Feng Christophel, Dragic Valter, Geffry Bernard, Denis Christine and Maise Pascau, ¹Thomson R&D, Cesson-Sevigne, France; ²Laboratoire Cellules et Composants, CEA Saclay, Gif sur Yvette, France.

It has been demonstrated that optical interference effects can dramatically modify the emission’s properties of Organic Light Emitting Diode (OLED). However, few comprehensive comparisons between the theoretical predictions and the experimental data are currently available. This kind of study allows us to distinguish between the optical phenomenon and the intrinsic QE, and can be a very useful tool in order to optimize and tailor the external light output of an OLED structure. In order to test our optical model, we have realized a series of samples where the excitons can be confined to a well defined region at the Alq3-NPB interface. The thickness of this region, and therefore the intensity of excitons confined and controlled by interferences, results from the presence of a thin hole-blocking layer (BAP) deposited at a fixed distance from the Alq3-NPB interface. The interference mechanisms become unquestionably evidenced when looking at a series of samples where the exciton thickness was varied from 60 nm up to 180 nm. We show that excitons confinement can produce dramatic spectral changes when tuning the optical cavity. These results are in excellent agreement with the predictions generated by our optical modeling. Furthermore, we show that in this simple excitons confined structure, all variations in external QE observed when tuning the optical cavity can be ascribed solely to interference effects. Removing the excitons confinement by removing the BAP layer shows a totally different change in emission spectra when tuning the optical cavity. This result can be explained in terms of variation of the excitons recombination profile. Finally, we will show that we can successfully apply our model to our latest high efficiency and low driving voltage OLED structures, employing n and p doped charge transport layers.


Highly conductive and transparent CdO thin films have been grown on glass and on single-crystal MgO(100) by MOVD at 400 °C, and were used as transparent anodes for fabricating organic-light-emitting diodes (OLEDs). Device response and application potential have been investigated and compared with those of control devices based on commercial ITO anodes. It is demonstrated that highly conductive CdO thin films of proper morphology can efficiently inject holes into such devices, rendering them promising anode materials for OLEDs. Importantly, this work also suggests the feasibility of employing other CdO-based TCOs as anodes for high performance OLEDs.

19.15 Effcient and Stable Organic Light-Emitting Diodes using Carbon Nanotube-Surfactant Layer at Metal-Organic Interface. Sumit Chaudhary¹, Krishna Veer Singh³ and Mihrinlah Ozkur¹,²; ¹Electrical Engineering, UC Riverside, Riverside, California; ²Chemical and Environmental Engineering, UC Riverside, Riverside, California.

Organic Light-Emitting Diodes (OLEDs) are in dire need of simple metal-organic interfacial solutions to reduce quenching, increase electron-injection and improve air-stability of these devices. Here, we demonstrate an OLED with carbon nanotube-surfactant (CNT-S)layer at the aluminium cathode-organic polymer interface. The CNT-S layer was spin-coated from aqueous solution. Our devices showed turn-on voltage of 2-3 Volts, compared to 12 Volts in the control device without the CNT-S layer. The external quantum yield and air-stability of the
devices also showed promising improvement. This was probably due to encapsulating nature of CNT-S film and better adhesion between metal and organic species owing to the amphoteric nature of the film.

19.16
Single-Walled Carbon Nanotube Composites as Hole Injection Layer for Organic Light Emitting Diode Applications. Ching Ching Oey1, Aleksandra B. Djurisic2, Chung Yin Kwong3, Chi Hang Cheung2, Po Ching Widmann-Loi2, Seok Jong Lee2 and Jong-In Hong2

Since the discovery of carbon nanotubes in 1991, they have gained much attention in both scientific and commercial community because of their unique nanostructures with improved electrical and mechanical behaviour. In the same time, there has been great interest in using organic and polymeric materials in electronic devices such as organic light emitting diodes (OLEDs) and photovoltaic cells due to their low cost, ease of fabrication and other advantageous properties over inorganic materials. As a result, it is of interest to study the incorporation of carbon nanotubes in polymer matrix for device applications. In this work, blend of dispersed short (~500nm) single-walled carbon nanotubes (SWCNTs) with polyc(3,4-ethylenedioxythiophene):poly(styrene sulfonic acid) (PEDOT:PSS) were investigated as radiation layers in OLEDs consisting of N,N’-di(naphthalene-1-yl)-N,N’-diphenylbenzidine (NPB) as a hole transporting and tris-(8-hydroxyquinoline) aluminum (Alq3) as electron transporting and emitting layers. The devices were characterized by electroluminescence and current-voltage measurements. By comparing the performance of devices fabricated using different surfactants (polystyreneimine (PEI) and Gum Arabic (GA)) in dispersing SWCNTs and those prepared without surfactants, it was found that the use of appropriate surfactants can improve the OLED performance. Improved efficiency was achieved for optimized SWCNTs concentration compared to the devices with pure PEDOT:PSS, although maximum luminance is lower. PEDOT:PSS:SWCNT nanocomposite layers are characterized and the reasons for the improved OLED performance are discussed.

19.17
Syntheses of White-Light-Emitting PAl-Conjugated Polymers and their Application to OLEDs. Junji Kido, Masataki Iwasaki, Takayuki Ito and Hisa-Ling Lan; Polymer Science and Engineering, Yamagata University, Yamagata, Japan.

Copolymers consisting of blue-emitting 9,9-dioctylfluorene units (PF) and orange-emitting units, 2,6-bis(2-phenylvinyl)pyridyl-4,7-diphenyl-1,10-phenanthroline (BCP), were prepared using the Suzuki coupling method. The BPPM contents of the copolymers varied from 0.2 to 1.0 percent. All the copolymers exhibited blue electron transporting and emitting layer. The devices were characterized by electroluminescence and current-voltage measurements. Improved efficiency was obtained for optimized BPPM contents of the copolymers were varied. The emission mechanisms are understood. We were interested in developing blue phosphorescent materials by changing the structure of the ancillary ligand. In this work, the core and valence levels of poly (p-phenylenevinylene) (PPV) based oligomers and polymers have been studied with X-Ray Photoelectron Spectroscopy of Organic Polymer/Metal Interfaces For OLEDs. Subramanian Vaidyanathan, Mary Galvin and Robert L. Opila; Department of Materials Science & Engineering, University of Delaware, Newark, Delaware.

In this work, the core and valence levels of poly (p-phenylenevinylene) (PPV) based oligomers and polymers have been studied with X-Ray Photoelectron Spectroscopy (XPS) and Synchrotron Ultraviolet Photoelectron Spectroscopy (UPS). From UPS results, the valence bands of these PPV based polymers with respect to the Fermi level of different metal substrates have been investigated. By comparing oxadiazole-containing PPV based polymers, the gap between the valence band and Fermi level was found to increase with increasing oxadiazole content. The interface formation between poly (2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene) (MEH-PPV) and deposited Al has been studied by XPS and UPS. The results show that the deposited Al electrode chemically reacts with MEH-PPV, modifying the structure of the conjugated polymer. Angle resolved XPS and XPS depth profile analysis showed that at the initial stages of the Al deposition, Al oxidizes forming an insulating layer between the metal and the MEH-PPV. A band bending of about 0.5 eV at the interface of Al and the MEH-PPV has also been measured. The results lead to a better understanding of the polymer/metal interfaces, which is crucial to designing higher efficiency organic electronic devices.

19.22
Modified HOST Materials having Higher Energy Band Gap in Organic Light Emitting Diodes (OLEDs): Synthesis of CBP Derivatives through the Birchwald Reaction. Hye-Hok Ahn, Su-Soon Cho1, Myoung Ki Kim2, Kwan Hee Lee2, Su Jin Park2 and Jong-In Hong1; School of Chemistry, Seoul National University, Seoul, South Korea; 2Corporate R&D Center, Samsung SDI, Seoul, South Korea.

A fluorene-containing arylamine (DFPA) was synthesized, which can be spun-casted to form amorphous films and can be evaporated in the vacuum. Various kinds of OLEDs using DFPA were fabricated. One of the OLEDs with a DFPA doped with Sb compound, TBP/AH, as a hole-injection layer and a conventional arylamine, NPD, as a hole-transport layer, aluminum complex, Alq, as an emission layer, exhibited a high luminous efficiency of 2.3 lm/W. Charge injection characteristics of DFPA was also investigated and found to be different for the spin-casted film and the vacuum deposited film. The details are reported.

19.20
Tuning the Emission Wavelength of Heteroleptic Iridium Complexes by Varying the pKa of the Ancillary Ligands. Seok Jong Lee1, Myoung Ki Kim2, Joon Yul Park2, Dung Hyun Jung2, Seok Jong Lee2 and Jong-In Hong2; School of Chemistry, Seoul National University, Seoul, South Korea; 2Corporate R&D Center, Samsung SDI, Seoul, South Korea.

In OLED displays, blue phosphorescent materials still remain elusive because their color index and efficiency have not been fully optimized. Color tuning through the modification of the main ligand on iridium (III) complexes has been extensively studied. However, the effect of the ancillary ligand on the emission wavelength have not been fully understood. We were interested in developing blue phosphorescent materials by changing the structure of the ancillary ligand. In this work, we report synthesis, characterization, PL data, and EL data of a series of iridium complexes with various ancillary ligands. In order to understand the effect of the ancillary ligand on the emission wavelength of iridium complexes, we used various ancillary ligands derived from N-containing heterocyclic carboxylic acids such as isouquinolinocarboxylic acid, pyrazolecarboxylic acid, and oxazolocarboxylic acid. Emission wavelength of the iridium complexes seems to well correlate with the pKa values of the ancillary ligands, which was further supported by extensive DFT calculations.
Much interest is currently devoted to organic light-emitting diodes (OLEDs) for flat panel display. Phosphorescent materials as dopants have been used because internal quantum efficiency in devices can potentially reach 100%. Design of suitable host materials for the use in phosphorescent light-emitting devices is a challenging task because the triplet energy of host materials should be larger than that of phosphorescent dopants but not greatly exceed the triplet energy of the guest. To address the above issues, we designed new host materials with higher energy band gap by the modification of known carbazole derivatives by DFT calculations and synthesized them via Buchwald nitrene insertion reactions. Time-of-flight (TOF) technique, the ROT compounds were found to be ambipolar with competitive hole injection mobilities of about 10^-5 cm^2/Vs at room temperature under the electric field of 0.5 MV/cm. The frontier orbitals were examined computationally by an initial method. It was found that the highest occupied molecular orbital (HOMO) is localized on the phenylene moiety and is essentially fixed, whereas the lowest unoccupied molecular orbital (LUMO) is localized on the aromatic ring, and its position can be tuned by varying the size of the fused ring. Organic light-emitting diodes (OLEDs) were fabricated with a structure ITO/CuPc/ROT/Ca. Due to the ambipolar character of the ROT layer, both charge transport and EL took place within the same layer. The EL spectrum of the ROT device from 440-520 nm. The EL intensity and lifetime reaches 7500 cd/m², and the current efficiency ~2 cd/A. ROT materials can be used to fabricate efficient homojunction OLEDs with a very simple architecture.

19.27 High-Efficiency OLEDs using Hole-Injection Layer Consisting of Arylamine Doped with TCNQ Derivative.

Kuo-Lung Tsai, Cing-Tao Hsu, Jen Lin Lin, and Jun Li; Polytechnic Science and Engineering, Yonagawa University, Yonagawa, Japan.

Organic LEDs having triphenylene tetramer (TPT) doped with hexacyanoquinonodimethane (CN2-TCNQ) as a hole injection layer were fabricated by vacuum deposition. The OLED structure was ITO/TPT doped with CN2-TCNQ/NPD/Au/Al/LiF/Al. The drive voltages are lower than that of the OLED without the doped layer and the maximum luminous efficiency of 3.9 lm/W was observed. Due to the low resistivity of the doped layer, the thickness can be as thick as 120 nm. Charge injection and transport characteristics of doped and undoped TPT layer were also investigated and the details are reported.

19.28 Transverse Electrical Transport in Pentacene Photodiodes.

Cristobal Voz, Joaquim Puigdollers, Isidro Martin, Albert Orpella, Michael Vetter, Francisco Fabregat, Germa Garcia, Juan Bisquert, and Ramon Alcubilla.

Organic devices could be competitive for applications requiring low temperature processing compatible with inexpensive flexible or weightless substrates. In particular, conjugated polymers, oligomers and small molecules have attracted great attention last years. Among them, pentacene has performed exceptionally well in organic thin film transistors [1]. Thus, electrical transport mechanisms and the interface to the substrate have been intensively studied. However, although pentacene has evidenced significant photovoltaic conversion, very few applications in optoelectronic devices have been reported [2]. Besides, optical absorption and transverse electrical transport mechanisms are not completely understood. In this work, pentacene thin films are obtained by thermal evaporation at moderate substrate temperatures (<100 °C). X-ray diffraction measurements reveal that as deposited pentacene films are highly ordered with triclinic crystallographic structure. A detailed study of the optical absorption in pentacene thin films is presented, including optical transmission and photothermal deflection spectroscopy measurements. The absorption edge around 1.8 eV makes pentacene suitable for photovoltaic applications. Absorption peaks located at 1.97, 2.3 and 2.5 eV corresponding to singlet states of pentacene molecular orbital levels were clearly distinguished. Other observed peaks at 1.86 and 2.13 eV were related to Frenkel excitons with binding energies 0.11 and 0.17 eV respectively. In addition, organic photodiodes were fabricated by evaporating pentacene films on indium-tin-oxide, a transparent high work function electrode acting as anode. Low work function aluminium contacts evaporated on top are the cathode of these photodiodes. Thicknesses for the indium-tin-oxide, pentacene and aluminium layers were 250, 840 and 100 nm in that order. Dark current-voltage characteristics evidence forward/reverse ratios over 10^2 for applied voltages ranging from -5 to +5 V. Different forward regimes are observed, including ohmic, space-charge limited current and trap filled limit. The trap density calculated in the trap filled limit region is about 1.3 X 10^12 cm^-2. On the other hand, quantum efficiency curves show a broad response band related to direct photogeneration of free carriers, but also clear antibonding features which evidence transverse excition transport mechanisms. Results can be interpreted considering that exciton dissociation occurs mainly at pentacene/electrode interfaces. Finally, the time of flight in indium-tin-oxide/pentacene/gold structures was measured to determine the transverse carrier mobility. Preliminary results will be discussed.


19.29 Photovoltaic Cells Based on Multilayers of Ionic Poly(p-phenylene ethynylene)s and a Water-Soluble Fulleren Derivative. Jeremiah Meyers, Mauricio Pinto, Nisha Anandakhel, David Wirtz, Kirk S. Schranz and John R. Reynolds; Chemistry, Center for Macromolecular Science and
We describe the layer-by-layer (LbL) fabrication of multilayer films and photovoltaic (PV) cells using poly(phenylene ethynylene) based anionic conjugated polyelectrolytes as electron donors and a water-soluble cadmium fullerene (CdSe) derivative as acceptor. LBL film deposition was used to linearly relate the number of layers as monitored by UV-Vis absorption. Atomic force microscopy (AFM) and scanning electron microscopy (SEM) of the multilayer films revealed an aggregated, but relatively uniform morphology. The incident monochromatic illumination to achieve current conversion efficiency (ICE) of the PV-cells ranged between 10-12%. The thin film PV-cells do not provide complete absorption of the incident light and therefore the current generation per photon captured should be above 20%. The highest efficiency reported to date using the LbL fabrication technique. The cells exhibited open circuit voltages of 200-250 mV with the highest measured short circuit currents of up to 0.5 mA/cm². The power conversion efficiencies measured at AM1.5 solar conditions (100 mW/cm²) were as high as 0.04% for the best performing cells and similar to the ICE results, the efficiency is a function of the thickness of the PV active layer.

19.30 Electrical Properties of ITO/CdSe/P30T/Au Heterojunction. Osvaldo Hilario Salinas1, Cecilia Lopez-Mata1, Haolin Hu1, Ma. Elena Niche-Diaz2 and Oscar Gomez-Duaz1, 1Solar Materials, CIE-UNAM, Temixco, Morelos, Mexico; 2CICIAp - UAEM, Cuernavaca, Morelos, Mexico.

Conducting polymer based heterojunctions have been intensively studied because of their prominent application in photovoltaic solar cells. It is reported in this work the formation of heterojunctions of cadmium selenide (CdSe) with poly(3octylthiophene) (P30T) by casting a chemically synthesized P30T solution onto screen printed CdSe coatings. The CdSe coatings were obtained by oxidation polymerization of poly(3octylthiophene) with FeCl3 as a catalyst. The obtained product was in intrinsic or undoped form and can be dissolved in a common organic solvent such as chloroform or toluene. Screen printed CdSe coatings on conducting glass substrates (ITO) were prepared and annealed. Then by drop-casting the polymeric solution, either undoped or doped P30T were deposited on top of the CdSe coatings. Since the screen printed coatings are quite porous, the solution of P30T was rapidly absorbed by the inorganic one. By using ITO as back contact and the gold film as metal contact, the electrical properties of the heterojunctions of CdSe/P30T were studied at room temperature under ambient conditions. The curves of current density vs. applied potential of a screen printed CdSe coatings indicate that the contact is quasi ohmic. When the inorganic semiconductor forms a heterojunction with a doped P30T, which represents a 10 wt% in the junction, the electrical behavior becomes more rectifying at a potential value of 1 V, the current density of the heterojunction shows about 50% less than that of the single CdSe coating. When the percentage of the polymer in the heterojunction is increased up to 20 wt%, this exhibits a rectifying factor of one order of magnitude at 1 V of applied potential. In the same time, a major concentration of P30T also reduces notably the forward current of the junction. The rectifying behavior should be related with the heterojunction because both ITO/P30T and Au/P30T form ohmic contacts.

19.31 Photovoltaic Devices Based on a Donor/Sensitizer/Acceptor Architecture Utilizing Phthalocyanine Cyanide and Layer-By-Layer Electrostatic Deposition. Susan E. Bailey, Kristin L. Mutolo and Mark E. Thompson; Department of Chemistry, University of Southern California, Los Angeles, California.

Layer-by-Layer (LbL) electrostatic deposition of thin films is being investigated for use in organic photovoltaic devices. The LbL technique utilizes the self-limiting deposition of alternating layers of oppositely charged polymers. In this way multilayer films are constructed with controlled placement of function. Poly (p-xyleneetetrahydrothiophenium chloride) is co-deposited with poly(styrenesulfonate). The pair can be thermally converted to produce self-doped conjugated poly(p-xylene(diyleneylene)). Poly (butylenevinylether) dibromide is a polycationic salt that is used as the electron conducting layer. Copper (I) phthalocyanine-tetrasulfonic acid is used in increase photon absorption in the photovoltaic devices. Deposition conditions were investigated to build smooth films of a desired thickness or optical absorbance. Absorption is used to characterize the optical properties of the films. Thickness and surface roughness are investigated by ellipsometry and Atomic Force Microscopy (AFM). The films were built on ITO coated glass. The donor/sensitizer/acceptor device architecture was constructed using the LbL technique. The thickness of each component was controlled by the number of layers and the composition of the multilayer could be changed by polyelectrolyte in alternate layers. Devices were constructed with a salt methyl viologen mediator between the thin film coated ITO and a gold counter electrode. IV curves and the photo-response of devices give insight into problems and possible areas for future improvement.

19.32 Interface and Bulk Contributions of Metal/Polyaniline/Metal Structures. Rodrigo Fernando Bianchi1, 2, Helder Nunes da Cunha3, 4, Guillerme Fontes Leal Fernandez1 and Joao Mariz Guimaraes Neto3; 1Departamento de Fisica y Ciencia de los Materiales, University of Sao Paulo, Sao Carlos, Sao Paulo, Brazil; 2Departamento de Engenharia de Sistemas Eletronicos, Escola Politecnica, Sao Paulo, Sao Paulo, Brazil; 3Departamento de Fisica, Universidade Federal do Piaui, Teresina, Piaui, Brazil.

Current vs. voltage and complex impedance measurements of polyaniline (PANI) films were carried out in samples with different doping levels and Au and/or Al as electrode. The complex impedance of Au/PANI/Au films presents the typical behavior of a solid material with negligible electrode influence. DC measurements confirm these evidences. However, some additional influence of the interface was observed when Au was used as electrode. A phenomenological model employing the the Cole-Cole dielectric function for generating the conduction process is developed and the calculated both the real and imaginary components of the complex impedance as a function of the polymer doping level, bias polarisation and temperature are found to be in good agreement with experimental data. From the three experimental fittings were able to separate the bulk and the interface contributions to the complex impedance, as well as the evaluation of the PANI/Au interfaces thickness and resistivity. The experimental fittings are for 10 nm and 1013 Ohm, respectively. Papeep and MCT/IMM from Brazil sponsored this work.


A series of meso-meso ethyne-bridged (porphirinato)zinc(II) oligomers have been synthesized from dimer to oligomers. The electronic absorption spectra of these species feature S0 → S1 transitions that progressively red-shift (800-870nm) and increase dramatically in oscillator strength with increasing oligomer length, indicating polaron delocalization lengths that span the molecular length scales of these structures (20-75 Å). Bulk-phase resistivity measurements have been carried out for derivatives of these structures that bear a wide range of solubilizing groups via 2- and 4-point probe experimental methods. Charge transport properties are shown to be sensitive to the nature of oligomer peripheral substitution: for example, the resistivities measured for undoped oligomers can vary over 2-5 orders of magnitude bridging the gap between insulator and semiconductor (10^{11}-10^{-6} Ohm cm) for a given conjugation length. These changes in resistivity correlate with the nature of oligomer-oligomer intermolecular interactions made possible in the bulk phase.

19.34 Programmable Conductance Switching and Negative Differential Resistance in Nanoscale Organic Films. Troy Graves-Abe1, 2 and J. C. Sturm2; 1PRISM, Princeton University, Princeton, New Jersey; 2Department of Electrical Engineering, Princeton University, Princeton, New Jersey.

In this work, we report programmable switching in self-assembled multilayer organic devices. The devices consisted of self-assembled multilayers of the molecule 11-mercaptoundecanoic acid (MUA) contacted by gold electrodes. They showed programmable conductance switching or negative differential resistance, depending on the frequency region that was studied. Devices were fabricated by depositing a thin film of Au onto a Si substrate by thermal evaporation (with a 5-nm Ti layer for adhesion). Multiple self-assembled layers of MUA were grown on the Au film by alternate immersions in millimolar ethanol solutions of MUA and Cu(CIO4)_2, resulting in repeated bi-layers of MUA and Cu [1]. Following the growth of 7-8 layers of MUA (total thickness 11-13 nm), patterned layers of silicon oxide (SiO_x) (70 nm) and Au (30 nm) were deposited on the MUA by evaporation through shadow masks. The resulting
devices had active areas (defined by regions where the two gold layers overlapped with no SiOx present) of 50 to 300 μm². Low-frequency current-voltage characteristics (with applied voltage) showed a strong, symmetric negative differential resistance (NDR). Peak current occurred around 3 V with current densities up to 10⁴ A/cm². The NDR peak was reproducible over multiple scans, although some hysteresis was observed and peak current varied for different scans on the same device. Peak-to-valley ratios of 5:1 were typical, but ratios as high as 30:1 were measured. At higher measurement speeds (>100 V/s), the negative differential resistance peak was more reproducible, but the devices showed ionization effects and current collapse would be varied by up to a factor of 10² by applying short (<1 ms) voltage pulses. High voltages (>4 V) set the device in an insulating state, while lower-voltage (2-4 V) pulses programmed the device into a conducting state. The negative voltage pulse can remove the stored space charge and could be used to read the programmed state. Programmed states remained stable for several days, and the device could be programmed between high and low states many times without degradation in electrical characteristics have been observed previously, primarily in electroformed inorganic insulating films [2]. Other observations of bistable switching in organic devices [2] have been attributed to stored charge [4]. We will present evidence that for the system formation and destruction of conducting filaments is more appropriate. [1] S.D. Evans et al., J. Am. Chem. Soc. 131 5866 (1999). [2] A.K. Ray and C.A. Hogarth, Int. J. Electron. 57 1 (1984). [3] L. P. Ma, J. Liu, and X. Yang, App. Phys. Lett. 80 2979 (2002). [4] L. P. Ma et al., App. Phys. Lett. 82 1419 (2003); L. D. Bozanci et al., App. Phys. Lett. 84 607 (2004). [5] G. Dearnaley, A. M. Stoneham, and D. V. Morgan, Rep. Prog. Phys. 33 1129 (1970).

19.35 Memory Effect in the Current-Voltage Characteristics of Diodes based on PEDOT-PSS. Yu Liu, Fengliang Xue, Yi Su and Kody Varahramyan, Institute for Micromanufacturing, Louisiana Tech University, Ruston, Louisiana.

Polyethylene dioxythiophene doped with poly styrene sulfonate (PEDOT-PSS) is an air-stable, solution-processable, and commercially available conducting polymer. Its electrical properties have been intensively studied for electronic applications such as organic light emission diodes [1], organic solar cells [2], and thin film transistors [3]. Recently, we have developed a new method of memory devices were developed using PEDOT-PSS as a fuse material [4]. In this paper, we demonstrate a reversible memory effect of the diodes based on PEDOT-PSS. Diodes were formed by interdigitating a thin film of PEDOT-PSS between aluminum and heavily doped silicon. Both p-type and n-type Si substrates are used. Hysteresis loops were observed in their current-voltage (I-V) characteristics. Information can be written by applying a voltage pulse to aluminum electrode. The information of the device can be read out from the current under a small read voltage (0.3-0.6 V, to Al electrode). Applying ±1 V induces a "low" conductance state while applying ±1 V switches the device back to the "high" conductance state. The charge difference between two states is up to 3 orders of magnitude. The switching behavior of diodes using p-type Si as bottom electrodes is compared with that of diodes using n-type Si. The shapes of their I-V curves are very similar, suggesting that the effect of electrode and charge mobility is not significant. Therefore, the space charge storage in the polymer is believed to be responsible for the memory effect. Upon positive voltage pulse the charges are injected into the charge storage centers (traps) near the PEDOT-PSS interface. The charges are stored there, and will later reset under current injection, resulting in the "low" conductance state. The negative voltage pulse can remove the stored charges and recover the device back to "high" conductive state. Reference [1] C. C. Huang, H. P. Meng, and G. K. Ho et al., Applied Physics Letters, 84, 1105-1107 (2004). [2] S. E. Shaheen, R. Radspinner, and N. Poyghambarian et al., Applied Physics Letters, 79, 2996-2998 (2001). [3] J. Lu, I. N. Pinto, and A. G. MacDiarmid, Journal of Applied Physics, 52, 6033-6037, 9, C. Perlov, W. Jackson, C. Taussig and S. R. Forrest, Nature, 426, 168-169 (2003).

19.36 Charge Mobility Engineering of Organic Co-Host using Triphenylamine- and Rubrene-Mixed Alloy. H. H. Kong 1,2 and S. K. So 1,2 1Physics, Hong Kong Baptist University, Hong Kong 2Centre for Advanced Luminescence Materials, Hong Kong Baptist University, Hong Kong, Hong Kong.

Organic co-host system has been employed into doped organic light-emitting diodes (OLEDs) for improving the luminescence efficiency and the device stability. Recent research on the co-host OLED (e.g. Alq3 : polycyclic aromatic hydrocarbon-based transporter) show that mixing the organic host transporters not only alter the charge recombination process but also the luminescence efficiency and the device conductivity. Critically, the host composition determines the function of the co-host layer. Mobility evaluation is an invaluable tool to elaborate the electrical conduction of this organic alloy system. In typical N,N,N',N'-tetradodecyl-1,1'-bibiphenyl-4,4'-diamine (TDDBP) and N,N,N',N'-bis(3-methylphenyl)-1,1'-bibiphenyl-4,4'-diamine (TDDBP) functions as a triphenylamine hole transporter while rubrene (RB) is an effective electron transporter. Previously, time-of-flight (TOF) mobility measurements show that both TDDBP and TDDBP + Alq3 can be highly improved up to ~10⁻³ to ~10⁻⁴ cm²/V·s respectively [H. H. Kong et al., Chem. Phys. Lett. 353, 407 (2002), and Chem. Phys. 298, 119 (2004)]. In this study, the effect of composition on the RB:TPD co-host will be investigated. Results indicate that a significant increase in hole mobility is observed when the RB concentration approaches to ~2.5 wt%. It is proposed that at low doping of RB, the holes mainly conduct along TPD molecules. At higher RB incorporation, hopping conduction along RB molecules has been established and is responsible for the significant increase in hole mobility. The threshold hysteresis ratio for RB is about 3 nm in the RB:TPD alloy. It is suggested that the molecular separation and the HOMO-HOMO difference (HOMO = highest occupied molecular orbital) control the hole conduction in the RB:TPD alloy.

19.37 Investigation of Bipolar Carrier Transport Properties in Pentacene by Admittance Spectroscopy. Jin Au 1,2, Stephen S. W. Tsang 1,2 and J. B. Xu 1,2 1Dept. of Electronic Engineering, Chinese University of Hong Kong, Hong Kong; 2Centre for Advanced Luminescence Materials, Hong Kong Baptist University, Hong Kong, Hong Kong.

In the area of organic field-effect transistors (OFETs), pentacene has been widely studied [1]. The reported field-effect hole mobility is as high as 0.1 cm²/V·s. From the applications point of view, exploration of intrinsic carrier mobility of pentacene is highly desired. However, due to the high material cost and the large film thickness (50nm) and detection limitation, it is impractical to use conventional time-of-flight (TOF) method to study the carrier mobility of pentacene. Recently, admittance spectroscopy has been successfully demonstrated to study the carrier mobility of PPV and Alq3 with thinner organic films (<50nm). In this report, we will present a detailed phenomenological study of the intrinsic hole and electron mobilities by admittance spectroscopy at various electrical field strengths and temperatures. Two different kinds of device structures are prepared, namely, ITO/pentacene/Au and ITO/pentacene/Au configurations. They are used to study the unipolar (hole) and bipolar transport properties. The characteristics of field- and temperature-dependent hole mobility are compared in two different structures. The zero-field hole and electron mobilities are above 10⁻² to 10⁻¹ cm²/V·s, respectively, which are a few orders of magnitude lower than those form the reported field-effect mobilities. This provides a strong evidence that the influence on carrier mobility by the induced change carrier density in an OFET configuration [2] is negligible. 1. Au, J. et al., IEEE Transactions on Electron Devices, 1997. 44(8), p. 1325-1331. 2. Martens, H.C.F., J.H. Halbritter, and J.W. Blom, Applied Physics Letters, 2000. 77(12), p. 1852-1854. 3. Berleb, S. and W. Brütting, Physical Review Letters, 2002. 89(20), p. 226601. 4. Tannen, C., et al., Physical Review Letters, 2003 91(21), p. 216601.

19.38 Abstract Withdrawn


The chemical synthesis of bis-heterocycle-phenylene polymers has been investigated for use in thin-film organic optoelectronic devices. Two soluble polymer derivatives, poly(1,4-bis(2-thienyl)-2,5-dialkoxyphenylene) [PBEDOT-OR2] and poly(1,4-bis(3,3,4,4-tetraethylenedioxy)thiényl)-2,5-dialkoxy-benzene) [PBEDOT-B(OR)2] have been synthesized via Ni(COD)2 coupling reaction developed by Yamamoto and coworkers. For materials characterization, molecular weights were estimated using size exclusion chromatography and repeat unit molar mass analyzed by MALDI/TOF mass spectrometry. These polymers exhibit high solubility in common organic solvents and good film forming abilities. These are easily fabricated into films by either hot casting, spin-coating or spray coating techniques. The degree of order in the polymer films was evaluated by X-ray and DSC in order to study the influence of the regioregularity on charge transport for chemical applications. These polymers present low oxidation potentials and switch between deep colored states. The polymers also...
absorb strongly in the visible and exhibit band gaps ranging from 2-2.2 eV similar to MEH-PPV and P3HT. Fundamental optical and electrochemical results will be presented in order to establish the band structures and demonstrate why these polymers are attractive candidates for electrochromic and photosensitive devices.


Self-assembled monolayers (SAMs) are thin organic films which form spontaneously on solid surfaces. SAMs are the subject of intense study because of their potential utility in such applications as adhesion promotion, biomimetic systems (MEMS) lubrication, protection of metal corrosion, and low dielectric layer. We have been studying the formation of organic-inorganic hybrid self-assembled multi-layers using molecular layer deposition. The multi-layers have been investigated by means of photoelectron spectroscopy, contact angle analysis, atomic force microscopy (AFM) and transmission electron microscopy (TEM). The results showed that these self-assembled multi-layers have high efficiency.

19.41 New Conjugated Polymers Derived from Carbazole as Thermoelectric Materials. Isabelle Levesque1,2, Xing Gao1, Dennis D. Klug1, Christopher I. Ratcliffe2, John Tse1,4, Mario Leclerc1, Alphonse Levesque1 and Terry Bayot1; 1Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, Ontario, Canada; 2Chemistry, Universite Laval, Quebec, Quebec, Canada; 3Physics and Astronomy, Clemson University, Clemson, South Carolina; 4Physics, University of Saskatchewan, Saskatoon, Saskatchewan, Canada.

Conjugated polymers and oligomers derived from 2-carbazole have been synthesized for their use in light-emitting diodes and transistors. The doped polymers are usually electrically conductive, and show thermoelectrical behavior. In our search for new materials for transformation of thermal energy to electrical energy, conducting polymers would allow advantages such as processability, flexibility, light weight and low cost. Thermoelectrical measurements also allow us to understand energy transport properties of these novel materials. Theoretical calculations performed on these polymers and other conjugated polymers show that their electrondonor electron acceptor band structures are adequate for thermoelectric materials. An efficient thermoelectric material must possess a large Seebeck coefficient (ΔV/ΔT), moderate electrical conductivity and a low thermal conductivity. In the search for advanced high thermopower materials, low band-gap polymers appear to have all these characteristics. It is possible that high electronic density of states near the Fermi level can be manipulated by careful adjustment of the concentration of valence electrons of such polymers via n- or p-doping. In this way, a favorable balance between electrical conductivity and a large Seebeck coefficient may be achieved. In this study, we combined theoretical and experimental approaches to investigate this possibility. Theoretical calculations have been performed on several representative conjugated polymers (polythiophene, poly(2,7-carbazole derivatives). We will describe the synthesis of new polycarbazole derivatives, as well as some optical, physical and electrochemical properties of the obtained samples. Polymers are soluble in common solvents and can form free-standing films. Thermoelectric measurements on selected conjugated polymers will be compared to theoretical calculations.

19.42 Water-Soluble Paracyclophane Chromophores with Large Two-Photon Action Cross Sections. Han Young Woo1,2, Alexander Mihailovsky1, Dmitry Korystov2 and Guillermo C. Bazan2; 1MIC-CAM, University of California, Santa Barbara, California; 2Chemistry, University of California, Santa Barbara, California.

Two-photon absorption (TPA) and two-photon induced fluorescence (TPIF) materials are an important consideration due to their potential applications such as 3D optical data storage, micro-fabrication, optical power limiting, biological imaging, etc. Especially, water-soluble TPA fluorophores can be used as biomolecular tags for two-photon fluorescence microscopy (TPM). TPM and higher multi-photon variations provide the best non-invasive means of fluorescence microscopy for biological imaging. Two parameters need to be optimized for the design of TPA fluorophores. One is the two-photon absorption cross section (δ, expressed in GM), which provides the probability of TPA at a particular frequency. A large fluorescence quantum yield (η) is also desired for better signal to noise. Currently most of the fluorophores being used as biomolecular tags in TPM are those that have been developed for one-photon excitation, so they have relatively small values of two-photon action cross section (δη < 10 GM). In this contribution, we report molecular design and characterization of TPM-specific chromophores based on [2-2]paracyclophane with exceptionally large η. Different azobenzene molecules were chosen to strengthen the bond based on different methods and to allow the molecules to be neutral, and soluble in organic solvents or charged and water-soluble. The specific neutral structures are (in order of increasing donor strength): 4,7,12,15-tetra[N-(6'-chlorohexyl)carbazol-3'-yl]vinyl-[2-2]paracyclophane (1N), 4,7,12,15-tetra[N-(6'-chlorohexyl)carbazol-3'-yl]vinyl-[2-2]paracyclophane (2N) and 4,7,12,15-tetra[N-(6'-chlorophenyl)phenyl]-4'-aminostyryl-[2-2]paracyclophane (3N). The charged species: 4,7,12,15-tetra[N-(6',N,N-trimethylammonium)hexyl]-4'-aminostyryl-[2-2]paracyclophane octaiodide (1C), 4,7,12,15-tetra[N-(6',N,N-trimethylammonium)hexyl]carbazol-3'-ylvinyl]-[2-2]paracyclophane octaiodide (2C). The overall set of compounds shows the evaluation solvent influence on fluorescence quantum yield and photophysical effects on η. Two-photon excitation spectra, measured using TPIF technique, show δ values of 1200 ~ 2080 GM in toluene and a substantial decrease of δ in water. Significantly, the fluorescence quantum yield in water decreases much more for 1, relative to 2 and 3. The combined η of 2C and 3C are determined to be 294 GM and 359 GM, which are the highest reported action cross sections for chromophores in water. These results show that to maximize the η in this class of chromophores, one needs to fine tune the magnitude of the charge transfer character of the excited state, to minimize fluorescence quenching in polar media. We will discuss structural guidelines for water-soluble TPM fluorophores and also explore medium effects on η.

19.43 Thin Films of Phthalocyanine/Perylene Tetracarboxyldilimide Blends for Organic Solar Cells. Alexandre Vlad1, Pascal Viville2, Dania Serban1, Vinciane De Cuper3, Gael Zucchi2, Vincent Bayot1, Roberto Lazzaroni2 and Yves Geerts3; 1IDICE, Universite catholique de Louvain, Louvain-la-Neuve, Belgium; 2SCMN, Universite de Mons-Hainaut, Mons, Belgium; 3LCP, Universite Libre de Bruxelles, Brussels, Belgium.

The performances of organic photovoltaic (solar) cells are governed by three important parameters: (i) the efficiency of the active layer to absorb light in the visible range, (ii) the efficiency of the dissociation mechanism of the optical excitations into charge carriers and, (iii) the efficiency of the charge transport towards the electrodes. Liquid crystal p-n heterojunctions consisting of electron donor dicystic-like phthalocyanines (PcH2) and electron acceptor calamic-like perylene tetracarboxyldilimide (PTCDI) are shown to be promising materials to fulfill these three conditions for the elaboration of organic solar cells. Both compounds absorb in the visible range and present a high electrical conductivity. In addition, thanks to their liquid crystal nature, they both exhibit an interesting columnar organisation at ambient temperature that can favour the vertical migration of the charge carriers towards the electrodes. In particular, PcH2 molecules are soluble in common solvents such as toluene, meaning that the thin films can be easily processed. In this work, we characterize the morphological structure of perylene-doped phthalocyanines thin films prepared from PcH2/PTCDI toluene solutions with various proportions. The optimization of the blend morphology is targeted to allow an efficient charge separation process at the p-n junction while keeping a sufficient phase separation needed for the migration of the charge carriers towards the electrodes. Special emphasis is thus given here to the control of the miscibility between the two active compounds. To reach that goal, spin casting, spin coating and drop casting deposition methods are investigated on ITO. Parameters such as the spin rates, along with the volume of the deposited solution and its concentration have been tested to tune the roughness and the thickness of the films. We use Tapping-Mode Atomic Force Microscopy to characterize the film morphology and thickness, and the morphology of the thin films. It is shown that, depending on the parameters listed above, a high degree of mixing between PcH2 and PTCDI, along with partial phase separation, can be obtained. The electrical properties of these organic layers, as candidates in organic solar cell devices, are also reported.

19.44 Supramolecular Organization of Thiophene-based Oligomers: From Solution to Solid-state Nanostructures. Philippe Leclerc1,2, Mathieu Surin1, Gwennalle Derue1, W. James Feast2, Pascal Jonkhoeij2, Albertus H. J. Schenning2, E. W. (Bert) Meijer2 and Roberto Lazzaroni1; 1University of Maastricht, Maastricht, Netherlands; 2IRC, Durham, United Kingdom.

Well-defined conjugated oligomers play an important role in the field of organic electronics because their precise chemical structure and
conjugation length give rise to well-defined functional properties and facilitate control over their supramolecular organization. Until recently research in this field has been focused mainly on methodologies for the synthesis and characterization of pi-conjugated oligomers with long axis dimensions up to 10 nm. Another major issue, which attracts increasing attention, is the control of the spatial orientation and packing of oligomers through the design of micellar and supramolecular architectures. The role of self-assembling processes (pi-pi interactions, hydrogen bonding) of these systems is demonstrated here for disubstituted oligothiophene derivatives (n = 3, 6 and 7). This allows to prepare materials with a high degree of structural order of the constituent building blocks. During these processes, the interplay between the conjugated molecules, the solvent and the substrate surface is of primary importance. This can be clearly observed. Depending on the interactions between the molecules and the substrate, one-dimensional (nanowires) or two-dimensional (platelets) objects can be generated.

Moreover, molecular modeling calculations are primordial in the understanding on how the molecules are organized within these nanostructures and therefore rationalize the experimental data. In this work, some attempts to use spatial deposition or soft-lithography-derived techniques are also presented and show very promising results. In combination with scanning probe microscopy-derived techniques, they constitute a determining and pertinent approach to create organized nano-conducting architectures. For this purpose, we propose here to use an AFM tip as a pencil to organize at the local scale the nanoobjects along a given axis. The construction of nanoscopic and mesoscopic architectures represents a starting point for the construction of molecular electronics or even nanoscopic devices. 1. L.S. Hung, C.H. Lee, S.T. Lee, and L.S. Hung, Appl. Phys. Lett. 82: 840, 2003.

Polysilanes are a well studied class of inorganic polymers. Their most interesting feature is that of es-bond delocalization. This process accounts for their UV activity, thermochromism and a number of other interesting properties. So far mainly polymeric chains have been the subject of studies. Theoretical studies, however, have revealed that polysilanes may be attractive semiconducting materials. These compounds would be rigid rod-like structures with the main chain consisting of siloxane cages. Recent synthetic efforts have provided us with a simple access to bicyclo[2.2.2]siloxanes. These compounds can be converted into diamines, which are well known precursors for polymer synthesis. Theoretical calculations predicted a smaller band gap for these polymers compared to conventional polysilanes. Investigations concerning electronic properties of a number of compounds with different spacer groups between the siloxane cages will be the subject of discussion.

SESSION 110: LEDs
Chair: Ghebremichael Yohannes
Friday Morning, April 1, 2005
Room 201 (Moscone West)

8:30 AM 110.1 Organic Solid Solution: Formation and Application in Organic Light Emitting Diodes. Yang Yang and Yan Shao; Materials Science & Engineering, University of California, Los Angeles, Los Angeles, California.

Research attentions have been paid to organic electronics in recent decades and currently organic materials have found promising applications, such as display and transistors. To enhance the performance of organic LEDs, dipolar and gap-doped mixed junction structure by co-evaporation method have been extensively adopted in formation of organic thin films. In the criteria of material system selection, most (if not all) attentions have been paid to material energy band structure for carrier transport behavior. As a result, some important characteristics may be overlooked, such as material compatibility or solvability. In this presentation, we propose a novel doping method taking advantage of fused organic solid solution process, which is a high pressure and high temperature processing to ensure that organic host and dopant are fully fused. By proper preparation of fused solutions of organic compounds, stable material systems can be selected for device application. Furthermore, with the help of the fused organic solid solution, doping concentration and uniformity could be precisely controlled by only one thermal source. As examples for forming organic thin films, high performance organic light-emitting diodes with both single color and white color have been demonstrated by this new method. Compared with traditional co-evaporation method, fused organic solid solution provides us a more convenient way to optimize doping system and fabricate relatively complicated organic devices. 1. L.S. Hung, C.H. Chen, Materials Science and Engineering 2002, R39, 139. 2. A.B. Chwang, R.C. Kwong, and J.J. Brown, Appl. Phys. Lett. 2002, 80, 745. 3. D. Ma, C.S. Lee, S.T. Lee, and L.S. Hung, Appl. Phys. Lett. 2002, 80, 3641.

8:45 AM 110.2 Light Emitting Devices from Ionic Transition Metal Complexes. George Malliaras, Materials Science and Engineering Department, Cornell University, Ithaca, New York.

Ionic transition metal complexes have emerged as promising candidates for applications in solid-state electroluminescent devices. These materials serve as multifunctional chromophores, into which electrons and holes can be injected, migrate and recombine to produce light emission. Their device characteristics are dominated by the presence of mobile ions that redistribute under an applied field and assist charge injection. As a result, efficient single-layer devices that use air-stable electrodes can be fabricated from solution. We present recent experimental results and show various approaches to study the mechanisms of these devices and to construct novel device structures. By depositing an array of electrically floating aluminum strips on top of the exposed polymer film, the device can be turned on by simultaneous formation of multiple light-emitting p-n junctions in series. In normal large planar LEDs, the emission zone is approximately 6% of the total exposed area between the electrodes. The multiple-junction LED can offer nearly 50% emitting area and uniform light emission to a naked eye. Moreover, when the device is operated as a photovoltaic cell in frozen-junction mode, extremely large open circuit voltage proportional to the number of junctions has been observed. In this system we report planar LEDs with up to 53 formed p-n junctions in series between two electrodes 0.5cm apart, which offers uniform light emission and an open circuit voltage of 63.3V. All the metal deposition was done in single step through a shadow mask. The device can be easily scaled down by using microfabricated electrodes which will offer more junctions and/or improved light-emitting and photovoltaic performance. Reference 1. “Planar Polymer Light-Emitting Electrochemical Cells with Extremely Large Inter-electrode Spacing”, J. Gao and J. Dur, Appl. Phys. Lett. 83: 3027-3029 (2003). 2. “Visualization of electrochemical doping and light-emitting junction formation in conjugated polymer films”, J. Gao and J. Dur, Appl. Phys. Lett. 84: 2778-2801 (2004). 3. “Imaging the degradation of polymer light-emitting devices”, J. Dur and J. Gao, Appl. Phys. Lett., in press Oct.25 (2004)

9:00 AM 110.3 Planar Polymer Light-Emitting Devices and Photovoltaic Cells with Multiple p-n Junctions. Corey Tracy and Jun Gao; Department of Physics, Queen’s University, Kingston, Ontario, Canada.

Recently we have demonstrated planar polymer light-emitting electrochemical cells (LEC) with extremely large inter-electrode spacing (mm to cm). The vast exposed polymer allows a unique approach to study the mechanisms of these devices and to construct novel device structures. By depositing an array of electrically floating aluminum strips on top of the exposed polymer film, the device can be turned on by simultaneous formation of multiple light-emitting p-n junctions in series. In normal large planar LECs, the emission zone is approximately 6% of the total exposed area between the electrodes. The multiple-junction LEC can offer nearly 50% emitting area and uniform light emission to a naked eye. Moreover, when the device is operated as a photovoltaic cell in frozen-junction mode, extremely large open circuit voltage proportional to the number of junctions has been observed. In this system we report planar LEDs with up to 53 formed p-n junctions in series between two electrodes 0.5cm apart, which offers uniform light emission and an open circuit voltage of 63.3V. All the metal deposition was done in single step through a shadow mask. The device can be easily scaled down by using microfabricated electrodes which will offer more junctions and/or improved light-emitting and photovoltaic performance. Reference 1. "Planar Polymer Light-Emitting Electrochemical Cells with Extremely Large Inter-electrode Spacing”, J. Gao and J. Dur, Appl. Phys. Lett. 83: 3027-3029 (2003). 2. "Visualization of electrochemical doping and light-emitting junction formation in conjugated polymer films”, J. Gao and J. Dur, Appl. Phys. Lett. 84: 2778-2801 (2004). 3. "Imaging the degradation of polymer light-emitting devices", J. Dur and J. Gao, Appl. Phys. Lett., in press Oct.25 (2004)

9:30 AM 110.4 High Efficiency Blue-Emitting OLED using Wide-Gap Arylamines. Junji Kido1,2, Daisaku Tanaka1, Yuya Agata1 and Hitoshi Shimizu1; 1Polymere Science and Engineering, Yamagata University, Yonezawa, Yamagata, Japan; 2Optoelectronic Industry and Technology Development Association, Bunkyo-ku, Tokyo, Japan.

Various kinds of blue-emitting phosphorescent OLEDs were fabricated using wide-gap arylamine derivatives. Carbazole derivatives, having a wide energy gap of over 3.4 eV, were used as a host material in the emitter layer and triphenylamine derivatives, having a wide energy gap of 3.5 eV, were used as a hole-transporting layer. OLEDs with a structure of TTO/p-doped buffer layer/wide-gap arylamine hole-transporting layer/blue-emitting carbazole laver doped into carbazole-containing quaternary derivative/electron-transporting layer/LiF/Al were fabricated. A high luminous efficiency of 23 lm/W and the external quantum efficiency of over 15 percent were observed. These are the highest values so far reported for blue OLED. Design of
the materials and the device structure are discussed.

OLED Degradation Described by Using a One-Free-Parameter Time-Dependent Diffusion Model. Beneoit Raccuia, Salvatore Cnaa, Armand Bettinelli and Henri Doeyts; Thomson, Cesson Cevigne, France.

The luminance decay mechanism in Organic Light Emitting Diode is a complex and important problem. The major improvements in lifetime achieved recently in excess of 100 cd/m² make hard to reliably estimate the lifetime after a relatively short experimental time. Even when accelerating the degradation, either by increasing the initial luminance or the temperature of the sample, thousands of hours of lifetime might be necessary before having a correct estimation of the device lifetime. A combination of at list two exponential decays is normally used as a fit function, in order to account for the initial rapid exponential decay as well as for the long term decay behavior mainly observed during degradation of an OLED. We will show that the predicted LT can dramatically change depending on the fitting model used. By using a simple time-dependent diffusion model, already successfully used to explain the degradation process observed in fluorescent tubes as well as in luminophores employed in plasma displays, we derive a new function able to fit the whole OLED lifetime by using a single free parameter.

We made experiments on the luminance decay of green and red OLEDs with various degree of complexity, from simple bi-layer structures up to phosphorescent devices using electrically doped interfaces; all experimental results were successfully fitted by our model. Further results were also analysed using various fitting models with one or two exponentials. We observe that early estimations (based on few hundred hours) of the accelerated lifetime using these models, leads to a large errors when compared with the experimental data. Using our model we produce a small fitting error, despite having a single fitting parameter, therefore allowing for reliable estimation of the lifetime, vital when testing new materials or new device architectures.

10:00 AM I10.7

Organic semiconductors such as conjugated polymers provide a new way of looking at many of the broad fundamental scientific issues related to molecular electronics. A great deal of the physics, which governs the behaviour of devices fabricated with these organic semiconductors, occurs at the organic-organic interfaces. Therefore, understanding of the organic interfaces is crucial to the success of molecular electronics. Here we report the detailed studies of a range of well-controlled organic-organic interfaces with different length-scales, in both inter-chain and intra-chain. Our study of electronic structures and processes focus on two conjugated homo-polymers; poly(9,9-dioctylfluorene-co-benzothiadiazole) F8BT [acceptor] and poly(9,9-dioctylfluorene-co-(4,7-diphenyl-1,10-phenanthroline) TFB donor) with different chain-lengths, their blends and random copolymer (The Dow Chemical Company) have been investigated. Our results show that the molecular-scale electronic processes such as energy transfer within these materials are very different when these processes occur at intra- or inter-chain interfaces with different length-scales. In particular, the F8BT shows the effects of intra-chain heterojunction state (formed by random copolymerrisation with TFB) in its luminescence lifetimes and spectrum, which are different from those induced by the inter-chain heterojunction states (formed by blending with TFB). Using the copolymer as an active material in devices such as organic light-emitting diodes, we observed that the large number of donor-acceptor interfaces in the copolymer is able to provide good charge balance leading to better recombination rates and more steady output efficiencies compared to blend devices. The presence of these interfaces also enhances charge dissociation in organic photovoltaics. However the absence of domains and matrices rich in any one particular homo-polymer has reduced the charge transport abilities of the copolymer. In this presentation, we will discuss in detail the role and implication by these inter- and intra-chain interfaces formed in organic semiconductors and their devices and demonstrate how we are able to improve the charge transport within devices using the copolymer by making controlled multilayer devices that combine the advantages of the different polymer systems.

10:30 AM I10.8
Light-Emitting Liquid Crystals: From Red, Green and Blue Light-Emitting Materials to Full Color and Polarisated OLEDs. Adam E. A. Contoret, Simon R. Farrar, W. Chung Tse; Kai L. Woon, Mary O'Neill, Matthew P. Aldred, Pano S Vlachos and Stephen M. Kelly; 1Department of Physics, University of Hull, Hull, United Kingdom; 2Department of Chemistry, University of Hull, Hull, United Kingdom.

We have recently pioneered a liquid crystal approach to organic electroluminescence, whereby thin, uniform films of electroluminescent and charge-transporting liquid crystals are formed as insoluble polymer networks by photo-polymerization using ultraviolet light [1]. Here we report new material and device developments to show that liquid crystalline polymer networks provide a practical alternative to the standard polymer and small molecular approaches to Organic Light-Emitting Displays (OLEDs). We describe the design and synthesis of novel polarizable red, green and blue light-emitting liquid crystals (reactive mesogens). We show how molecular design can be used to optimize the orbital energies and charge-carrying mobility of such reactive mesogens for electron and hole injection and transport. We show that the optical and electrical properties of the chromophores can be improved by crosslinking. Red, green and blue OLEDs are shown with luminances up to 560 cd/m² at V. Efficiencies up to 2.2 cd/A are reported. We demonstrate the first full-colour multilayer OLED produced by photolithographic patterning of nematic light-emitting reactive mesogens. Another advantage of the fluid nematic state is the capability of polarized light emission. This can provide improved viewing in bright light conditions for standard OLEDs and is also required for a number of 3D display configurations. We report a new class of organic copolymers designed specifically as conducting photoluminescent OLEDs with chartographically patternable polarized emission. Illumination with polarized ultraviolet light causes a surface anisotropy to the alignment layer and hence a preferred in-plane orientation of the overlying light-emitting liquid crystal. We demonstrate the patterning of the polarization direction of luminescence by simply changing the polarization direction of the ultraviolet light. Linearly polarized emission has been achieved with a polarization ratio of 1:3.1 is demonstrated.

10:45 AM I10.8

Organic light-emitting diodes (OLEDs) are promising for full color displays and lighting applications. New readily processible and thermally robust emissive and charge transport materials are needed for developing the next generation of high performance blue, green, red, and white OLEDs. In this talk, I will present recent work in our laboratory on new emissive and charge transport materials, including oligomers, dendrimers, and polymers. A series of n-type, blue-light-emitting oligoquinolines based on the 6,9-bis(4-phenylquinoline) core has been synthesized and used as emissive and electron transport materials by blue OLEDs. The white OLED EL with CIE coordinates at (0.15, 0.16), a maximum brightness of > 4000 cd/m², and maximum luminous efficiency of 7.9 cd/A at 945 cd/m² was achieved using simple bilayer diode architectures. A series of new light-emitting conjugated dendrimers based on the benzene core, poly(phenyl-phenylenevinylene) dendrons, and diphenylquinoline peripheral groups has been synthesized, characterized and used as emissive and charge transport materials in efficient light emitting diodes (LEDs). The performance of bilayer LEDs using the dendrimers as the electron transport layers and poly(2-methoxy-5-(2-ethyl-hexyloxy)-1,4-phenylenevinylene) (MEH-PPV) as the emissive layer increased with generation and number of electron-acceptor phenoxy groups. This yielded a maximum external efficiency of 5.0 %, a power efficiency of 1.3 lm/W, and a brightness of up to 2000 cd/m² in ambient air using aluminium cathodes. White OLEDs were fabricated from blends or multilayers based on poly(9,9-dioctyfluorene) (PFO) and MEH-PPV. Efficient white light with CIE coordinates of (0.33, 0.34), a luminance level of 4000 cd/m², an external quantum efficiency of 3.1% (photons/electron) and a device efficiency of 3.7 cd/A was obtained from the blend LEDs.

11:15 AM I10.9
Highly Efficient Red, Green, Blue and White Emission from Small-Molecule Organic Light-Emitting Diodes (OLEDs). Karsten Walter, Quan Huang, Gufeng Ho, Rico Meerheim, Gregor Schwartz, Karsten Fehe, Martin Pfeiffer and Karl Leo; Institute of Applied Photophysics, Dresden University of Technology, Dresden, Germany.

In this talk we present an overview over our current activities on highly efficient RGB OLEDs for display applications, and first data on white OLEDs for lighting. Common for all devices is an efficient...
charge carrier injection both from the cathode and the anode side via doped organic transport layers, and a charge carrier confinement within the emissive layer to eliminate Auger recombination. Red and green phosphor dots were co-deposited onto polyfluorene-based triplet emitters, while fluorescent emitter materials are used for blue.

A well-balanced carrier ratio inside the emissive zone is achieved by different means, such as the use of appropriate matrix materials and the application of well-distributed emission zones by double emission layers. For green OLEDs this approach lead to a record-breaking power efficiency of 82 lm/W.[1] Another advantage of double emission OLEDs is the significant increase in device lifetime, which e.g. for red p-i-n devices over extended time periods, which could lead to device lifetimes up to 150,000 hours. Consequently, the double emission layer approach was applied to top emitting OLEDs as well. We will show that top emitting p-i-n type OLEDs can possess even higher efficiencies than bottom emission devices with still very low operating voltages. Finally, we will show first results on white OLEDs with doped transport layers.[1] G. He et al., APL 85 (2004) 3911

11:30 AM I10.10
Fluorenone Incorporation Effect on Optoelectronic Properties of Blue Light-Emitting Polymers and Devices. Craig Murphy, Ian Rees, Nathan Phillips, Mark Lonsbater, Haris Grizzi and Carl Towns; CDT Ltd., Cambride, United Kingdom.

Recently, fluorenone defects in conjugated polymers, particularly in poly(di-alkyl-fluorene) systems, have been widely studied with a focus on their emission properties. Although these fluorenone defects have been assigned to be the origin of a low-energy green emission band appearing in polyfluorenes, there has been little work to address the direct fluorescence incorporation effect on the optoelectronic properties of blue light-emitting polymers (LEPs) and devices, in particular after prolonged operation of the devices, which has implications for the further use of polyfluorenes as active materials for displays. Here we report the effect of fluorenone deliberately incorporated into commercial blue LEPs, focusing on the emission (photoluminescence and electroluminescence) and device characteristics (luminance-current-voltage and lifetime). Materials with a range of fluorenone incorporation from 0.005% to 30% mol were synthesized and compared to a pristine material with nominally 0% fluorenone content. We first observe in the PL spectra and efficiency that, for fluorenone contents of 0.2% and above, the green emission from the fluorenone units (570nm) is more intense than that from the original material (450nm). Second, for the light-emitting diodes, even 0.005% causes a large increase in green emission features with a related decrease in the lifetime. For 0.05% fluorenone, the green emission feature becomes as intense as the original blue emission peak, indicating a much stronger fluorenone incorporation effect for charge injection than for photoexcitation. Third, most importantly, we find a large reduction of the green peak after DC lifetime test in the devices fabricated with the highest fluorenone content polymer. A similar massive suppression of the green peak is also observed in the EL spectrum, resulting in the recovery of blue emission from the device. Interestingly, a low-intensity red peak (640nm) apparent in the driven device set-ups may indicate the existence of fluorenone 'aggregate' states. In this presentation, we will discuss in detail the results described above.

11:45 AM I10.11
Efficient, Blue-Green Electrophosphorescence using Fluorenone-Free Small Molecules - A New Route to Saturated Blue Phosphorescence. Russell J. Holmes1,2, Stephen R. Forrest1,2, Tissa Sajo1,2, Arnold Tamayo1, Xiaofan Ren1, and Mark E. Thompson1,2; 1Department of Electrical Engineering, Princeton University, Princeton, New Jersey; 2Princeton Institute for the Science and Technology of Materials (PRISM), Princeton University, Princeton, New Jersey; 3Department of Chemistry, University of Southern California, Los Angeles, California.

The study of blue electrophosphorescence has to date been centered on molecules that include electron withdrawing functional groups, necessary to blue shift molecular phosphorescence. We have developed a new class of molecules capable of saturated blue electrophosphorescence without the need to attach fluorine groups. Organic light emitting devices were constructed using the blue phosphor fac-tris(9,9’-dimethyl-2-fluoropyridine)perylenesulflato, Na, C33H13I3N3O4 (F113), doped into host matrices of N,N-dicarbazolyl-3,5-benzene (mCP) and p-bis(triarylilidene)benzene (UH2). Peak quantum and power efficiencies of (6.7± 0.3)% and (11.9 ± 3.2) lm/W in mCP, and (5.7 ± 0.6)% and (10.5 ± 1.1) lm/W in UH2 respectively are obtained, while the emission in both cases is characterized by Commission Internationale de l’Eclairage co-ordinates of (x=0.25, y=0.53).

SESSION I11: Display and RFID
Chair: Devin MacKenzie Friday, April 1, 2005 Room 201 (Moscone West)

1:30 PM I11.1
Inkjet Technology for Printed Organic Electronics. Christopher Newsome, Cambridge Research Laboratory of Epson, Cambridge, United Kingdom.

Epson’s research into the concept of the ‘micro liquid process’ aims at realizing functional electronic devices by depositing materials from the liquid form using drop on demand piezoelectric inkjet heads technology. Such production technology is targeted at improving the efficiency of material and energy consumption, thus reducing the impact on the environment as compared to conventional manufacturing methods based entirely on evaporation or subtractive photolithographic techniques. The additive nature of the micro liquid process is intrinsically efficient in terms of material consumption, and is also a flexible production tool as the patterning is directed by digital information. Once deposited in the desired location, the material is then converted to the solid form to realise the required material characteristics. In addition to liquid to solid transformations, post deposition treatments may even include solid to liquid transformations such as self organisation in a liquid crystalline phase. The micro liquid process has been implemented to fabricate (among others) thin film transistors based on polymer materials. Devices incorporating printed conducting patterns from materials such as PEDOT-PSS and semiconductor materials such as those based on a fluorene co-polymer have been fabricated. The analysis of the device operation encompasses the bulk properties of the semiconductor and material properties of the interfaces between adjacent layers in the transistors as well as the source & drain electrodes influence the device operation in terms of the threshold voltage for example. Device performance in terms of the field-effect mobility has been investigated and correlations can be made to the film morphology and homogeneity of the semiconductor. Self assembly of enhanced structural phases have been realised to improve the field effect mobility in top gate configuration devices. In addition to mobility considerations, the switching characteristics of polymer transistors are crucial to realise display oriented applications. The off-on current ratios observed in printed arrays of polymer transistors are sufficiently high to switch films of electrophoretic capsules acting as display elements in active matrix arrays. Examples of these devices will be presented.

2:00 PM I11.2

There is currently a large effort in the display and lighting community to develop mechanically flexible OLEDs both to enable unique applications and to reduce manufacturing costs. In order to achieve this, low cost roll-to-roll or sheet-processing methods must be developed in place of the classic semiconductor manufacturing methods currently used. At present, completely new deposition methods for both polymer and small-molecule devices are being developed in order to evaluate the utility of such methods, it is advantageous to have a robust and fast method to evaluate the thickness uniformity of the deposited organic layers. Non-uniformities at all spatial length scales from sub-mm to several cm can occur and need to be understood as a function of the relevant parameters for each deposition method. Non-uniformities on a larger scale, several cm or even feet, are also inherent in web coating due to difficulties of controlling process parameters across and along the web, and over long periods of time. Numerous techniques such as ellipsometry, interferometry, and optical profilometry can non-destructively measure thin films but it is difficult to quickly obtain a spatial map of thickness variation over a large length scale with adequate resolution. Here we demonstrate a simple and fast method to quantify non-uniformities in thin films over arbitrarily large length scales. Our method utilizes the color of light reflected from the coated substrate and its variation with polymer layer thickness. This concept of color change is well known, and is due to constructive interference of light of particular wavelengths related to polymer layer thickness and optical constants. In our modification, a digital camera is used to capture images of the coated substrates, and hue is extracted from the image data file. We show that hue can be linearly correlated with polymer thickness. We demonstrate this for polymer based OLEDs using poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT-PSS) and various light-emitting polymers (LEP) deposited on ITO/PEI substrates. The correlations were successfully used for 40-150nm PEDOT-PSS layers and 20-120nm LEP layers over length scales greater than 1 inch. The method sensitivity is estimated to be better than 0.6 μm. We show examples of
We present a unique fabrication process for inexpensive optoelectronic devices on flexible PET substrates. The objective of this research was to explore the device characteristics of screen-printed light-emitting electrochemical cells. Various device structures are discussed with reference to cost effective construction, optimum performance and stability. We also discuss the electroluminescence (EL) properties depending on factors such as substrate cleaning method, wet-etch technique, ink processing and drying, and device driving schemes. Processing conditions and challenges associated with patterning substrates, ink formulation, printing active layers, and encapsulation will be presented. We also examine the relationship between change transport and doping of the light-emitting polymer (LEP) layers. The electrochemical behavior of the display proves to be strongly correlated to the nature and quantity of dopants incorporated into the structure. The nature of the dopants affects the print quality, the LEP layer thickness, the turn-on time, the device efficiency and stability. The dopants induces a phase separation, of various degrees, within the printed LEP, which affects the morphology and proves to be intricately related to the EL properties. The luminance output shows an inverse relationship between doping levels and EL. Lower doping concentrations lower the electroluminescence efficiency but compromise the switching time of the display. This switching, or turn-on time, is correlated to the rate of charge injection at the electrodes. Increasing the doping levels promotes faster injection formation so the display switches on faster, but impacts the EL uniformity and the stability of the displays in both dry nitrogen and air atmospheres. Results for light-emitting electrochemical cells created by a fully screen-printed process including J-V-L characteristics, external quantum efficiency and lifetimes are presented. Lifetime measurements, complimented by microscopy images suggest a number of degradation mechanisms. Device failure may be affiliated with surface defects in the flexible substrates or tin oxide, impurities or insoluble material in the charge transport or emissive layers, irreversible electrochemical reactions, delamination of electrodes, or chemical reaction with air and water. Variation in dopant concentration, LEP thickness, encapsulation method and driving conditions all contribute to device stability and will be discussed.

3:00 PM 111.4 Integrated Organic Semiconductor Optics for Miniaturised Analysis. Oliver Hofmann1, Paul Miller1, Xuhua Wang2, Jingsong Huang2, Donal D. C. Bradley3, Andrew J. de Mello4,5 and John C. de Mello3,5; 1Department of Physics, Imperial College London, South Kensington, United Kingdom; 2Department of Chemistry, Imperial College London, South Kensington, United Kingdom; 3Diagnostics Lab 5Molecular Vision Ltd, London, United Kingdom.

Miniaturisation of conventional analytical instrumentation has been one of the dominant themes within the physical and biological sciences during the last decade. In particular, development of the concept of a miniaturized total analysis system (μ-TAS) or Lab-on-a-Chip has yielded distinct systems for genetic analysis, clinical diagnostics, chemical synthesis, drug screening, and environmental monitoring. In analogy to microelectronic development, the downsizing and integration of chemical processes leads to huge gains in performance, speed, size, throughput, cost and automation. Lab-on-a-Chip devices have shown themselves to be highly effective for laboratory-based research, where their superior analytical performance has established them as efficient tools for complex tasks in genetic analysis, drug discovery and medical diagnostics. However, to date Lab-on-a-Chip systems have not been well suited to point-of-care applications, where cost and portability are of primary concern. Although the chips themselves exhibit small instrument footprint, they cannot be fabricated at low unit cost, thus must generally be used in conjunction with bulky optical detectors, which are needed to identify and quantify the analytes or reagents present. We report the successful use of organic light-emitting diodes and photodetectors as a device of the conventional microelectronic optics that are typically used for optical detection in Lab-on-a-Chip applications. The organic devices add minimal size and weight to the μ-TAS chip, allowing for the creation of fully integrated, precise analytical devices in a disposable, printed form. We describe a range of chemical and diagnostic assays that have been successfully performed using organic-semiconductor based detection, and examine the sensitivity limits of these integrated sensors.

3:15 PM 111.5 Polymer Based Rectifiers and Integrated Circuits for Portable RFID Tags. Dietmar Zipperer, Wolfgang Clemens, Andreas Ullmann, Markus Boehm and Walter Fix; PolyIC GmbH & Co. KG, Erlangen, Germany.

Radiofrequency identification (RFID) tags have been named as a potential application for polymer electronics for a long time. Besides integrated circuits, also rectifiers are necessary for the realization of such tags. We developed rectifier diodes based on poly styrene (Styrene-phenylene) as semiconducting polymer and capacitors and combined them into integrated rectifiers in order to rectify radio frequency alternating currents. As a.c. voltage supply we used the induced voltage of a resonant antenna circuit in a radio frequency electromagnetic field. The d.c. output voltage of the rectifier was used to drive polymer based integrated circuits, e.g. ring oscillators. A polymer RFID-tag was assembled with these devices, using an output transistor to back couple the signal by load modulation. We present our latest developments in this field as well as the roadmap towards printed electronics for low cost RFID tags and other applications.

3:45 PM 111.6 13.56 MHz Organic Transistor based Rectifier Circuits for RFID Tags. Robert Rotzoll1, Siddharth Mohapatra2, Viorel Olariu2, Robert Wenz3, Michelle Grigs4, Oleg Shekhtin5,6, Klaus Dimm2 and Ananth Dodabalapur1,7,8, 1Organic ID, Austin, Texas; 2Organic ID, Colorado Springs, Colorado; 3The University of Texas at Austin, Austin, Texas.

One of the potential application areas for organic and polymer transistors is in radio-frequency identification (RFID) tags. The miniaturization of organic transistor-based circuitry for low-cost-sensitive application stems from the low-cost that can potentially be achieved with organic electronics. One of the key components of an RFID tag is the front-end rectifier that must rectify an AC signal received from the antenna which is tuned to the RFID regime such operating speeds can be achieved in rectifier circuits. The circuits were fabricated on flexible plastic substrates and employed a solution-cast dielectric. The pentacene mobilities are in the range 0.1 to 1.0 cm2/V-s. The channel lengths of the transistors are in the range 2-4 mm. The half-wave rectifiers employed a diode-connected transistor. The voltage rectification efficiency was in excess of 28% at 14 MHz, demonstrating that such circuits can be used in RFID tags. We have also implemented monolithically integrated full-wave rectifier circuits with 4 pentacene transistors connected to take advantage of NQS mode operation. These circuits also operated successfully at speeds up to 15 MHz. The rectifier output was measured both with an oscilloscope and with a high-impedance voltmeter. We will also describe the essential features of a system level design of an all-organic RFID tag.

4:00 PM 111.7 High Performance Organic Schottky Diode. Soren Steudler1,2, Maritjn Lenes1, Carsten Deibel1, Stijn De Vusser1,3, Jan Genois1,3 and Paul Heremans2,3; 1Polymer and Molecular Electronics, EMEC, Leuven, Belgium; 2E.E.Dpt. K.U.Leuven, Leuven, Belgium.

With ongoing improvements in the performance of small molecule organic thin film transistors (OTFT) and the first demonstrations of Inversors and oscillators the route towards circuits based on organic small molecules like pentacene is open. A special focus in the development of organic circuits is the radio frequency identification tag. One of the main challenges is the rectification stage that rectifies the incoming high frequency signal, preferable at the radio frequency identification tag. We like to present an organic Schottky diode based on pentacene that shows a superior performance to previous organic diodes as well as compared to silicon diodes. This Schottky diode achieves a current density above 200A/cm2 with a mobility of 0.13cm2/Vs. In a rectifying stage the diode has been able to follow a frequency of more than 5MHz, supplying a DC output of 10V. These findings represent a step in the realization of an organic radio frequency identification tag and might be of further interest in driving organic memories as well.

4:15 PM 111.8 Fabrication of OLED Displays on a Dome using a Deformable Polymeric Hole Injecting Anode. Rabin Bhattacharya1,2, Sigurd Wagner1, Yue-Jin Tung1,2,3, Eric Jones1,2, Janie Jo1,2, Melissa Ann Kreger1,2, 1Organic ID, Austin, Texas; 2Universal Display Corporation, Ewing, New Jersey.
The fabrication of organic light emitting diode (OLED) displays on conformally shaped surfaces is a fascinating and evolving new field that calls for new patterning techniques and materials, in addition to the marriage of OLEDs with deformable substrates. Applications of shaped OLED arrays include displays that are fitted onto spherical surfaces of goggles or cell phones. The entire structure must withstand the strain of shaping to a dome. We have been developing the necessary materials and processes for conformally shaped passive OLED displays, and we present here the use of PEDOT:PSS as the anode contact to obviate the need for an otherwise rigid and brittle conventional transparent conducting oxide. Our approach is to (1) fabricate gold interconnects on polyethylene terephthalate (PET), which is plastically deformable, (2) spin coat a uniform film of the conductive polymer PEDOT:PSS over the interconnects, (3) evaporate a blanket green phosphorescent OLED (PHOLED) structure over the PEDOT film along with an aluminum cathode, (4) deform the entire structure to a dome with 9-cm radius of curvature. This produces an average radial strain of 2%. We use the PEDOT, a hole conductor, as the transparent anode for the bottom emitting display. PEDOT's mechanical ductility allows it to survive strains that would normally fracture a film of the commonly used anode material, indium tin oxide (ITO) on PET. To date, we have obtained OLEDs on the dome that have a luminance of 112 Cd/m². We present the fabrication, the electrical and optical characteristics, as well as the spatial distribution of the light emission. This work is supported by the Army’s Night Vision and Electronic Sensors Directorate.

4:30 PM 111.9
Ambipolar Organic Transistors and Complementary-Like Logic Circuits. Thomas Dimitrios Anthopoulos1, Dago M. de Leeuw1, Sepas Setayesh1, Cristina Tanase2, Jan C. Hummelen1 and Paul D. M. Blom1; 1Philips Research Laboratories, Eindhoven, Netherlands; 2Molecular Electronics, Materials Science Centre, University of Groningen, Groningen, Netherlands.

As the complexity of organic integrated circuits increases there is an increasing need for higher yield, better noise immunity and lower power dissipation [1]. One route that can meet all these requirements is the use of complementary transistor circuitry. Despite the advantages, however, organic complementary circuits prepared by thermal evaporation [2] are difficult to fabricate and hence potentially expensive. In this context, solution processable devices are potentially cheaper alternatives in terms of manufacturing cost. Here we report on an approach towards organic complementary-like circuits based on ambipolar transistors using solution processible organic compounds. In particular, we show that ambipolar transport can be achieved within a single transistor channel by employing a polymer-small molecule blend or simply by using a single narrow-band gap molecular semiconductor. Despite the fact that we employ exclusively high work function gold electrodes for the source and drain we observe ambipolar operation over easily accessible operating voltages. To demonstrate the suitability of ambipolar organic transistors for practical utilisation in logic circuits we realise complementary-like inverters based on two ambipolar transistors. Furthermore, by integrating several such inverters we are able to demonstrate more complex organic circuits such as ring oscillators. REFERENCES [1] Gelinck G. H. et al. Nat. Mater. 3, 106 (2004). [2] Crone B. et al. Nature 403, 521 (2000).